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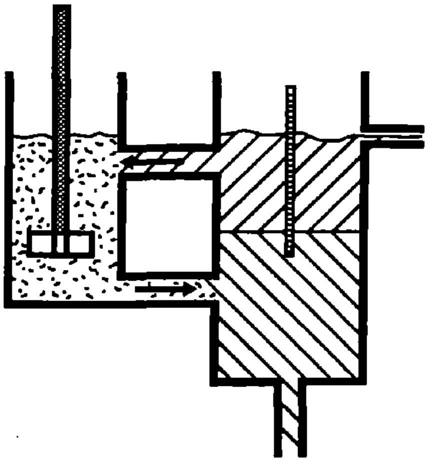
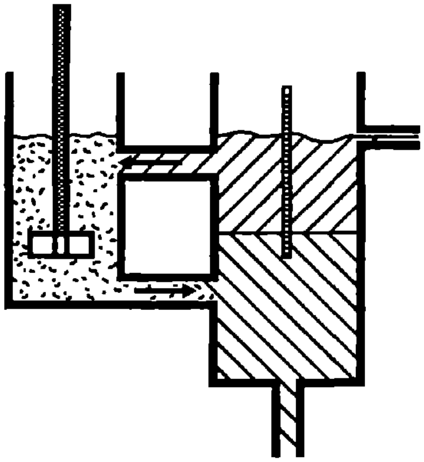
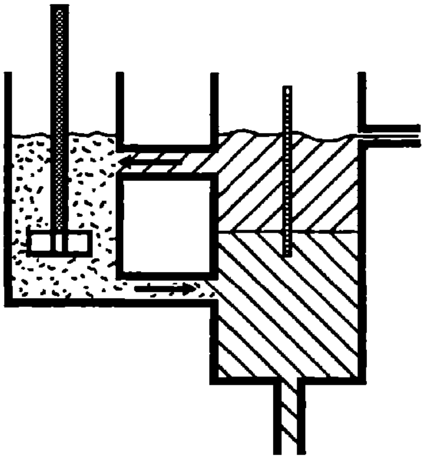
INFORMATION CIRCULAR/1995

PB97-198972

Laboratory Procedures for Hydrometallurgical-Processing and Waste-Management Experiments







UNITED STATES DEPARTMENT OF THE INTERIOR

UNITED STATES BUREAU OF MINES

REPRODUCED BY: NTIS
U.S. Department of Commerce
National Technical Information Service
Springfield, Virginia 22161

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Information Circular 9431

Laboratory Procedures for Hydrometallurgical-Processing and Waste-Management Experiments

By D. C. Seidel

UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES
Rhea Lydia Graham, Director

Library of Congress Cataloging in Publication Data:

Seidel, D. C. (Don C.)

Laboratory procedures for hydrometallurgical-processing and waste-management experiments / by D.C. Seidel.

p. cm. — (Information circular; 1995); 9431.

Includes bibliographical references.

Supt. of Docs. no.: I 28.27:199 . 9431.

1. Hydrometallurgy—Experiments. 2. Factory and trade waste—Experiments. I. Title. II. Series: Information circular (United States. Bureau of Mines); 1995. 9431.

TN688.S43 . 1995 669'.028'3—dc20 95-4202 CIP

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TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Metric Units

cm	centimeter
cm^2	square centimeter
cm^3	cubic centimeter
cm^3/min	cubic centimeter per minute
g	gram
g/L	gram per liter
h	hour
h/d	hour per day
kg	kilogram
kg/m^2	kilogram per square meter
kg/t	kilogram per metric ton
L	liter
L/min	liter per minute
(L/min)/m^2	liter per minute per square meter
m	meter
m^2	square meter
m^3	cubic meter
m·d	meter day
m/min	meter per minute
(m^2/t)/d	square meter per metric ton per day
mg	milligram
mg/L	milligram per liter
mg/m^3	milligram per cubic meter
min	minute
min/rev	minute per revolution
mL	milliliter
mL/min	milliliter per minute
(mL/min)/cm^2	milliliter per minute per square centimeter
mm	millimeter
mV	millivolt
ppm	part per million
rph	revolution per hour
rpm	revolution per minute
s	second
t	metric ton
t/m^3	metric ton per cubic meter
vol %	volume percent
wt %	weight percent
μm	micrometer
°C	degree Celsius

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

U.S. Customary Units

atm	atmosphere
BV	bed volume
BV/h	bed volume per hour
cfm	cubic foot per minute
cfm/ft^2	cubic foot per minute per square foot
ft	foot
ft^2	square foot
ft^3	cubic foot
ft/min	foot per minute
ft^3/rev	cubic foot per revolution
(ft^3/rev)/ft^2	cubic foot per revolution per square foot
(ft^2/st)/d	square foot per short ton per day
gal	gallon
gal/ft^2	gallon per square foot
(gal/ft^2)/rev	gallon per square foot per revolution
gpm	gallon per minute
gpm/ft^2	gallon per minute per square foot
gpm/ft^3	gallon per minute per cubic foot
hp	horsepower
in	inch
in Hg	inch of mercury
lb	pound
lb/ft^3	pound per cubic foot
(lb/ft^2)/rev	pound per square foot per revolution
lb/gal	pound per gallon
(lb·gal)/ft^4	pound gallon per foot to the fourth
lb/h	pound per hour
(lb/h)/ft^2	pound per hour per square foot
lb/st	pound per short ton
oz/st	troy ounce per short ton
psi	pound per square inch
psig	pound per square inch gauge
st	short ton
°F	degree Fahrenheit

Some traditional laboratory equipment, procedures, and data calculations are given in customary units of measure only. The following conversion factors can be used to calculate metric equivalents for these measurements.

To convert from—		To—	Multiply by—
in	inch	centimeter	2.54
ft	foot	meter	0.34
ft^2	square foot	square centimeter	929.03
		square meter	0.092903
ft^3	cubic foot	liter	28.316
gal	gallon	liter	3.7853
lb	pound	kilogram	0.45359
		gram	453.59

Disclaimer of Liability

The procedures described in this report may involve hazardous materials, operations, and equipment. The procedures do not purport to address all of the safety problems associated with their use. It is the responsibility of the user of these procedures to establish appropriate safety and health practices and to determine the applicability of current regulatory limitations prior to use.

LABORATORY PROCEDURES FOR HYDROMETALLURGICAL-PROCESSING AND WASTE-MANAGEMENT EXPERIMENTS

By D. C. Seidel[1]

ABSTRACT

This report describes generic procedures and equipment arrangements for conducting laboratory-scale hydrometallurgical and related waste-management experiments. It provides a starting point for personnel who have received or are receiving professional training, but do not have specific experience in laboratory procedures. With guidance, it also has application as a resource for technician training. The publication contains chapters on laboratory safety, feed-sample preparation, leaching, solids-liquid separation, and recovery from solution.

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INTRODUCTION

Over the years, U.S. Bureau of Mines (USBM) researchers have developed, adapted, and used a wide variety of experimental techniques for bench-scale hydrometallurgical research. Many of these techniques also have application for waste-treatment studies. Descriptions of these procedures are scattered throughout USBM publications, the general technical literature, and company brochures, but no aggregate reference has been available. The purpose of this report is to provide a resource that can be used both for training personnel and for planning mineral processing and waste-management experiments; the scope focuses primarily on equipment and techniques applicable for initiating a new experimental program. The approach assumes that the researcher has studied the literature related to the investigation, but has limited experience in specific experimental techniques. It provides a starting point for personnel who have received or are receiving professional training. With appropriate supervision, it also has application as a guide for technician training.

The report presents a series of monographs on subjects such as laboratory safety, sample preparation, leaching, solids-liquid separation, and recovery from solution. Each chapter includes an extensive list of references.

Hydrometallurgical research is based on scientific principles, but in many ways conducting experiments is an art form. The following quotation from "Leadership Is an Art,"[2] by Max DePree applies for both the technical and safety aspects of every experiment.

> Those of you who have had real experience with machinery and equipment and even buildings know that they have personalities of their own. Intimacy with a job leads one to understand that when training people to do a job, one needs to teach not only the skill of the job but the art of it as well. And the art of it always has to do with the personality of both the operator and the machine. Intimacy is the experience of ownership. This often arises out of difficulty or questions or exasperation, or even survival.

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[2] DePree, M. Leadership Is an Art. Dell, 1989, 148 pp.

CHAPTER 1.—LABORATORY SAFETY OVERVIEW

1.1 INTRODUCTION

Everyone has a responsibility for safety; it is both a legal and moral obligation. Management must establish and maintain a positive, safety-conscious atmosphere, and supervisors must ensure that safety precautions and regulations are followed and that deficiencies are identified and promptly corrected. Laboratory workers are responsible for following procedures for handling and processing chemicals and raw materials safely and for reporting unsafe working conditions to their supervisor.

"All accidents are caused; none are fortuitous. The predominant cause of laboratory accidents is probably the laboratory worker who knowing takes a chance." (Young, 1991, p. 43). In effect, the laboratory worker says, "Even though I know better, I'll do it—just this once!" In conjunction with accidents, Young (1991, p. vii) has presented the following first and second laws of safety, their corollaries, and the conclusions drawn from them:

The first law of safety states—To occur, an accident requires that at least two mistakes occur simultaneously, or almost simultaneously, at the same location. Corollary to the first law: If the required mistakes are not confluent in time and space, one has either a "close call" or a "nonevent."

A close call may or may not be noticed. Close calls involving toxic overexposure, for example, are rarely dramatic and may be missed entirely; a close call that is a small fire instead of a large explosion is usually noticed.

A nonevent is either a single mistake by itself, hence no accident, or two or more mistakes sufficiently separated in time and/or space as not to be even a close call.

The second law of safety states—All accidents prophesy; like other coming events they cast their shadows before them.

Corollary to the second law: The prophecy that an accident will happen appears in the form of a close call or a nonevent.

The conclusions are threefold

- By eliminating the causes of close calls and nonevents, accidents will be avoided.
- If we learn how to identify that a close call or a nonevent has in fact happened, we can then know there was a cause, or causes, which can be identified.
- Once identified, a cause can be eliminated.

Nearly all workplaces have some hazards, but laboratories usually involve a greater variety of potential hazards than most and call for precautions not ordinarily encountered elsewhere. Both physical and chemical hazards exist in hydrometallurgical laboratories. Physical hazards can include fire, explosion, electrical shock, and dangerous equipment. Chemical hazards derive from the acute or chronic toxic effects produced by either the reagents or raw materials being treated. Nearly all laboratory chemicals present some degree of hazard, and all new substances should be handled as though they are toxic.

The primary objective of every safety program is to prevent the occurrence of accidents and, thereby, protect people and property. Related benefits include prevention of unnecessary human suffering, reduction of lost work time from accidents, lower health care and insurance costs, a positively motivated work force, and increased productivity. To be effective, laboratory safety requires a continuous and coordinated effort. Experience shows that piecemeal safety programs do not do the job. Effective laboratory safety requires a formal, written program and mandatory safety rules. Everybody must "get into the act" as a regular routine for safety programs to work.

In the United States, Federal regulations governing laboratory safety and health have been established by the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA). Some individual States have promulgated similar, but generally more restrictive, regulations. Therefore, each laboratory location requires a careful study of applicable regulatory requirements. In general, laboratory activities related to chemical health and safety are governed by more than 100 separate regulations (Clark, 1991, p. 221).

OSHA regulations pertaining to laboratory safety and health are found in Title 29, Code of Federal Regulations (CFR), Part 1910.1000-1500, published by the Office of the Federal Register and sold by the U.S. Government Printing Office, Washington, D.C. Related EPA regulations are located in Title 40, CFR. EPA regulations under the Superfund Amendments and Reauthorization Act (SARA) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) also affect laboratory procedures, related reporting, and notification requirements. Clark (1991, pp. 221-237) has abstracted the OSHA regulations relating to laboratory health and safety and referenced the 29 CFR 1910 sections that apply to specific elements such as personal protection, flammable liquids, compressed gases, air contaminants, etc. Clark has also summarized and referenced the related EPA requirements in 40 CFR for reporting spills and leaks of hazardous chemicals, emergency preparedness programs, and toxic releases. Varnerin (1991, pp. 239-259) has summarized and referenced EPA regulations that apply to the safe disposal of hazardous wastes.

Appendix A of 29 CFR 1910.1450 presents National Research Council (NRC) guidelines for handling hazardous chemicals in laboratories. These recommendations can be used by laboratory personnel to help develop a chemical hygiene plan that will satisfy the requirements of paragraph e of the standard (29 CFR 1910.1450). The following section (1.2) summarizes these recommendations. The complete recommendations are published under the title "Prudent Practices for Handling Hazardous Chemicals in Laboratories" (NRC, 1981). This reference (hereafter referred to as "Prudent Practices") also includes extensive recommendations on other aspects of laboratory safety such as fires and explosions, electrically powered equipment, pressurized and vacuum operations, low-temperature procedures, and corrosive agents.

Each of the chapters in this guidebook also contains a section on safety considerations that apply specifically to subjects treated in that chapter.

Additional laboratory safety references include ACGIH (1992), Alden (1981), Furr (1990), Mahn (1991), MCA (1972), RSC (1983), and Tomb (1985).

1.2 CHEMICAL SAFETY, PLANNING, AND PRACTICE

Paragraph e of title 29 CFR, part 1910, section 1450 requires that a written chemical hygiene plan shall be developed and followed in laboratories where hazardous chemicals are used. The standard defines a "hazardous chemical" as follows:

> "Hazardous chemical" means a chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term "health hazard" includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes or mucous membranes.

Sections .1000 - .1101 of 29 CFR 1910 and appendixes A and B of the "Hazard Communication Standard" (29 CFR 1910.1200) provide further guidance in defining the scope of health hazards and determining whether or not a chemical is to be considered hazardous for purposes of this standard.

The chemical hygiene plan shall indicate the specific measures that will be taken to ensure laboratory employee protection. Elements such as the following must be included:

- Standard operating procedures that will be followed when hazardous chemicals are being used.
- Criteria that will be used to determine and implement control measures to reduce employee exposure to hazardous chemicals.
- Specific measures that will be taken to ensure that fume hoods and other protective equipment are performing properly.
- Provisions for employee information and training as required by the standard.
- Circumstances under which a particular laboratory operation will require prior approval before implementation.
- Provisions for medical consultation and examinations as required by the standard.
- Designation of personnel responsible for implementation of the chemical hygiene plan.
- Provisions for additional employee protection for work using particularly hazardous chemicals such as "select carcinogens" and substances with a high degree of acute toxicity.

All laboratory workers should know and follow the rules and procedures of the chemical hygiene plan.

The following sections (1.2.1 to 1.2.5), which have been abstracted from appendix A of 29 CFR 1910.1450, contain guidelines and recommendations for preparing a chemical hygiene plan. Users should also consult both appendix A and the original "Prudent Practices" (NRC, 1981) reference for more detailed information and justifications. Changing regulatory requirements may supersede any of these general recommendations.

Sections 1.2.1 - 1.2.4 contain recommendations directed primarily at administrators and supervisors. Section 1.2.5 relates primarily to employees who actually handle and work with laboratory chemicals.

1.2.1 General Principles

"Prudent Practices" (NRC, 1981) recommends several general principles for working with laboratory chemicals that include the following:

- *Minimize all chemical exposures*—Because nearly all laboratory chemicals present some hazard, it is prudent to adopt general rather than specific precautions for handling chemicals (see 1.2.5). As a cardinal rule, skin contact with chemicals should be avoided.

- ***Don't underestimate risks***—Even for substances with no known significant hazard, risks should not be underestimated, and exposure should be minimized. One should assume that all substances of unknown toxicity are toxic, and that any mixture will be more toxic than its most toxic component.
- ***Provide adequate ventilation***—Installing and using hoods and other ventilation devices is the best way to prevent exposure to airborne substances. Adequate protection requires careful monitoring of hood performance.
- ***Institute a chemical hygiene program***—Every laboratory should establish a mandatory chemical hygiene program. This program, which must be a regular and continuing effort, should be designed to minimize all chemical exposures.
- ***Observe the permissible exposure limits (PEL) and threshold limit values (TLV)***—OSHA and the American Conference of Governmental Industrial Hygienists have established PEL and TLV. If differences exist, the OSHA limits are primary, and should not be exceeded.

1.2.2 Chemical Hygiene Responsibilities

All levels have responsibility for chemical safety and hygiene. Specific responsibilities include the following:

Chief executive officer—The ultimate responsibility for chemical hygiene within an organization rests with the chief executive officer. This officer and other administrators must provide continuing support for institutional chemical hygiene.

Supervisor of a department or other administrative unit—His level of management carries the responsibility for all chemical hygiene and safety within their respective department or unit.

Chemical hygiene officer—Appointment of a chemical hygiene officer is essential. The chemical hygiene responsibilities, which are usually a component of the laboratory safety officer's duties, must include the following functions:

- Work with administrators and other employees to develop and implement appropriate chemical hygiene policies and practices.
- Monitor the procurement, use and disposal of chemicals and other potentially toxic materials used in the laboratory.
- See that appropriate audits are maintained.
- Help project directors develop precautions and adequate facilities.
- Know the current legal requirements concerning regulated substances.
- Seek ways to improve the chemical safety and hygiene program.

Laboratory supervisor—This supervisor's direct chemical hygiene responsibilities include the following:

- Ensure that workers know and follow the chemical hygiene rules.
- Ensure that appropriate protective equipment is available, that it is in working order, and that adequate training has been provided. Training related to the use of material safety data sheets (MSDS) is particularly important (see section 1.2.4.10).
- Provide regular, formal hygiene and housekeeping inspections including routine inspections of emergency equipment.
- Know the current legal requirements concerning regulated substances being used in the laboratory.
- Determine the required levels of protection and equipment.
- Ensure that facilities and training for the use of any material being ordered are adequate.

Laboratory worker—Each laboratory worker is responsible for:

- Planning and conducting each operation or experiment in accordance with the institutional chemical hygiene and safety procedures. Laboratory workers should become thoroughly familiar with the MSDS (see 1.2.4.10) information available for each chemical or substance used.
- Developing and maintaining good personal chemical hygiene and safety habits.

1.2.3 Laboratory Facility

Chemical hygiene and safety plans must thoroughly consider factors such as the design, maintenance, usage, and ventilation of the laboratory.

Design—All laboratory facilities should be designed to have

- An appropriate general ventilation system with all air intakes and exhausts located to avoid intake of contaminated air.
- Adequate, well-ventilated stockrooms and storerooms.
- Laboratory hoods and sinks.
- Other safety equipment including eyewash fountains and drench showers.
- Arrangements for waste disposal.

Maintenance—All chemical safety- and hygiene-related equipment such as hoods, safety showers, etc., should undergo continuing appraisal and be repaired or modified if inadequate.

Usage—Both the type of work conducted and its scale must match the physical facilities available, especially the ventilation capacity.

Ventilation—Adequate ventilation is a critical requirement for all laboratories. Factors to be considered include the following:

- General laboratory ventilation should provide a source of air for breathing and for input into local ventilation devices. The overall ventilation system should ensure that the laboratory air is continuously being replaced so that concentrations of toxic or odoriferous substances do not increase during the working day. The system should not be relied upon for protection from toxic substances released into the laboratory from experiments or other sources.
- If laboratory workers spend most of their time working with chemicals, the laboratory design should provide at least 2.5 linear feet (0.75 m) of hood space for every two workers. "Prudent Practices" (NRC, 1981, pp. 201-206) recommends that for work with substances of unknown toxicity each hood should have a continuous monitoring device to allow convenient confirmation of adequate hood performance before each use.
- Canopy hoods, snorkels, ventilated storage cabinets, etc., should be provided as needed. Each canopy hood and snorkel should have a separate exhaust duct.
- Some ventilation areas require special precautions. For example, exhaust air from glove boxes and isolation rooms should be passed through scrubbers or other treatment before release into the regular exhaust system.
- Normally 4 to 12 room air changes per hour will provide adequate general laboratory ventilation, if local exhaust systems such as hoods are used as the primary method of control. The airflow into and within a hood should not be excessively turbulent. For most hydrometallurgical experiments hood face velocities of 100 linear feet per minute provide adequate pickup. When highly toxic chemicals, carcinogens, or radioactive agents are being used, the minimum hood face velocity should be 150 linear feet per minute.
- Trained personnel should monitor the ventilation system performance on a regular basis (at least every 3 months). Whenever changes are made in local ventilation, the monitoring and evaluation should be repeated.

1.2.4 Chemical Hygiene Plan

Section 1.2 outlined the basic components of chemical hygiene plan. The following sections (1.2.4.1 to 1.2.4.11) provide additional information and recommendations on various components that should be covered by the chemical hygiene plan.

1.2.4.1 Basic Rules and Procedures

The basic rules and procedures that laboratory workers should know and follow are discussed in section 1.2.5. These rules and procedures constitute a critical component of the chemical hygiene plan.

1.2.4.2 Chemical Procurement, Distribution, and Storage

The following paragraphs review the related subject areas that should be covered in the chemical hygiene plan. Part II of "Prudent Practices" (NRC, 1981, pp. 215-219) presents additional recommendations.

- *Procurement*—Before a substance is ordered and received, those who will be using the substance should know the proper handling, storage, and disposal requirements. No container should be accepted without a complete identifying label and the appropriate MSDS (Genium, 1993) information. Preferably all substances should be received in a central location for cataloging and inventory control.
- *Stockrooms-storerooms*—Chemicals known to be highly toxic should be stored in locally ventilated storage areas in unbreakable chemically resistant secondary containers. These chemicals should be kept in a locked storage cabinet with controlled access. Qualified personnel should examine stored chemicals at least annually for replacement, deterioration, and container integrity. Any preparation of repackaging should be carried out in an area separated from the stockroom.
- *Distribution*—When chemicals are hand-carried within the laboratory, the worker should place the container in an outside container or bucket.
- *Laboratory storage*—Only minimum working quantities of toxic materials should be present in the work area; the amounts permitted should be as small as practical. Storage on bench tops and in hoods is inadvisable. Periodic inventories should be conducted, and unneeded items should be either returned to the storeroom or properly discarded.

1.2.4.3 Environmental Monitoring

Although regular instrumental monitoring of airborne concentrations is usually not justified or practical in laboratories, such monitoring becomes desirable when testing or redesigning hoods or other ventilation devices. Also, when highly toxic substances are continuously used or stored in the laboratory, frequent monitoring (e.g., three times per week) may be appropriate, and in some instances may be required by pertinent regulations.

1.2.4.4 Housekeeping, Maintenance, and Inspections

A schedule should be established for housekeeping, maintenance, and inspections. When housekeeping standards fail, safety performance inevitably deteriorates. A clean, orderly laboratory promotes safety. For example, work areas should be kept free of obstructions and floors should be cleaned on a regular schedule. Stairways and halls should not be used as storage areas, and emergency equipment or utility controls should never be blocked.

Formal housekeeping and equipment inspections should be conducted at least quarterly, and informal inspections should be continual. Safe, efficient laboratory operations require good equipment maintenance. Maintenance plans should include procedures to prevent restarting out-of-service equipment. Regular inspection and maintenance of safety equipment are particularly critical. Safety showers and eyewash fountains should be inspected at intervals of not less than 3 months.

1.2.4.5 Medical Program

Regulatory requirements specify that medical surveillance programs should be established for some operations. For example, anyone whose work involves regular and frequent handling of toxicologically significant quantities of substances such as arsenic-bearing materials or chemicals should be included in a medical surveillance program.

Every laboratory should have trained first-aid personnel available during working hours. Arrangements should also be made for emergency room service that includes medical personnel trained in the proper treatment of chemical exposures.

1.2.4.6 Protective Apparel and Equipment

Every laboratory area should have available protective equipment and apparel such as the following:

- An eyewash fountain.
- An easily accessible drench-type safety shower.
- Appropriate fire extinguishers.
- Protective apparel compatible with the required degree of protection for the substances being handled.
- Equipment for suitable respiratory protection for emergencies or when effective engineering controls are not possible.
- Fire alarms and emergency communication equipment.

1.2.4.7 Accident Reporting and Records

Every laboratory should establish a system to ensure that all accidents or emergencies are promptly reported to the persons responsible for safety matters. Accident records should be written and retained.

Inventory and usage records for substances with moderate chronic or high acute toxicity, e.g., HF or HCN, should conform to regulatory requirements. These records should document the quantity on hand, the amounts used, and the workers involved. For substances with high chronic toxicity, e.g., dimethylmercury and nickel carbonyl, the records should also include the dates of use.

The chemical hygiene plan and the laboratory records should document that the facilities available and the precautions taken comply with the current state of knowledge and regulatory requirements.

1.2.4.8 Signs and Labels

Prominent signs and labels of the following types should be posted throughout the laboratory:

- A list of emergency telephone numbers to be called in the event of fire, accident, or hazardous chemical spill should be available at every telephone. "Prudent Practices" also recommends posting the telephone numbers of laboratory workers and their supervisors.
- All containers including waste receptacles should have labels that identify their contents.
- Signs should be posted to identify clearly the location of safety showers, eyewash stations, other safety and first-aid equipment, and areas where food and beverage consumption or storage are permitted.
- Specific warning signs should be posted for any area where special or unusual hazards exist.

1.2.4.9 Spills and Accidents

A written emergency plan should be established and communicated to all personnel; it should include procedures for evacuation, medical care, reporting requirements, and drills. The plan should also define procedures for incidents such as ventilation failures and chemical spills. Each laboratory should have a well-marked and readily accessible looseleaf binder containing MSDS for all chemicals being used. All laboratory workers should know and regularly review the "Section 7. Spill, Leak, And Disposal Procedures" summarized on these sheets. In addition to chemical spill containment and cleanup procedures, the spill control policy should also consider prevention strategies.

The laboratory should install an alarm system to alert people in all parts of the facility including isolated areas such as coldrooms.

Not only should all accidents or near accidents be reported, but they should also be carefully analyzed and the results distributed to all who might benefit.

1.2.4.10 Information and Training Programs

Safety information and training programs should be designed to ensure that all individuals at risk are adequately informed about their work in the laboratory, its risks, and what to do if an accident occurs. Every laboratory worker should know the location and proper use of available protective apparel and equipment, and some full-time laboratory personnel should receive specific training on emergency procedures and the proper use of emergency equipment. First-aid training for all personnel should also be available and encouraged. To be effective, all of these training programs must be regular continuing activities.

Literature and consulting advice concerning laboratory hygiene and general safety should be readily available to all laboratory personnel. The availability of information such as MSDS for the chemicals being used in the laboratory is mandatory. These sheets, which contain descriptive toxicity and handling information, are designed to serve as the basis for all chemical-hazard communication programs. The MSDS use an extensive list of acronyms and abbreviations; detailed definitions and explanations of these terms are presented in the glossary section of the MSDS collection published by Genium Publishing Corp. (1993, v. 3, pp. 1-18). Currently, every MSDS contains nine sections; the topics discussed in each section are listed below.

Section 1. *Material Identification*

Material name, description (origin and uses), other designations, manufacturer

Section 2. *Ingredients and Occupational Exposure Limits*

OSHA PEL (skin), ACGIH TLV (skin), National Institute for Occupational Safety and Health (NIOSH) REL, toxicity data (human oral)(human inhalation), etc.

Section 3. *Physical Data*

Boiling point, melting point, vapor pressure, vapor density, molecular weight, specific gravity, water solubility, percent volatile by volume, appearance and odor, etc.

Section 4. *Fire and Explosion Data*

Flash point, autoignition temperature, lower explosive limit LEL, upper explosive limit UEL, extinguishing media, unusual fire or explosion hazards, special fire-fighting procedures, etc.

Section 5. *Reactivity Data*

Stability-polymerization, chemical incompatibilities, conditions to avoid, hazardous products decomposition, etc.

Section 6. *Health Hazard Data*

Carcinogenicity, summary of risks, medical conditions aggravated by long-term exposure, target organs, primary entry, acute effects, chronic effects, first-aid (eyes) (skin) (ingestion), etc.

Section 7. *Spill, Leak, and Disposal Procedures*

Spill leak, waste management and disposal, OSHA designations, EPA designations, etc.

Section 8. *Special Protection Data*

Goggles, respirator, warning, ventilation, safety stations, contaminated equipment, other, comments, etc.

Section 9. *Special Precautions and Comments*

Storage requirements, special handling-storage, engineering controls, other precautions, comments, transportation data, etc.

Laboratory workers should be encouraged to use and regularly review the MSDS and all other safety information resources.

1.2.4.11 Waste Disposal Programs

The objective of a laboratory waste disposal program is to meet Federal and State requirements and to ensure that chemicals are disposed of in such a way that people, other living organisms, and the environment are subjected to minimal harm. Specific recommendations related to the waste disposal component of the chemical hygiene plan include the following:

- The waste disposal program should specify how waste is to be collected, segregated, stored, and transported. The waste transportation must conform to Department of Transportation regulations.

- Unlabeled containers of chemicals should be disposed of promptly by using appropriate procedures. In at least some instances, this may require analyses to identify the contents.
- Laboratory workers should remove waste from laboratories to a temporary central location at least once a week. Accumulated wastes should be removed from this central storage area on a regular basis. The schedule will depend on the type and amount of waste generated and also on the laboratory's Waste Generator Classification as defined by applicable Federal and State regulations.
- Final disposal procedures depend on the type of waste being generated. Incineration is acceptable for many combustible laboratory wastes, but solid wastes usually require burial in an approved disposal site. Indiscriminate disposal by pouring waste chemicals down the drain or adding them to mixed refuse for landfill burial is unacceptable. Also, hoods should not be used as a means of disposal for volatile chemicals. Disposal by recycling or chemical decontamination should be used when possible.

1.2.5 Basic Rules and Procedures for Working With Chemicals

In addition to the rules and procedures cited in sections 1.2.1 to 1.2.4, the chemical hygiene plan developed for a hydrometallurgical laboratory should include rules and procedures such as those presented in this section. Both general rules and rules for several specific types of chemicals are discussed.

1.2.5.1 General Rules

"Prudent Practices" (NRC, 1981) recommends that the following general rules should be followed for all laboratory work with chemicals:

- *Accidents and spills*

Eye contact: Promptly flush eyes with water for a prolonged period (15 min) and seek medical attention.

Ingestion: Encourage the victim to drink large amounts of water.

Skin contact: Promptly flush the affected area with water and remove any contaminated clothing. If symptoms persist after washing, seek medical attention.

Cleanup: Promptly clean up spills, using appropriate protective gear and equipment as stated in the MSDS. The cleanup should be carried out by properly trained personnel. Section 7 of each MSDS contains concise information on applicable cleanup procedures and precautions.

- *Avoidance of "routine" exposure*

Avoid unnecessary exposure to chemicals by any route. For example, (1) do not smell or taste chemicals, (2) vent apparatus that may discharge toxic chemicals (e.g., vacuum pumps, distillation columns, etc.) into local exhaust device, and (3) test glove boxes and carefully inspect the gloves before use.

- *Choice of chemicals*

Use only those chemicals for which the quality and capacity of the available ventilation system is adequate. If changes have been made in the ventilation system, the capacity should be thoroughly tested to ensure that workers have adequate protection.

- *Eating, smoking, etc.*

Contamination of food, drink, and smoking materials is a potential route for exposure to toxic substances. Well-defined areas should be established for storage and consumption of food and beverages. No food should be stored or consumed outside of these areas. Smoking areas should also be well-defined.

- *Equipment and glassware*

Handle and store laboratory glassware with care to avoid injury or damage; do not use damaged equipment or glassware. Use extra care with Dewar flasks and other evacuated glass apparatus; tape or shield them to protect workers should an implosion occur. Adequate hand protection should be used when inserting glass tubing into rubber stoppers or making hose connections.

- *Exiting*

Wash areas of exposed skin well before leaving the laboratory; washing hands before eating is particularly important.

- *Horseplay*

Avoid all horseplay, practical jokes, or other behavior that might confuse, startle, or distract another worker.

- *Personal apparel*

Confine long hair and loose clothing. Wear shoes at all times in the laboratory, but do not wear sandals, perforated shoes, or sneakers.

- *Personal housekeeping*

Keep the work area clean and uncluttered; properly label and store all chemicals. Clean up the work area on completion of an operation or at the end of each day.

- *Personal protection*

Ensure that appropriate eye protection is worn by all persons, including visitors, in all areas where chemicals are handled or stored. Wear appropriate gloves when the potential for contact with toxic materials exists; inspect the gloves before each use and wash them before removal. Use appropriate respiratory equipment when air contaminant concentrations are not sufficiently restricted by engineering controls; consult and follow specific regulatory requirements. Remove laboratory coats immediately upon significant contamination. Avoid use of contact lenses in the laboratory; if contact lenses are necessary, special precautions will be required. In general, use any other protective apparel or equipment as appropriate for the work being conducted.

- *Planning*

Seek information and advice about hazards, and plan the positioning of equipment before beginning any new operation. The planning process should include a job safety analysis for every new experimental operation (see 1.2.5.3).

- *Unattended operations*

Leave lights on, place an appropriate sign on the door, and provide for containment of toxic substances in the event of failure of a utility service (such as cooling water) to an unattended operation.

- *Use of hood*

Use the hood for any operation that might release toxic chemical vapors or dust. As a rule of thumb, use a hood or other local ventilation device when working with any appreciably volatile substance with a time-weighted average (TWA) of less than 50 ppm. Confirm adequate hood performance before use; keep hood closed at all times, except when adjustments within the hood are being made; do not store chemicals in hoods; equipment in hoods should be positioned so that it will not block vents or airflow.

- *Vigilance*

Be alert to unsafe conditions and see that they are corrected as soon as detected.

- *Waste disposal*

Ensure that the plan for each operation or experiment includes provisions and training for waste disposal. Deposit chemical wastes in appropriately labeled receptacles and follow all other waste disposal procedures of the chemical hygiene plan. Do not discharge to the sewer concentrated acids or bases, highly toxic, malodorous, or lachrymatory substances. Also do not discharge any substance that might create fire or explosion hazards, cause structural damage, obstruct the flow, or interfere with the biological activity of waste water treatment plants.

1.2.5.2 Working With Moderate and High Toxicity Chemicals

Before working with any chemical, laboratory workers should consult and become thoroughly familiar with the information presented on the MSDS for that substance. This procedure is particularly important for substances that have moderate or high toxicities. For example, "Prudent Practices" (NRC, 1981, pp. 39-56) classifies hydrofluoric acid and hydrogen cyanide in the category of chemicals with moderate chronic or high acute toxicity, whereas nickel carbonyl is in the category that includes substances with high chronic toxicity. All of these substances require special precautions.

1.2.5.3 Job Safety Analysis (JSA)

A JSA breaks a job or operation down into its component parts, identifies the potential hazards in each component, and develops safe procedures to eliminate the hazards. For existing operations, the JSA is based on detailed observation of the worker performing the job. In hydrometallurgical research operations, the JSA examines proposed laboratory procedures to prevent an accident from happening. When properly implemented, it constitutes one of the foremost proactive steps in a safety program.

The National Safety Council has developed and published guidelines for performing a JSA (1988). The general procedure consists of the following four steps:

a. ***Job selection***—The term "job" in a JSA is defined as a task, procedure, or activity that a worker performs as part of his or her duties. When establishing job priorities for JSA's, the "worst first" criteria is a good approach and likely to yield the quickest results. Factors to consider in job selection for existing operations include:

- Accident frequency.
- Accident severity.
- Potential for severe injuries.

Even if accidents have not occurred, the JSA should be performed on the following type of jobs:

- New jobs (always).
- Special jobs (e.g., those that may expose many employees to risk, and also those covered by strict standards or regulations).
- Routine jobs with unknown accident potential.

The following references contain relevant information on job selection factors: Peterson (1975), and Rankin (1986).

b. ***Job breakdown***—Before attempting to define the hazards, a job should be broken down into a sequence of steps. This is the most difficult part of a JSA. Detailed information on job breakdown techniques has been published by Moore (1981) and by OSHA (1981). The key is to list those steps that advance the work. Experience helps to overcome the problem of being either too narrow or too broad. The job breakdown sequence includes the following components for jobs that are already in operation:

- Designate the right individual to break down the job or operation into its critical components. Desirable qualifications include experience, capability, a cooperative approach, and a willingness to share ideas.
- Brief the designee on the purpose and expected benefits of the JSA and how the information will be used.
- The designee should observe the worker performing the operation in a normal manner.
- The designee should break the job down into 5 to 15 steps beginning with action words such as remove, lift, open, etc.
- The designee should review the steps with the worker to confirm their accuracy and completeness.

If the job or operation is a new one, such as often occurs in hydrometallurgical research and development projects, the JSA procedure uses the same general approach to evaluate the projected steps of the research program. The supervisor and workers jointly develop a task analysis for the projected research.

c. ***Identify hazards***—For either an existing operation or a planned research project, this critical step involves identifying and examining all potential hazards. These hazards include both those created by the research or operational procedures as well as those produced by the environment. Again, for research projects and other new operations, both supervisors and workers should participate in this process. Input from others experienced with the type of work to be performed is highly desirable.

d. ***Hazard elimination and control***—The process for eliminating hazards and developing safe job procedures should include input from everyone associated with the work. Invariably, eliminating a job hazard will involve changing the job in some manner. In general, solutions fall into the following four categories:

- Find a new way to do the job. In research work this option may prove limited, but all options should be explored.
- Change the environment. This may involve such things as a different type of equipment or the installation of special exhaust ventilation.
- Modify operating procedures. It may be possible to change or modify the specific actions that workers must take or not take to avoid harm while they carry out the job. This can also include special training for project personnel.
- Reduce the frequency of doing the job. This approach applies primarily to repetitive jobs such as those encountered in manufacturing. Research work, however, may be able to accomplish this objective to a degree by careful planning and using statistically designed experimental programs.

The National Safety Council recommends using a form such as that shown in figure 1.1 for developing a JSA. This general form is applicable for operations such as hydrometallurgical research experiments.

The overall JSA process should include review of the initial JSA draft by the responsible safety office and a safety committee or other appropriate review group. The review and final approval are usually an interactive process, and several modifications or revisions of the proposed experimental procedures may be necessary.

An effective JSA program takes time, both to develop and implement, but it has proven to be a productive accident prevention tool. It also can indirectly benefit a laboratory group because the procedure encourages teamwork between supervisors and their employees and empowers employees to decide about the critical components in their own jobs. The overall approach should focus on the process rather than the written JSA product. The major benefit derives from having supervisors and employees go through the JSA experience.

1.2.6 Other Safety Recommendations

The recommendations in sections 1.2.1 through 1.2.5 relate primarily to the prevention of toxic exposure. Subsequent chapters present additional recommendations such as those directed toward prevention of physical injury. These additional recommendations are as follows:

Chapter 2.—Feed Sample Preparation
  2.7 Safety
    2.7.1 Dust Collection
    2.7.2 Equipment Guards
    2.7.3 Noise Protection

Chapter 3.—Leaching
  3.7 Safety
    3.3.1 Introduction
    3.3.2 Corrosive or Toxic Agents
    3.3.3 Explosive Characteristics
    3.3.4 Other considerations

Chapter 4.—Solids-Liquid Separation
    4.4.1 Introduction
    4.4.2 General Practices
    4.4.3 Specific Considerations

Chapter 5.—Recovery From Solution
    5.2.6 Safety (Ion Exchange)
    5.3.2 Safety (Carbon Adsorption)
    5.4.6 Safety (Solvent Extraction)

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Figure 1.1

(Page __of__)

Written by:	Concurred by:	Approved by:
For:		Number:
Location:		Date:

OPERATION	DETAILS OF OPERATION	HAZARD	PRECAUTIONS

Sample for job safety analysis of hydrometallurgical laboratory operating procedures.

CHAPTER 2.—FEED SAMPLE PREPARATION

2.1 INTRODUCTION

Experimental results cannot be better than the sample being tested. Consequently, both sample selection and preparation become particularly crucial steps in the overall metallurgical evaluation process.

A sample can be defined as a small representative portion of a relatively large amount of material. For relevant test results it must contain, in unchanged percentages, all of the constituents in the original material. The sample must be selected in such a manner that it closely represents the parent material in its physical and chemical properties, e.g., particle size, distribution, and chemical or mineralogical composition. Particle-size segregation is particularly important because every time an ore is handled segregation occurs, and typically both the mineral composition and other properties vary with particle size. Also, the sample size must be convenient for analysis and testing. The sampling error should not exceed the error in assaying. Metallurgical test samples are, therefore, nearly always based on a combination of acknowledged compromises. Obtaining samples that are completely representative of the whole in all aspects, except bulk, is seldom realized when heterogeneous mineral mixtures are sampled. In hydrometallurgical experiments, the potential for variability between samples must always be considered.

2.2 TYPES OF SAMPLES AND SAMPLE COLLECTION

Hydrometallurgical research is typically conducted on either raw ore samples or physical beneficiation concentrates. Related waste management investigations most often focus on tailings or other solid wastes.

No single ore is identical to another because the rocks that make up an ore are complex assemblages of minerals and can differ widely in composition and texture. Even within a given deposit, significant variations can be encountered from one part of the deposit to another. A process flowsheet cannot be realistically optimized for all variations; invariably it is a compromise of many factors. Collecting and studying two classes of samples almost always pays dividends. The first class of sample attempts to simulate an overall composite or average mill feed. The second should be a group of samples representing the variability that may be encountered in various parts of the deposit.

Preferably, the team that selects even the preliminary metallurgical test samples should include geologists, mineralogists, mining engineers, and process metallurgists. Participation in the sampling operation significantly improves the potential for successful process development because it gives the metallurgist a better appreciation of both the variability that may be encountered and the sampling process limitations. The team approach also helps to ensure that effective communication and compatible records will be maintained throughout the overall project development program.

2.2.1 Sample Sources

Metallurgical samples can derive from a variety of different sources, such as outcrops, mine faces, drill cores, stockpiles, etc. The character and quantity of the required sample will vary greatly with the complexity, type, and mineralization of the source. The following definitions for samples collected from mine face and other sources have been adapted from "A Dictionary of Mining, Mineral, and Related Terms" (Thrush, 1968).

- *Channel samples*—A channel sample consists of all particles, fragments, and dust from a channel of uniform width and depth cut across the face or bank of an exposure of ore or mineralized rock. Typically, channel sampling yields a reliable representation of the grade and characteristics of the sampled occurrence. Dimensions of the channel vary with the material being sampled. As a general guideline, Compton (1962, p. 183) states that the dimensions of a typical channel in a rock face would be approximately 1 in deep and 2 to 4 in wide. McKinstry (1948, p. 40) recommends that the channel sample length should be relatively short. A 20-ft-wide vein of homogeneous ore should be sampled in four 5-ft sections. Separate samples should be collected from each ore zone, and a relatively constant ratio between sample length and sample weight should be maintained.
- *Chip samples*—Chip sampling is a variation of channel sampling, in which, because of the hardness of the rock, shape of the deposit, or other working difficulty, a true channel sample cannot be taken. The chip sample consists of a regular series of ore chips or rock chips taken either in a continuous line across an exposure or at uniformly spaced intervals. Samples are usually collected using a pick, but on extremely hard rock a hammer or a moil, which is typically a short pointed length of drill steel, may be required. When possible, chip samples should be taken in such a manner that the chips fall directly onto a clean collecting sheet or into a collecting vessel. Chip samples are less accurate than conventional channel samples because, for example, it is difficult to

avoid oversampling in the softer ore zones and undersampling in hard zones. Preliminary prospecting often uses the chip-sampling technique.

- *Grab samples*—A grab sample consists of mineral or rock fragments collected more or less at random from an outcrop, or as float, or from a dump or pile. When sampling piles, it is usually desirable to lay off the surface of the pile in squares by more or less accurately measured lines, and a grab is taken at each intersection. In general, the grab-sampling process depends on the judgment and experience of the individual collecting the samples.

Grab samples are used primarily in connection with examination of the characteristic minerals present rather than for valuation. When using grab samples for process evaluation studies, the potential variability of the material should be carefully considered. In fact, grab samples can often be applicable for evaluating the variability of a deposit. If at all possible, grab samples collected from piles or dumps should be supplemented by trench samples.

- *Trench samples*—The term trench sampling refers to a refinement of grab sampling. The material to be sampled is spread out flat and channeled in one direction. Trench samples are taken at regular intervals along the channel. Preferably, the procedure is repeated with several other channels in different directions until a sample of the desired size has been collected.
- *Drill samples*—Various types of drill samples are often used in process research and development studies. Sections of the core or cuttings from the drilling operations are generally split or quartered. One of these splits or quarters may be reserved for metallurgical investigations. Preparing meaningful composites from drill core or cuttings requires close coordination and communication among the geologists, mining engineers, and the metallurgists.
- *Auger samples*—Samples of relatively soft materials such as tailings, laterites, and some placers can be recovered by various types of auger drills. Holes are augered using a grid system, and the sample intervals within each hole are usually no more than 5 ft (1.5 m). If the material being drilled is not at least relatively cohesive, extensive mixing can occur during the augering operation.

Exploration programs should include provisions for collecting metallurgical samples. For example, field personnel can place excess drill cuttings or trench samples in plastic-lined sacks. These sacks can be stored in drums near the sample site. The metallurgical samples can be selected from these materials after the drilling data and other exploration information are available. It is also desirable to save the plus 6-mesh reject material produced during the preparation of the exploration program analytical samples. The samples should be labeled and kept separate until sufficient information is available to prepare meaningful composites.

2.2.2 Sample Size

A relevant test sample must contain, in unchanged percentages, all of the constituents in the original material. The weight of sample required to contain this statistically valid representation of the whole depends on interrelated factors such as the following:

- The particle size.
- The grade of the material.
- The homogeneity.

Usually the method used to determine the required sample weight is based on experience with a particular ore or material or experience with ores in general. An example of the general experience approach is shown in table 2.1, which has been adapted from information assembled by Richards and presented by Behre and Hassialis (1945, pp. 19-22). Columns 1 through 6 show the minimum sample weights required for various passing sizes (diameter of the largest piece). The ore types range from very low grade or very uniform materials to very rich or exclusively spotty ores. In general, column 1 applies to iron ores. Column 2 applies to low-grade lead, zinc, copper, and most sandstone uranium ores. The weights in column 2 may also apply to uniformly distributed low-grade pyritic gold ores that do not contain native gold. If the valuable minerals are less uniformly distributed, then columns 3 and 4 apply. Columns 5 and 6 apply to ores containing fine particles of native gold or silver, and also to other spotty ores. Column 7 lists the minimum permissible sample weights suggested by Richards for gold ores. For silver ores, Richards suggests one-tenth of these amounts. When using this table, one should carefully consider that the terms "grade" and "uniform" (as used in columns 1 and 2) are not always synonymous. For example, an ore may be very low grade and at the same time very spotty.

Figure 2.1 shows a second set of conservative guidelines (Cooper, 1985, p. 30-14). These guidelines are based on the probability of a single particle containing a proportion of the minerals for which the material is to be sampled and analyzed. The sample size versus maximum particle-size relationships in figure 2.1 are based on the following general equation:

$$m = k\,d^n$$

Table 2.1.—Sample weights at different particle sizes, pounds

Diameter of largest piece			1	2	3	4	5	6	7
in	mm	mesh	Very low grade or very uniform ore	Low-grade or uniform ore	Medium ore	Medium ore	Rich or spotty ore	Very rich or exclusively spotty ore	Gold ore, minimum
8	203.2	NAp	19,200	64,000	—	—	—	—	—
6	152.4	NAp	10,800	36,000	80,000	—	—	—	—
5	127.4	NAp	7,500	25,000	55,550	—	—	—	—
4	101.6	NAp	4,800	16,000	35,556	80,000	—	—	—
3	76.2	NAp	2,700	9,000	20,000	45,000	—	—	—
2.5	63.5	NAp	1,875	6,250	13,888	31,250	80,000	—	—
2	50.8	NAp	1,200	4,000	8,889	20,000	51,200	—	10,000
1.5	38.1	NAp	675	2,250	5,000	11,250	28,800	—	5,000
1.25	31.7	NAp	469	1,563	3,472	7,813	20,000	—	—
1.0	25.4	NAp	300	1,000	2,222	5,000	12,800	—	2,000
0.75	19.05	NAp	169	563	1,250	2,813	7,200	—	1,000
0.625	15.87	NAp	117	391	868	1,953	5,000	—	—
0.500	12.70	NAp	75	250	556	1,250	3,200	—	400
0.375	9.525	NAp	42	141	313	704	1,800	—	300
0.3125	7.938	NAp	29	98	217	488	1,250	—	—
0.250	6.350	NAp	19	63	139	313	800	27,550	200
0.1875	4.763	NAp	10.5	35	78	176	450	15,500	100
0.131	3.327	6	5.15	17.2	38.1	86	220	7,560	75
0.093	2.362	8	2.6	8.65	19.2	43	111	3,810	50
0.065	1.651	10	1.29	4.3	9.5	21.5	55	1,890	—
0.046	1.168	14	0.65	2.16	4.8	10.75	28	953	25
0.0328	0.833	20	0	1.075	2.37	5.38	13.76	473	10
0.0232	0.589	28	0.322	0.539	1.20	2.69	6.90	238	—
0.0164	0.417	35	0.162	0.269	0.59	1.345	3.44	118	4
0.0116	0.295	48	0.081	0.135	0.30	0.673	1.73	60	1
0.0082	0.208	65	0.041	0.067	0.15	0.336	0.86	30	—
0.0058	0.147	100	0.010	0.034	0.075	0.168	0.43	15	—
0.0041	0.104	150	0.005	0.017	0.038	0.084	0.215	8	—
0.0029	0.074	200	0.0025	0.009	0.019	0.042	0.107	—	—

NAp Not applicable.

NOTE.—Dashes are used to indicate data not available.

Source: Arranged by Richards; presented in Taggart (1945, pp. 19-22).

where m is the minimum weight of sample to achieve a specified sampling accuracy, k is a probability constant, and d is maximum particle size. For the ore types shown, the probability constant k and the value of the exponent n are derived from actual sampling experience.

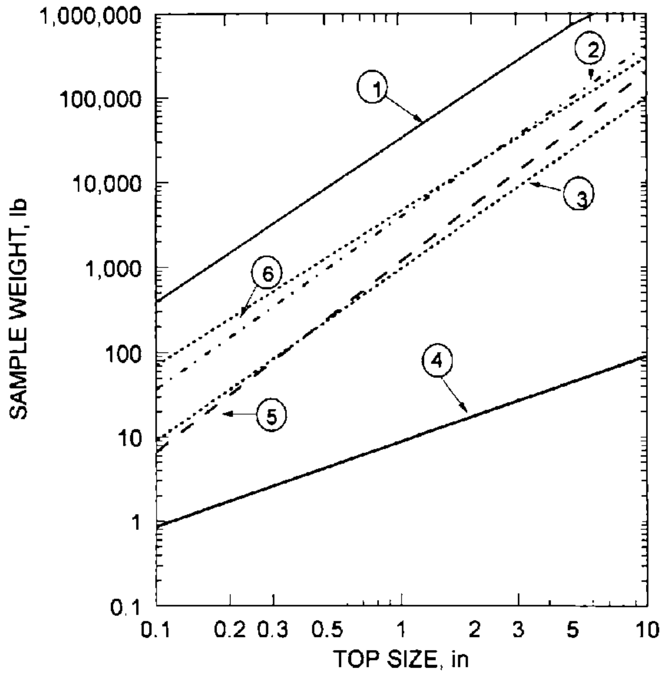
The information presented in table 2.1 and figure 2.1 can be used as general guidelines, but if spotty ores or materials are being tested, a more comprehensive approach, such as the procedures developed by Gy (1976), should be carefully considered. For example, the variability of the ore at different sizes and the distribution of the values among the various sizes may be critical. In nearly all instances, the between-sample variation of both the test samples and the analytical samples should be evaluated.

If only a relatively small amount of ore or other feed material is available, reducing the total quantity of material to minus 1/4-in or minus 10 mesh before proceeding is usually prudent.

When an ore or other material contains relatively large pieces of malleable minerals such as native gold, silver, or copper, the above guidelines will not hold, particularly during the final stages of the sampling procedure. Malleable materials may roll out as flat scales, cylinders, or spheres, and require special handling (see section 2.4.6.2).

Advanced methods for computing sample weights required to give the desired limits of error have been developed by Gy (1963) and summarized by Cooper (1985, pp. 30-06 to 30-10). A description of the sampling slide rule developed by Gy was presented by Ottley (1966). Gy

Figure 2.1



KEY

No.	k	n	Ore type application
1	30,000	2	Gold.
2	3,000	2	Silver.
3	1,000	2	Low grade, uniform distribution.
4	9	1.5	Base metals, high grade.
5	1,000	2.13	Base metals, low grade highly variable composition.
6	3,500	1.8	Average grade, variable distribution.

k probability. n experimental exponent.

Sample weight versus particle size.

(1976) published a comprehensive article on a general theory of sampling particulate material. Sample-size calculations based on fundamental probability theory have also been discussed by Behre and Hassialis (1945) and by Becker and Hazen (1961). These procedures can have significant applications, but during the initial phases of a metallurgical investigation, the required data and information may not be available.

2.2.3 Sample Handling and Preservation

Appropriate sample-handling and preservation procedures depend upon the type of material being handled. For example, a material that tends to oxidize may require storage in sealed containers or even purging with an inert gas. This approach may be particularly important if surface characteristics are critical. Preserving the moisture content of the ore will also require sealed containers. Another preservation technique involves freezing the sample and storing it in this condition. This procedure suppresses not only chemical oxidation, but also biological activity.

The type and strength of the sample container used must correspond to the particle size and other characteristics of the sample. If the sample is to be shipped for any distance, metal containers will probably be needed if the particle size is 3 in (7.6 cm) or larger. Cloth or even paper sacks may be appropriate for materials such as dry percussion drill cuttings. Using double sacks, i.e., one inside the other, is nearly always desirable. Full plastic liners are recommended for moist samples. The thickness of the liner material depends on both the sample particle size and the size of the container. Polyethylene liners suitable for 55-gal barrels normally have a thickness of at least 6 to 8 mils.

2.3 SAMPLE IDENTIFICATION

In every metallurgical processing evaluation, a sample numbering and identification system should be set up at the very start of the sampling program. When working with samples from exploration or mining programs, it may be desirable to adopt an identification system that extends the system used by the geologists or mining engineers to designate the various ore types or horizons. In all cases, a permanent, detailed record should be established that references the sample number to all critical information such as the location where the sample was taken, the sampler, the sampling dates, shipping information, all known mineralogical information, and analysis data. This database should also include a comprehensive record of all associated observations by both field and laboratory personnel. In some instances, regulatory requirements may specify that a "chain of custody" record be maintained for waste products containing hazardous substances. These records document who has the samples and how they are stored.

Ore samples and other feed materials should be stored in clean containers labeled with at least the full sample identification number. The label should be permanent. If steel drums are used, the label should be painted on the outside of the drum and a duplicate cardboard or plastic label placed inside the drum. Placing the cardboard label inside a sealed plastic envelope will keep the label dry and clean if the ore is somewhat damp. If a large sample requires more than one drum or other type of container, then each should be labeled to show the total number of containers used. This procedure is particularly important for nonhomogeneous or spotty ores in which a single container may not be representative.

Cloth sacks should be labeled both inside and out. If a tag is tied to the outside, than a second tag should also be placed inside the sack. Preferably, the inside tag should be placed in a sealed plastic envelope. Paper sacks should be labeled directly on the sack with a permanent marker. All sample containers should have closures that prevent any leakage or cross contamination.

Both during and after completion of the metallurgical evaluation program, a permanent record of all sample storage locations should be maintained. This record can be particularly valuable when, as typically happens, repeat tests or analytical determination are needed.

2.4 SAMPLING PROCEDURES

2.4.1 Introduction

As discussed in section 2.1, sampling is the operation of removing a portion of a bulk material in such a way that the portion represents the physical and chemical properties of the bulk material. Sampling pure liquids and gases is relatively easy, but when particulates are present the difficulties increase. For example, every time an ore is handled, the particles tend to segregate according to size and specific gravity. In a heap of particulate material, the coarse particles collect near the bottom perimeter of the heap, whereas the fine particles concentrate in the center core. This occurs because the coarse particles roll down the sloping surfaces of heaps, and the fine ones percolate through the larger particles at the apex and build a central core. Sampling theory based on probability cannot account for segregation because by its very nature segregation invalidates the basic assumption that deviations are due to chance causes.

Woodbridge (1916, p. 8) makes the following statement:

> In considering the reliability of any sampling method the tendency to segregate should be constantly borne in mind. Any system or any detail of a system that may tend to make possible the selection or rejection of the finer or coarser particles should be considered inaccurate. So absolutely does the accuracy of a sampling method depend on freedom from selection that one may forget that gold, silver or other metals are to be determined by the process and examine the method solely as to its ability to take from a lot of ore the same proportion of all the various sizes of particles.

The tendency to segregate can also significantly limit the effectiveness of mechanical blending devices. For some materials, even extended mixing in a revolving receptacle may only make the segregation somewhat less apparent to the eye.

Occasionally, it may be possible to collect samples for metallurgical or environmental testing from moving or flowing streams such as ore on a conveyor belt or a slurry flowing in a launder or pipeline. This type of sampling has typically been referred to as "incremental sampling." In general, the technique involves taking small portions of the entire moving stream at frequent intervals rather than large quantities at infrequent intervals. The cut should be taken through the complete cross section of the moving stream and not from just part of it. This type of sampling must consider not only the particle sizes, but also factors such as the degree of stratification in the material stream. When planning an incremental sampling program, references such as the following should be consulted: Cooper (1985, 1978), Gy (1965), and Behre (1945).

The size reduction, coning and quartering, and splitting procedures discussed in the following sections are designed to minimize the effect of particle segregation.

2.4.2 Sample Drying

Experience shows that consistent drying procedures can be a significant factor in hydrometallurgical testing. For example, if the test feed material and the analytical head sample have not been dried under the same conditions, then material balance and recovery calculations can be biased. For optimum results, the test feed and the analytical sample should be dried for the same time at the same temperature and preferably in the same drying oven. If for some reason, the test feed material and the analytical head sample cannot be dried at the same temperature, then the difference in moisture content, if any, between these two materials should be determined and used in the metallurgical balance calculations. An equivalent relationship applies for leach residues.

Bulk samples are often air dried before the sampling operations are started, particularly if the "as-received" material is sticky. The damp material is spread out on a hard, clean, crack-free surface that is protected from the weather. A 2- to 4-in bed depth is usually desirable. Fans can be used to promote air circulation over the bed, but the airflow should be kept low enough to prevent any dust losses. Turning the ore bed with shovels also reduces the drying time; it also helps to blend the material and minimize the formation of hard lumps. Heated floors or steam tables have also been used in some laboratories. If there is a question as to whether the drying procedure may affect subsequent experimental results, then exploratory tests should be conducted before the bulk sample is dried. Also, it is almost always desirable to determine at least the approximate moisture content of the as-received bulk sample. This determination is usually made on a composite grab sample taken from the material as it is being spread out to air dry.

Suitable temperatures for oven drying depend upon the nature of the minerals present in the material being dried and also on the local altitude. In most instances, a temperature a little above the local boiling point of water is applicable. In general, sulfide-bearing materials dry successfully at near 100 °C with minimal oxidation. It is a good idea, however, to experiment because even the same mineral in different deposits may show a varied response to heating. Some oxide minerals, such as those found in iron ores can be dried at 170 °C, but again testing is recommended.

Samples should be dried until a constant weight is reached. For convenience, most laboratories use overnight drying, but tests are recommended to determine the time required to achieve constant weight for a given material at the temperature chosen.

When appreciable clay or other fine materials are present in a sample, oven drying can produce almost brick-like masses. Frequent stirring can help to minimize this problem. If hard clumps have formed, then fine crushing or even grinding may be required before accurate blending and sampling can be achieved.

After drying, it is desirable to store both analytical head samples and test materials in closed containers. In some ores, such as laterites and garnierites, the moisture content in samples exposed to the air can vary with the relative humidity. In most instances, measure the sample weights both before and after drying so that the moisture content of the undried material can be determined.

2.4.3 Size Reduction

Becker (1968, p. 1) has defined sample reduction as "The processes of alternately crushing or grinding and sampling mineral particles prior to assaying." The same sequence of operations also applies to preparing samples for metallurgical testing. At each stage of the process, the sample is crushed, mixed, and a suitable portion selected for further size reduction. The end product of this sequence is normally one or more finely pulverized head samples for analysis and a series of coarser feed samples for the experimental studies.

In hydrometallurgical research, it is not unusual to find that only relatively limited amounts of the feed ore are available. In these instances, after suitable mineralogical samples have been selected, the entire lot of ore is often crushed to approximately minus 10 mesh before blending or splitting takes place. If the amount of available material meets or exceeds the quantities discussed in section 2.2.2, then interstage blending and splitting between the size-reduction steps becomes appropriate.

The following general procedures are based on the assumption that the crushing equipment listed below is available:

- One 5- by 6-in jaw crusher.
- One 3- by 4-in jaw crusher.
- One set of 8- by 12-in rolls.
- One Hammer mill (approximately 15- by 8-in).
- One 8-in cone crusher (Gy-Roll).
- Screening equipment (laboratory vibrating screen or Gilson Shaker).

The procedures listed are designed to minimize the production of excess fines, but modifications may be needed to fit the particular ore or other material being crushed. For example, a procedure applicable for a low-grade oxidized gold ore or sandstone uranium-vanadium ore may not be suitable for hard-rock ores.

Before starting crushing operations, all equipment and containers in the crushing circuit should be thoroughly cleaned to prevent salting or contamination from previous operations. Usually, wire brushes can adequately clean crushing circuit equipment. For some high-grade or clayey ores, however, it may be necessary to put a charge of quartz rock through the crushing circuit before initiating the brush-cleaning operation.

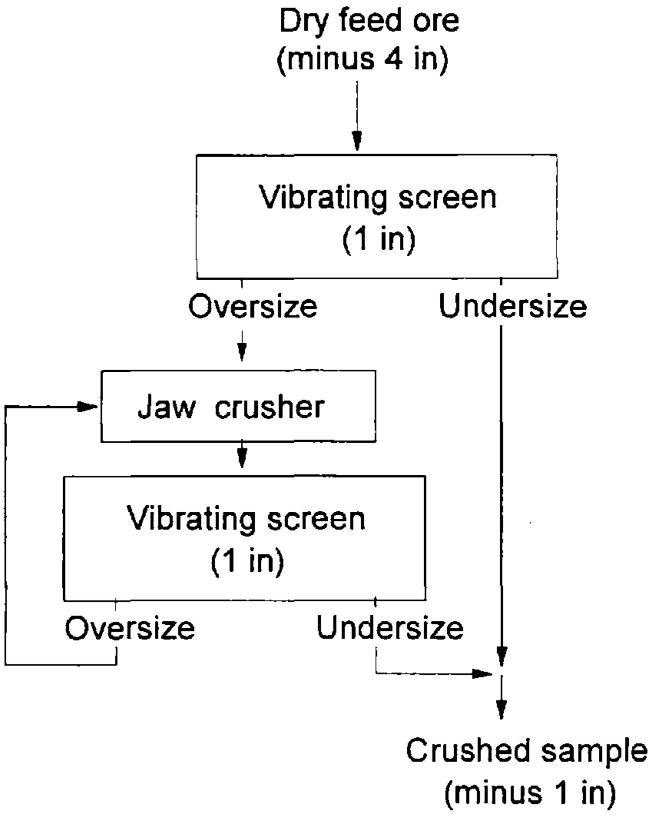
2.4.3.1 Coarse Crushing (to approximately minus 1-in)

The procedure shown in figure 2.2 is based on the assumption that the "as-received" ore sample is approximately minus 4-in. Any plus 4-in pieces are broken with a sledge or other suitable method after taking suitable safety precautions for protection from flying pieces. This material (preferably a standard weight such as discussed in section 2.2.1) is screened at the designated size on a vibrating screen or Gilson Shaker. The oversize passes through the jaw crusher (approximately 5- by 6-in size) with the jaws set to discharge slightly coarser than the desired product size. The crushed product feeds to rescreening, and the oversize returns to the crusher. This process continues until all of the oversize has been reduced to the desired size.

2.4.3.2 Intermediate Crushing (to about minus 1/2- or 3/8-in)

The general procedure for crushing to an intermediate size (such as minus 1/2- or minus 3/8-in) is the same as that shown in figure 2.2, except that the feed size is approximately minus 1-in, and the appropriate screens are used. A smaller jaw crusher (3- by 4-in size) can be used. Again, the feed weight should preferably be at least the quantity recommended by the guidelines in section 2.2.2.

Figure 2.2



Coarse-crushing procedure.

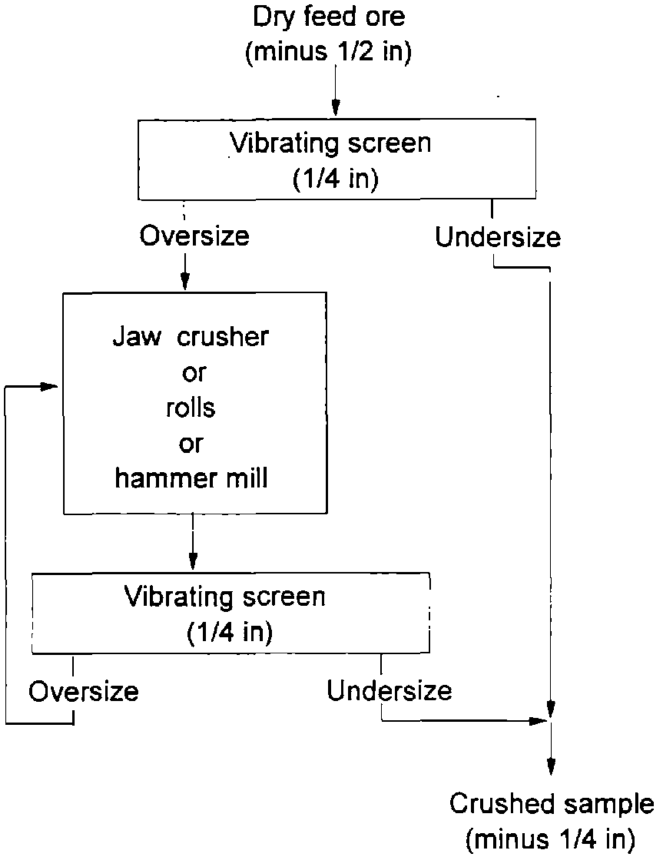
2.4.3.3 Fine Crushing (to approximately minus 1/4-in or minus 10 mesh)

The procedure for fine crushing generally follows flowsheets similar to those shown in figures 2.3 and 2.4. The standard weight of feed ore or other material feeds onto the screening unit. The oversize passes through the crushing equipment, which has been set to discharge at the desired product size. The screen undersize goes directly to the crushed product collector. The crusher product is rescreened; the oversize recycles to the crushing unit and the undersize goes to the crushed product collector. If relatively small amounts of material are to be crushed to the minus 1/4-in to minus 10-mesh size, the cone crusher and hand screening should be used.

2.4.4 Bulk Sampling

The term "bulk sampling," as used here, refers to the first step of the sampling procedure after the "as-received" ore sample has been reduced to about minus 2- or minus 1-in. Both coning and quartering and fractional shoveling are discussed.

Figure 2.3



Fine-crushing procedure (minus ¼ in).

2.4.4.1 Coning and Quartering

Behre and Hassialis (1945, pp. 19-27 to 19-28) have presented the following description of the coning and quartering technique; this procedure is probably the ancestor of all bulk sampling methods.

Coning and quartering was for many years the standard method of sampling throughout the western United States, especially for batches of ore whose value was to be determined between buyer and seller. It can be used on lots up to 50 tons. Where larger lots are to be sampled, the first cut is made by some other method and the sample thus obtained is further reduced by coning and quartering.

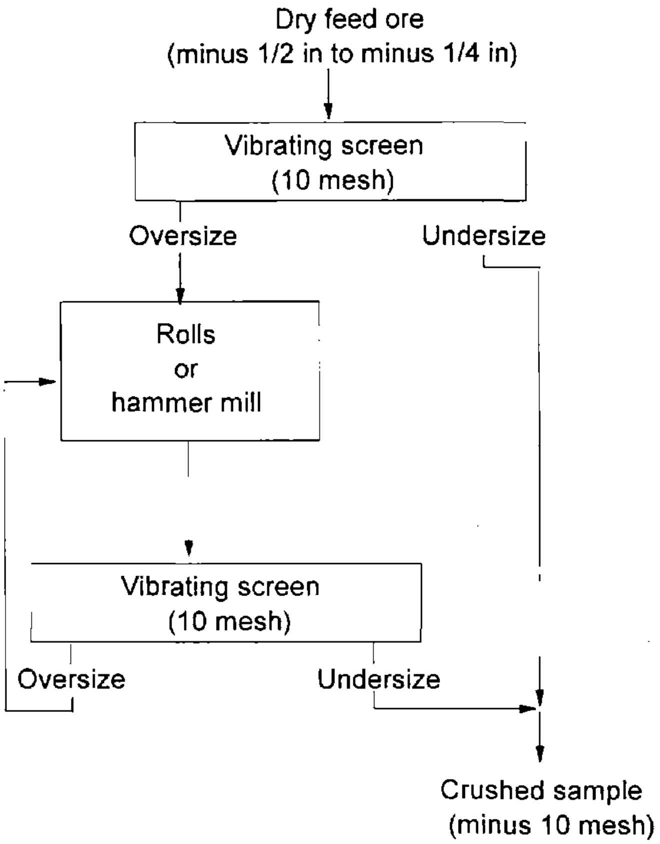
The procedure consists in piling the ore into a conical heap, spreading this out into a circular cake, dividing the cake radially into quarters, taking opposite quarters as sample and rejecting the other two. The ore should be crushed through 2-in or smaller ring. The operation should be carried on in a room of sufficient size to allow convenient handling of material. The floor should be smooth and free from cracks, preferably smooth concrete or steel sheets; it should first be swept thoroughly clean to avoid salting from a previous lot. The ore is dumped on the floor in two or four piles, or in a circular ring. Shovelers then pile this ore into a right-conical heap conveniently placed, taking care to drop each shovelful directly onto the apex. The object of coning is to form a heap in which segregation shall be symmetrical with respect to the vertical axis. To insure this, successive shovel loads should be so taken as to contain similar sizes similarly segregated on the shovel and should be so dropped onto the cone that the segregation therein is symmetrical. This end is attained by having the shovelers take successive shovel loads from adjacent places around the periphery of the heaps from which they are shoveling and drop these loads from successively adjacent points around the cone that they are building. Each man should take a shovel load of the same size as each other shoveler, and shovel loads should be made smaller as the size of the heap being shoveled becomes less. When the material is placed in a ring, the men move around the ring as they shovel into the cone. When the ore is all heaped up into a cone, the floor is carefully swept and the fines collected are placed on the apex, not swept up against the bottom of the pile. The men then start at point near the bottom of the cone and, with their shovels held tangentially, drag the material down radially so as to form, a truncated cone or flat circular cake. In this operation they should work around the cone. The cake is then marked off into quarters with a stick or board along diameters at right angles. Opposite quarters are shoveled out as reject. The remaining quarters, called the sample, are then shoveled into one or more piles or into a ring depending on the amount of material, and the coning and quartering operations repeated until the sample is so small that further crushing is necessary before further reduction in bulk can be made. A cross made of sheet iron or wood with sharpened edges is often used to mark the truncated cone into quarters. This is placed on top of the cake with the center of the cross directly over the center of the cone and is then pressed into the ore until it touches the floor. Such an arrangement is preferable to marking off with a single board. Lines of division will be more exact and the cross can be left in place to hold the sides of the sample quarters vertical while the reject quarter are being shoveled away. Or the cross may be laid on the floor before starting the pile and each shovelful dropped over the intersection. The cone is then spread out to the thickness of the cross and the reject shoveled away as above.

Coning does not mix the ore uniformly. As material is shoveled onto the cone the coarser pieces roll down the sides and come to rest on the floor while the finest particles remain near the apex. Pieces of intermediate size arrange themselves on the slopes of the pile according to their size. The ultimate result desired is that the segregation be symmetrical with respect to the axis of the cone. If this condition is attained, any sector taken should correctly represent the whole.

The "bench or cobbing" system, which is sometimes used to get better distribution of the material in the cone, consists in first making a small cone of some of the ore and spreading it out into a cake, then making another cone on the center of the cake and spreading it out and repeating until all the ore is this disposed of. This method tends to reduce the effects of accidental errors in flattening the cone.

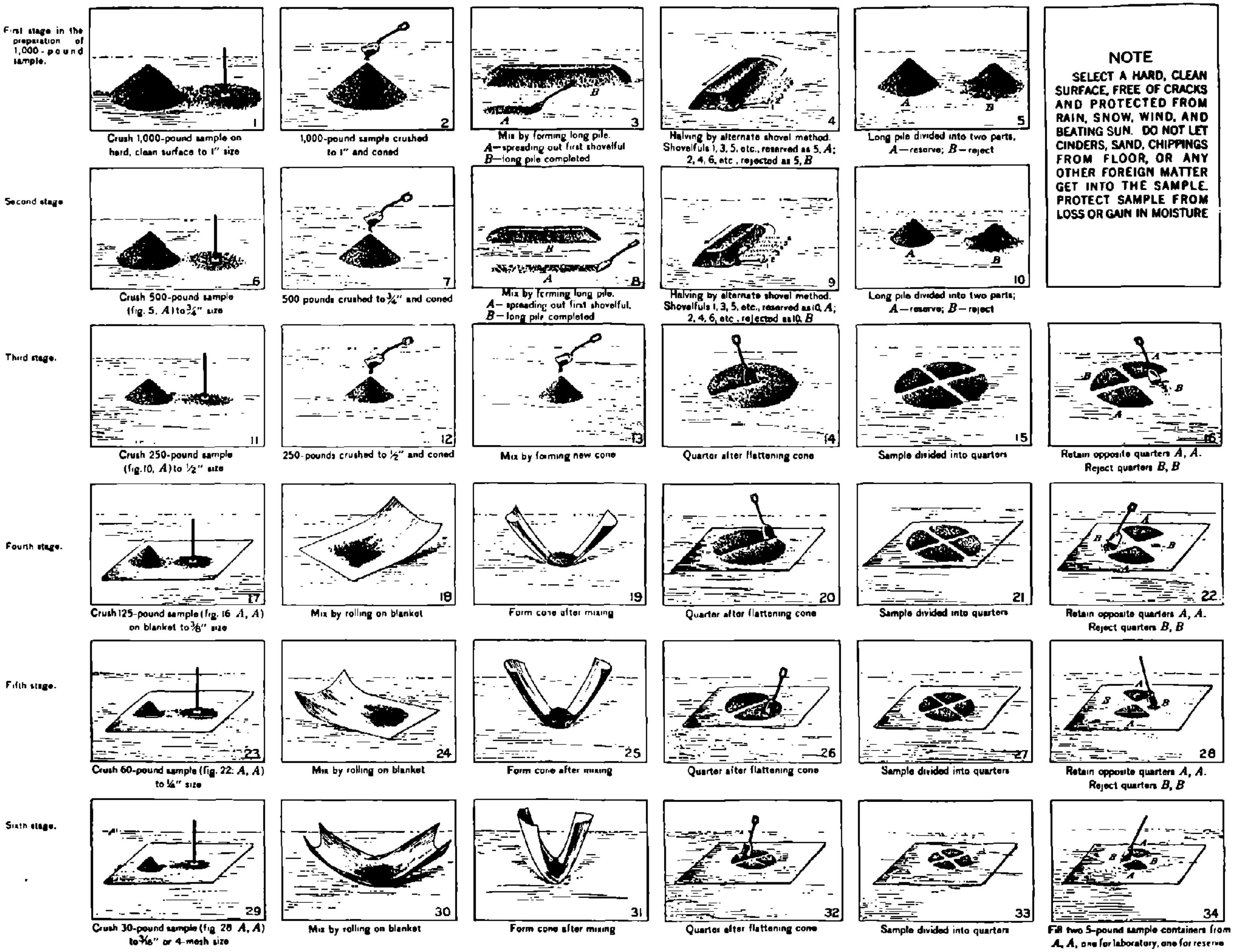
Pope (1916) presents a procedure for sampling coal; the same sequence of operations is also applicable for a variety of other materials. The procedure combines coning and quartering with several other hand-sampling techniques. Figure 2.5 presents both a symbolic representation

Figure 2.4



Fine-crushing procedure (minus 10 mesh).

Figure 2.5



First stage in the preparation of 1,000-pound sample.

1 Crush 1,000-pound sample on hard, clean surface to 1" size

2 1,000-pound sample crushed to 1" and coned

3 Mix by forming long pile. *A*—spreading out first shovelful *B*—long pile completed

4 Halving by alternate shovel method. Shovelfuls 1, 3, 5, etc., reserved as 5, *A*; 2, 4, 6, etc , rejected as 5, *B*

5 Long pile divided into two parts, *A*—reserve; *B*—reject

NOTE

SELECT A HARD, CLEAN SURFACE, FREE OF CRACKS AND PROTECTED FROM RAIN, SNOW, WIND, AND BEATING SUN. DO NOT LET CINDERS, SAND, CHIPPINGS FROM FLOOR, OR ANY OTHER FOREIGN MATTER GET INTO THE SAMPLE. PROTECT SAMPLE FROM LOSS OR GAIN IN MOISTURE

Second stage

6 Crush 500-pound sample (fig. 5, *A*) to ¾" size

7 500 pounds crushed to ¾" and coned

8 Mix by forming long pile. *A*— spreading out first shovelful. *B*— long pile completed

9 Halving by alternate shovel method. Shovelfuls 1, 3, 5, etc., reserved as 10, *A*; 2, 4, 6, etc , rejected as 10, *B*

10 Long pile divided into two parts; *A*—reserve; *B*—reject

Third stage.

11 Crush 250-pound sample (fig. 10, *A*) to ½" size

12 250-pounds crushed to ½" and coned

13 Mix by forming new cone

14 Quarter after flattening cone

15 Sample divided into quarters

16 Retain opposite quarters *A*, *A*. Reject quarters *B*, *B*

Fourth stage.

17 Crush 125-pound sample (fig. 16 *A*, *A*) on blanket to ⅜" size

18 Mix by rolling on blanket

19 Form cone after mixing

20 Quarter after flattening cone

21 Sample divided into quarters

22 Retain opposite quarters *A*, *A*. Reject quarters *B*, *B*

Fifth stage.

23 Crush 60-pound sample (fig. 22: *A*, *A*) to ¼" size

24 Mix by rolling on blanket

25 Form cone after mixing

26 Quarter after flattening cone

27 Sample divided into quarters

28 Retain opposite quarters *A*, *A*. Reject quarters *B*, *B*

Sixth stage.

29 Crush 30-pound sample (fig 28 *A*, *A*) to $\frac{3}{16}$" or 4-mesh size

30 Mix by rolling on blanket

31 Form cone after mixing

32 Quarter after flattening cone

33 Sample divided into quarters

34 Fill two 5-pound sample containers from *A*, *A*, one for laboratory, one for reserve

Method of preparing coal sample by hand [reproduction of plate V in USBM Bulletin 116 (Pope, 1916)]. Necessary tools of shovel, tamper, rubberized blanket (or plastic material measuring about 6 by 8 ft), broom, and rake. Coal is raked while being crushed with the tamper so that all lumps will be crushed. Floor or blanket is swept clean of discarded coal after each time sample is halved or quartered.

and discussion of the procedure. The sample weights for the various cuts correspond to the weights listed in column 2 (low-grade or uniform ores) of figure 2.1.

Each of the final 15-lb splits can be saved in a separate container and subsequently ground to the size desired for leaching or other type of test. Alternatively, the entire 60-lb sample (step 22) could be crushed to minus 10 mesh and then split down using a Jones splitter or equivalent type of riffle as discussed in section 2.4.5.

2.4.4.2 Fractional Shoveling

Bulk sampling can also be carried out using fractional shoveling. Gy (1976, p. 309) has stated that, when correctly carried out, it can be more reliable than coning and quartering or other splitting methods. It also requires less labor than coning and quartering. Gy defines fractional shoveling as follows:

> The lot of ore is moved with one or several hand or mechanical shovels. Shovelfuls are extracted from the lot and successively discharged on the top of one of the N heaps. At the end of the transfer, one of the N heaps is selected at random and retained as a sample. The sampling ratio is 1/N. The lot should contain at least 50 shovelfuls. For very large lots, it is advisable to choose N = 5 or 10. For small lots, with N = 2, fractional shoveling is known as alternate shoveling.

Fractional shoveling requires the same maximum particle size and/or sample weight relationships as those required for other sampling procedures. Also, the housekeeping and general shoveling techniques recommended for coning and quartering apply to fractional shoveling.

Gy (1976) states that the degenerated fractional shoveling method, which consists of discharging one shovelful on the top of heap A and N-1 shovelfuls (where N > 2) on the top of heap B, may be dangerous and should, therefore, be used only for very preliminary sampling.

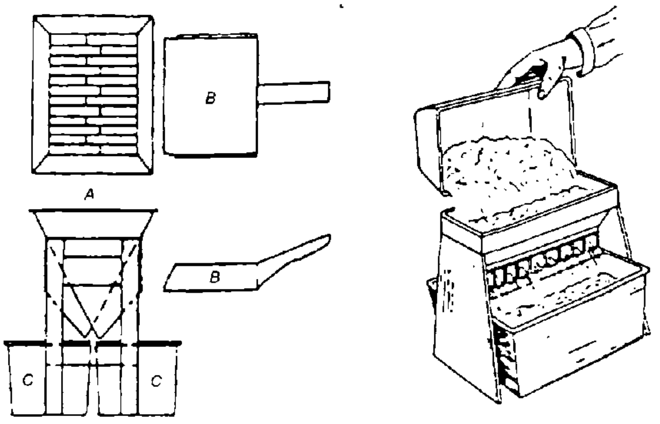
2.4.5 Splitting

After the bulk ore sample has been reduced to the 50- to 100-lb range, various splitting or riffling techniques are used to split out samples for test work and analyses. Depending upon the size of the sample and on the equipment available, both static and spinning riffles may be applicable.

2.4.5.1 Static Riffles

A variety of static riffles or splitters are available; the Jones splitter, shown in figure 2.6, is one of the most commonly used. It is used to divide the sample into two parts and consists of several equally sized chutes (figure 2.6*A*) discharging to opposite sides. Jones splitters come in a number of sizes, with chute openings ranging from 1/2- to about 2-in. Micro splitters with 1/4- and 1/8-in openings are also available. When splitting a sample, a splitter with a chute width somewhat larger than the largest particle in the sample should be selected. For example, a splitter with 1/2-in openings will usually ensure a free flow of 1/4-in particles through the chutes.

Figure 2.6



Jones splitter. A, Splitter; B, scoop for spreading ore over riffles; C, pans for receiving split sample rejects.

It is most important that the material be fed to the splitter from a shovel, pan, or scoop (figure 2.6*B*) that is the same width as the splitter. The lip of the scoop should be placed at the edge of the splitter hopper and the material then dumped into the splitter. The most common error is to pour the material onto the splitter in a small continuous stream that is moved back and forth across the splitter; this should never be done. The pans (figure 2.6*C*) that are provided with the splitter to catch the products are almost always of the same width as the splitter and can be used to feed the splitter if a suitable scoop is not available.

The following describes a typical example of the splitting process:

> Assume that the sample has been reduced to about 70 lb (32 kg), ground to minus 10 mesh, and blended. A final sample weight of about 1 kg is wanted. After the pans, splitter, and floor area have been thoroughly cleaned, the pans are placed below the splitter and the material fed onto the splitter with the proper scoop or pan. With successive deliveries, the material is fed first from one side of the splitter and then from the other. If a 3/4- or 1-in splitter has been used, it is likely that this splitting has

filled a total of four pans (two on each side). Therefore, two pans from one side are dumped into a holding container and the other two are split again. If the first pan is dumped onto the splitter from the right-hand side, the second is dumped from the left. The original sample has now been reduced to two pans, each containing approximately 8 kg. One pan is dumped into the holding container, and the other again put through the splitter. This process is continued, the quantity being reduced by about half each time, until the desired 1 kg of sample is reached. A larger splitter would be used for the initial 32 kg, but as the amount of material to be split becomes smaller, say less than a quarter panful, the final splits should use a smaller splitter. The splitter should be rapped smartly between splits to ensure that the slots are clean.

The Jones splitter can be used not only to reduce the quantity of material and produce a single sample for analysis, but also to divide a sample into several representative portions for leaching or other test work. As in all sampling procedures, the proper maximum particle size and/or sample weight relationship must be retained. For example, if 16 leach tests (500 g each) are to be made on an ore, the lot is split, as previously described, until one of the pans contains a little over 8 kg of ore. The material is then ground to the desired size, blended, and put through the splitter, as previously described, until two approximately 500-g samples have been produced by the last split. In this case, all of the previous reject splits are saved separately, and the splitting operation is performed on each of these until the entire 8 kg has been split into the desired 16 500-g test samples. When this operation is performed carefully, each portion will be of nearly the same weight, and only small subtractions or additions will be needed to bring the portion to the exact weight desired. Also, one portion may be pulverized and used as a head sample for this series of tests. If a statistical evaluation of the preparation and splitting procedure is desired, then multiple-head samples may be pulverized for analysis.

2.4.5.2 Rotary Riffles

Rotary (sometimes called spinning) riffles such as that shown in figure 2.7 are based on the following principles:

1. The sample should be taken when the system is in motion.
2. The sample cut should be taken through the complete cross section of the moving stream and not from a part of it.
3. Small quantities should be cut from the flowing stream frequently rather than large quantities taken infrequently.

Rotary rifflers have three primary components: a hopper, a vibratory feeder, and a rotating tray divided into separate compartments. The feed material should be blended before being placed in the feed hopper. The feeder discharges a continuous stream of the material from the hopper into the compartments on the rotating tray. A variety of sizes have been used. Capacities range from microsplitters for pulverized analytical samples to units that can handle 1/2-in particles.

A study by Allen and Kahn (1970) indicated that for accurate sampling each compartment should pass under the flowing stream at least 35 times, and all of the available sample should be fed through the device. The rotation speed of the collection tray should be low enough to prevent dusting losses. Table 2.2 shows a comparison of sampling reliability for rotary riffling and several other sampling techniques. These data indicate that when properly used, rotary sampling shows significantly better reliability than the other methods listed.

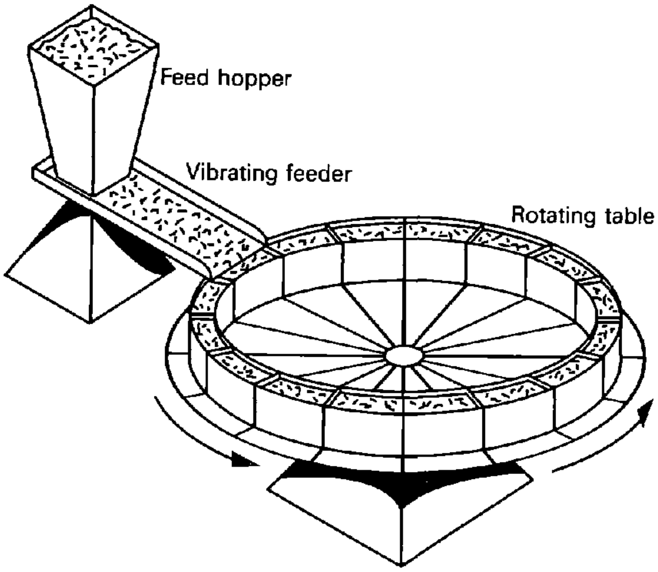
Table 2.2.—Reliability of sampling methods

Method	Standard deviation, %	Maximum sampling error estimated, %
Cone and quartering . . .	5.67	19.2
Chute riffling	1.10	3.7
Rotary riffling	0.27	0.9
Random variation	0.09	0.3

Source: Allen and Kahn (1970).

Rotary riffles can also be used as wet splitters. In one type of unit, the vibrating feeder is replaced with a stirred cone-bottom tank that holds the slurry to be sampled.

Figure 2.7



Rotary riffle.

The slurry feeds through an orifice into the containers on the rotating tray. Another type of wet splitter uses a rotating spout, and the receiving containers are stationary.

Typically, wet splitting is used when (1) the as-received sample is wet pulp or slurry, (2) drying the sample would produce undesirable chemical in the chemical or surface characteristics of the material, and (3) drying the sample would produce agglomerates that would not readily disintegrate during subsequent leaching operations. Condition 3 relates primarily to samples containing appreciable clay minerals. Condition 2 is not often encountered in leaching operations, but could be critical in physical beneficiation operations, such as flotation testing. Condition 1 might apply when either condition 2 or 3 are encountered, but it could also be just the most convenient method for splitting and sampling the as-received material.

2.4.6 Head Sample Preparation

The objective of the final head sample preparation is to reduce the material to a particle size that will permit cutting out a representative assay sample. The amount of material required for most wet-chemical analyses normally ranges between 0.5 and 1.0 g. When precious metal samples are being decomposed for Atomic Abortion analysis, the analyst typically takes a 5.0-g sample. Fire assaying requires a 29.17-g sample.

Typically, the final sample split is prepared for analysis by pulverizing to minus 150 mesh. Some materials, such as spotty ores, may require finer grinding. If an unknown ore or material is being sampled, an evaluation of the effect of maximum particle size on analytical accuracy and precision is warranted. Finely powdered samples are desirable because they can be more readily blended into a homogeneous mixture and can be subsampled with greater precision and accuracy. Also, finely powdered samples are easier to dissolve because they present a large surface area to volume ratio to the solvent or reagent used in dissolution.

The amount of material required for a representative sample depends upon the type of material being sampled and the particle size of the pulverizer feed. For example, if a minus 10-mesh, low-grade material such as that shown in column 2 of figure 2.1 is to be pulverized, approximately 2,000 g (4.3 lb) is required. If the 2,000 g of minus 10-mesh ore is ground to minus 28 mesh and blended, a split containing approximately 200 g becomes adequate. Mixing or blending the 2,000 g of minus 28-mesh material before splitting out the 200 g is important. A method called rolling is frequently used. The procedure consists of rolling the material back and forth upon itself on a piece of rubber-covered cloth. The rolling cloth should be square and a little larger than the area covered by the material so there will be no spillage while rolling. The material to be mixed is placed in the center of the cloth and diagonally opposite corners of the cloth are grasped. First with one corner and then the other, the cloth is drawn horizontally toward the opposite corner. This process is repeated using the other two corners, then the original two corners, etc., until the material has been rolled about 100 times. Persons unfamiliar with the proper rolling technique often make the mistake of merely lifting the corner instead of drawing it across the material. When this is done, the particles tend to slide along the cloth and mixing is not accomplished. The particles should "roll" over the particles below, and hence, the term "rolling." It is also important that the size of the cloth should fit the sample size. It is practically impossible to mix a small amount of material on an oversize cloth because the material will almost always slide rather than roll.

Blending can also be accomplished with the various types of cone or V-blenders on the market. Equipment capacities and blending times should follow the manufacturer's recommendations. In general, the blender should be less than 75% full, and the blending time should be at least 20 min.

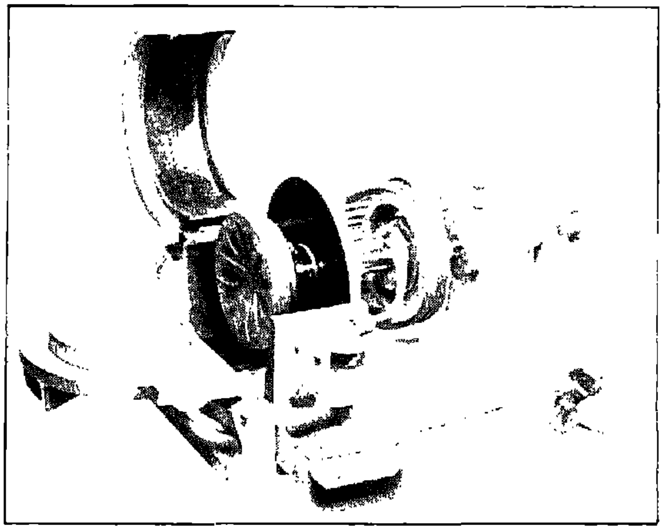
After mixing the 2,000 g of minus 28-mesh material, the 200-g sample can be split out using a small static riffle or a rotating riffle. As discussed in section 2.4.5.2, rotating riffles are particularly good for this operation. Drying the 200-g sample at approximately 100 °C before pulverizing is often recommended.

2.4.6.1 Pulverizing

Several forms of equipment can be used to pulverize head samples and other materials. These include disk pulverizers, rotary cup mills, and laboratory hammer mills. Thorough cleaning of these units between different types of samples is critical. One of the best methods is to brush it out, and then grind a quantity of barren material such as quartz sand. This is followed by a second brushing. Vacuum cleaners can also be used. Compressed air can be used if the nozzle design and air pressures meet regulatory requirements, and adequate dust collection is used (see 2.7.1).

- *Disk pulverizers*—The Bico-Braun-type pulverizers (see figure 2.8) grind the ore between two disks, one revolving and the other stationary. The dried material is fed through a spout in the door and passes into the grinding chamber through an opening in the center of the stationary plate. The small space that separates the plates determines the product fineness and is adjustable by a screw at the end of the shaft. Finished product falls through the plate spacing into the pan below. Feed previously crushed to minus 1/4-in or finer can usually be pulverized to about minus 100 mesh in a single pass. The standard grinding plates are a cast iron alloy, but a variety of other materials are available. These materials include manganese steel, hardened iron alloys, and alumina ceramics.

Figure 2.8



Disk pulverizer. (Courtesy SEPOR, Inc.)

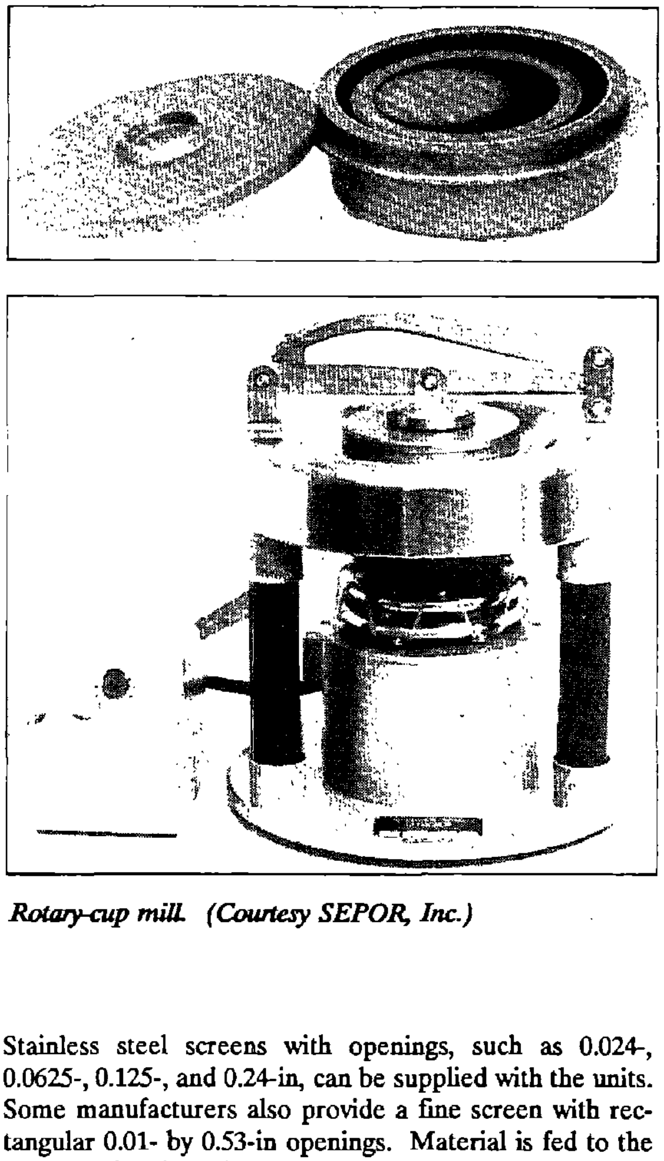
The McCool-type pulverizer is a similar machine, except that a slow gyratory motion of the disc centers is superimposed on the disc rotation. This helps to promote uniform disc wear.

- ***Rotary cup mills***—Rotary cup pulverizers, such as the Bleuler Mill shown in figure 2.9, grind the ore in a cup containing a puck and an anvil ring. A grooved lid closes the cup. The cup set is held in the drive unit with a quick-latch lever. The drive unit imparts an eccentric motion, which causes the puck to move likewise and pulverize the sample by both impact and attrition. The standard chrome steel grinding cup set is available in 50-, 100-, and 200-g sizes (based on 2.5 specific gravity glass). Manufacturer's can also supply a tungsten carbide grinding cup set. Grinding times are relatively short (usually <2 min), but the specific time required for each type of sample must be determined experimentally.

The cleaning procedure is similar to that outlined above; typically, it involves grinding out the unit with a charge of silica sand followed by thorough brushing. The sound level generated by rotary cup mills can exceed safe levels, and the units should be operated in a sound deadening chamber.

- ***Laboratory hammer mills***—A variety of laboratory hammer mill units are available. Applicability is limited primarily to relatively soft, friable materials, such as coal and many chemical compounds. Figure 2.10 illustrates a typical unit. The material is broken by impact with hammers mounted on a high-speed shaft rotating at near 10,000 rpm. The mechanism operates in a closed cylindrical chamber fitted with a replaceable screen bottom. Stainless steel screens with openings, such as 0.024-, 0.0625-, 0.125-, and 0.24-in, can be supplied with the units. Some manufacturers also provide a fine screen with rectangular 0.01- by 0.53-in openings. Material is fed to the grinding chamber with a manual auger. The ground material passes through the screen and collects in a metal sample container. All laboratory hammer mills are fitted with a removable cover that permits easy access for cleaning the mill and changing screens.

Figure 2.9

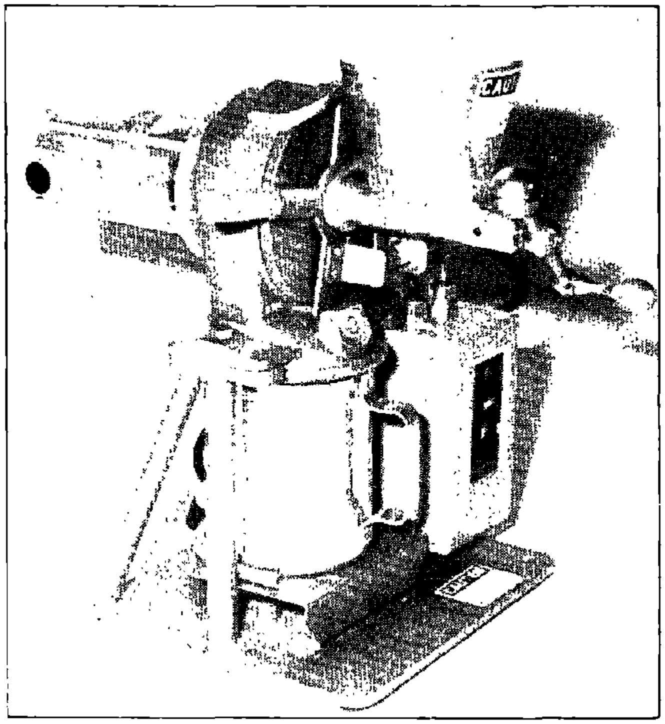


Rotary-cup mill. (Courtesy SEPOR, Inc.)

2.4.6.2 Ores Containing Malleable Minerals

Ores containing malleable materials such as native gold, silver, or copper present special sample preparation problems. When samples containing these materials are pulverized for analyses, the malleable minerals often end up as flat scales, cylinders, or spheres. If there is any expectation that an ore might contain metallics, identification of these materials by mineralogical examination or other means becomes particularly important. Information

Figure 2.10



Laboratory hammer mill. (Courtesy SEPOR, Inc.)

on ore characteristics such as the liberation size of the malleable minerals is usually needed for selecting prudent sample preparation procedures. The coarser the metallic particles, the more difficult it becomes to obtain an accurate sample.

Bugbee (1940, p. 70) makes the following recommendations for sample preparation when metallics are present:

> The original sample must be carefully weighed before pulverizing. After grinding, the particles found on the sieve being used to check the product size must be saved separately and accurately weighed. The material passing through the screen should also be weighed. This procedure not only gives the data required to calculate the true assay, but also acts to check on any carelessness in the overall sample preparation operation. If the particles on the screen are gold or silver, they are normally wrapped in lead foil, cupeled, weighed, and parted. The weights and gold or silver analyses of the two screen fractions can then be used to calculate a head assay.
>
> Metallic copper pellets may require fusion-type analyses to determine the actual copper content. When sampling molybdenum ores, flat scales of molybdenite may be found on the screen. These should also be weighed and analyzed separately. Various metallurgical products such as slag, matte, furnace or cupel bottom, and dross, very often contain metallics and must be handled in this way.

In some instances, malleable particles can smear on the working surfaces of the grinding equipment. This can both introduce a low bias to the current sample and salt subsequent samples. The bias can be critical if both high-grade and low-grade samples are being prepared for analysis. If there is any indication or suspicion that malleable particles have smeared on the grinding surfaces, then the pulverizer should be cleaned by grinding a suitable charge of quartz sand. The resulting cleanings should be collected, weighed, and analyzed separately. All cleaning operations become particularly important when samples containing malleable minerals are being prepared. Also, to minimize salting during any sample preparation, the lowest grade samples should be prepared first.

Even with painstaking care, sampling statistics may limit achieving metallurgical balances with these materials; calculated head analyses based, for example, on leach test products may be the only realistic approach.

2.5 TEST SAMPLE PREPARATION

2.5.1 Introduction

Particle size is often one of the most important leaching variables. It can interact with other variables such as leaching reagent concentration, time, temperature, and redox potential. In general, effective leaching requires only exposure of the valuable minerals and not the extensive liberation needed for flotation. Mineralogical examination can often bracket a particle-size range that will provide satisfactory exposure of the mineralization.

Industrial grinding operations have economic limits. This point occurs when the cost of further comminution is not covered by improved extraction, or when the greater extraction is offset by excessive reagent consumption or undesirable side reactions.

Woodcock (1985, pp. 13-24) has listed typical commercial practice leach feed sizings as follows:

Baxuite: minus 100 mesh
Copper ore (oxidized): minus 1/2-in to minus 20 mesh
Copper ore (oxidized slimes leach): 75% minus 200 mesh
Gold ores: minus 65 mesh to minus 200 mesh
Gold concentrates (sulfides): minus 325 mesh
Ilmenite: minus 200 mesh
Nickel laterite: 100% minus 20 mesh, 90% minus 200 mesh
Nickel concentrates (sulfide): minus 200 mesh
Uranium ores: minus 10 mesh to minus 100 mesh
Zinc calcines: minus 200 mesh

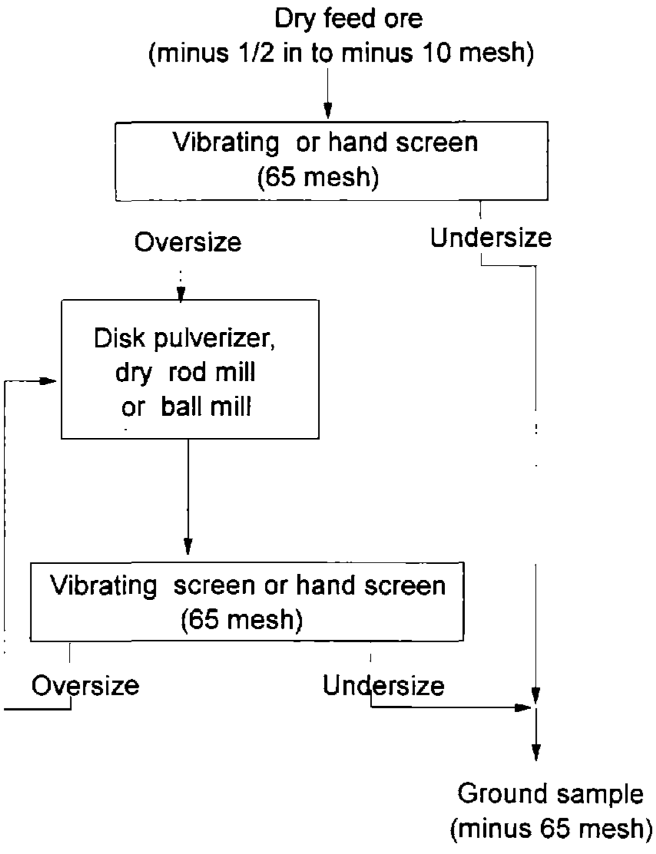
The following sections review methods that can be used for preparing leach-test feed materials. Both dry- and wet-grinding techniques are discussed.

2.5.2 Dry Grinding

Dry grinding has been used to prepare leach feed material from a wide variety of ores and concentrates, particularly for exploratory studies. The following procedure is based on the assumption that the ore or other material has been previously crushed to about the minus 1/4-in to minus 10-mesh size range as discussed in section 2.4.3.2. For most materials, either rolls or a small cone crusher can readily produce this grind. A few materials, such as sandstone uranium ores, can be ground to about minus 14 mesh with these units.

To produce a minus 65 mesh leach feed, a stage-grinding flowsheet such as that shown in figure 2.11 can usually give a product that does not contain appreciably more fines than that produced by an industrial circuit.

Figure 2.11



Dry-grinding procedure. (minus 65 mesh).

Before starting the grinding operation, the equipment should be thoroughly cleaned. The disk pulverizer or other grinding unit should be ground out with a clean quartz sand and carefully brushed. Adjusting the gap between the pulverizer plates to achieve the desired grind depends on a combination of experience and trial grinds at different settings.

When preparing relatively small amounts of material (e.g., less than 5,000 g), disk pulverizers are commonly used, but they are also often used for considerably larger samples. A similar relationship also applies for hand or mechanical screening. If only a small amount of plus 65-mesh material is produced during the final stage-grinding sequence, it can be ground in hand mortar and added to the minus 65-mesh product.

If a laboratory ball or rod mill is used to dry grind the ore, then a series of grinding tests will be needed to determine the required grinding time. A minus 10-mesh feed is desirable for most materials. In all instances, the relationship between the feed sample size and maximum particle size should meet the requirements for a representative sample.

An 8- by 8-in ball mill or an 8- by 12-in rod mill will usually be applicable for 500- to 2,000-g ore charges. The 10,000-g ball charge mixture supplied with an 8- by 8-in ball mill usually includes 1/2- to 1-1/4-in mild-steel balls. A typical ball-mill charge may consist of approximately the following weight percentages: 1-1/4 in - 49%, 1 in - 36%, 3/4 in - 10%, and 1/2 in - 5%. The 10,000-g rod charge for an 8- by 12-in rod mill is characteristically a mix of the following weight percentages: 3/4 in - 51%, 5/8 in - 32%, and 1/2 in - 17% mild-steel rods. The total mill loading (i.e., ball or rod charge plus the material to be ground) should not occupy more than approximately 60% of the mill volume. Typically, the ball or rod charge occupies about 40% of the mill volume, and the ore charge varies from 10% to 20% of the mill volume. Additional information on procedures for determining the size distribution of the grinding media is presented in the following references: Bond (1961, p. 8, and 1958).

The ground charge and the grinding balls are dumped onto a heavy screen with openings small enough to retain the grinding media. The ground product is collected in a suitable vessel positioned below the screen. The inside of the mill and the grinding media are brushed to recover as much as possible of the ground material. When a rod mill is used, the rods are removed and brushed individually.

After the grinding operation is complete, the product should be blended. It can then be split into individual samples, each with approximately the desired leach-feed weight. As mentioned previously, the final feed weight can be adjusted by adding or removing small multiple-grab samples. Either static or rotary riffles can be used to cut out the individual samples, but rotary riffles are recommended.

2.5.3 Wet Grinding

In some instances, wet grinding of a leach feed material may be desirable. For example, one objective may be to compare the effects of wet grinding and dry grinding. Also, in hydrometallurgical processes, such as alkaline leaching of uranium ores, the grinding operation uses recycle carbonate solutions, and some leaching occurs during the grinding step.

The 8- by 8-in ball mills and 8- by 12-in rod mills apply for wet grinding ore charges from approximately 500 to 2,000 g. The pulp densities usually range between 50% to 67% solids. Rod mills are often used for relatively coarse grinds (i.e., minus 65 to minus 100 mesh) because the size distribution of the product is closer to that of an industrial-scale, closed-circuit grinding operation. Experience indicates that it is always desirable to grind out the mill with a charge of clean silica sand before starting a test series because both the mill and the grinding media rust quickly when not in use. After the silica-sand grind has been completed, the balls or rods should be removed from the mill and thoroughly washed before the test material is processed.

The grinding time required for the desired product size is determined by conducting a series of preliminary tests. Depending on the feed material and the desired product size, times may range from a few minutes to 20 min or more. As grinding times increase, attrition effects become more pronounced.

The procedure for recovering the ground product parallels that for dry grinding, except that water or some other fluid is used to wash the pulp from the mill and the grinding media. The collected pulp is filtered, and the filtrate volume measured. In some instances, some water solubility occurs, and the filtrate must be analyzed so that material balance calculations can be made. A portion of the filtrate is often used as a dilution fluid to obtain the desired leach pulp density.

Additional information on several aspects of laboratory-scale batch grinding techniques have been discussed by Fahrenwald in USBM RI 2989 (1930) and USBM RI 2990 (1930).

2.6 SIZE ANALYSIS

2.6.1 Introduction

Particle size can be one of the most important variables in hydrometallurgical processing. This applies to raw materials, materials in process, leach residues, etc. For example, the relationship between particle size and leach extraction can have a critical effect on process economics. Size analysis is an almost universal component of nearly all hydrometallurgical process evaluation studies. The terms "screen analysis," "sieve analysis," "size analysis," and "size distribution analysis" are used interchangeably in the literature.

The physical and chemical properties of ores and other materials can vary widely. Therefore, it is not possible to establish a single procedure for all size-distribution tests. The variability relates to properties, such as particle shape, density, and friability, together with other factors that include the moisture content and hygroscopic nature of the material being characterized. The following discussion relates primarily to test methods for particle size or screen analyses of metal-bearing ores and related materials. The procedures are based on American Society for Testing and Materials (ASTM) standards E-389 and E-276. The ASTM has also published standard sieve analysis procedures for a wide variety of other materials. A list of these standard test methods is published in the ASTM Manual on Test Sieving Methods (ASTM, 1985, pp. 37-41).

2.6.1.1 Wire Cloth Sieves

Most particle-size determinations in hydrometallurgical experimentation use wire cloth sieves that should always conform to the ASTM specifications shown in table 2.3. The entire series as shown in the table is based on a $\sqrt[4]{2}$ factor. This means that the area of each successive opening in the series is one-fourth that of the next coarser sieve. Hydrometallurgical test work commonly uses size analyses based on the $\sqrt{2}$ factor Tyler screen series. The cross-sectional area of each successive opening is one-half that of the next coarser sieve. Screens in this series include the 4-, 6-, 8-, 10-, 14-, 20-, 28-, 35-, 48-, 65-, 100-, 150-, 200-, 270-, and 400-mesh sieves. The 325-mesh screen, which is in the $\sqrt[4]{2}$ series, is also often used in hydrometallurgical test work. Coarser screen sizes in the $\sqrt{2}$ series are also available; they include the 0.25-, 0.375-, 0.5-, 0.75-, and 1-in sieves.

The standard screen diameter is 8 in, which is available in both 2- and 1-in depths. For most screen analyses, the 8-in-diameter by 2-in-depth screens are recommended. Sieves with 3- and 12-in diameters are also produced.

Manufacturers produce test sieves in several different alloys. Brass wire cloth is commonly used for the coarser sieves, and phosphor bronze cloth for the finer sizes. Stainless steel cloth is increasing in popularity because of its greater strength, durability, and resistance to corrosion. Frames are either brass or stainless steel.

Table 2.3.—Standard testing sieves

Designations			Nominal dimensions	
NIST	Tyler mesh	ASTM sieve opening,[1] µm	Sieve opening,[2] in	Wire diameter, mm
3.5	3.5	5,660	0.223	1.68
4	4	4,750	0.187	1.54
5	5	4,000	0.157	1.37
6	6	3,360	0.132	1.23
7	7	2,830	0.111	1.10
8	8	2,360	0.0937	1.00
10	9	2,000	0.0787	0.900
12	10	1,700	0.0661	0.810
14	12	1,400	0.0555	0.725
16	14	1,180	0.0469	0.650
18	16	1,000	0.0394	0.580
20	20	850	0.0331	0.510
25	24	710	0.0278	0.450
30	28	600	0.0234	0.390
35	32	500	0.0197	0.340
40	35	425	0.0165	0.290
45	42	355	0.0139	0.247
50	48	300	0.0117	0.215
60	60	250	0.0098	0.180
70	65	212	0.0083	0.152
80	80	180	0.0070	0.131
100	100	150	0.0059	0.110
120	115	125	0.0049	0.091
140	150	106	0.0041	0.076
170	170	90	0.0035	0.064
200	200	75	0.0029	0.058
230	250	63	0.0025	0.044
270	270	53	0.0021	0.037
325	325	45	0.0017	0.030
400	400	37	0.0015	0.025
450	450	*32	0.0013	0.028
500	500	*25	0.0010	0.025
635	635	*20	0.0008	0.020

ASTM American Society for Testing and Materials.

NIST National Institute of Standards and Technology (formerly National Bureau of Standards.

[1] Openings correspond to those proposed as an international standard (International Organization for Standardization), except those designated by an asterisk (*).

[2] Only approximate to metric values of ASTM.

Rectangular screens, such as the Gilson Shaker, are also available. The screen-tray dimensions are approximately 18 by 26 by 3 in. This type of equipment is particularly applicable for coarse screening relatively large samples.

2.6.1.2 Other Types of Sieves

Perforated plate sieves with either square or round openings are manufactured, but not commonly used in metallurgical processing studies. Openings range from about 0.127 to 5 in. Round openings are used for some materials, such as molding plastics, when product specifications are based on round hole apertures.

Precision electroformed sieves are available with apertures ranging from 5 to 40 µm. Because of their very limited open area and small size (3-in diameter), only very small samples, 1 to 2 g often can be sized. Also, the electroformed screening surface is very delicate and special-handling procedures are necessary. The manufacturers' directions must be followed.

2.6.2 Screening Procedures

Screening procedures include dry screening, wet screening, and a combination of both. The following sections discuss these procedures together with preliminary preparations.

2.6.2.1 Preliminary Preparations

1. Gather the screens and other equipment together and check to see that all proper mesh sizes are present and that all screens are of the same standard series.
2. Examine all screens, particularly the finer sizes, for broken sections in the screen surface. Check all parts of the screen surface; tears often occur where the cloth is attached to the frame. Often small holes can be repaired by soldering, but care must be taken so that the wire cloth is not injured by excessive heat or an incompatible flux. In some instances, successful repairs have been made using a two-part epoxy cement, but soldering is usually more successful. Do not continue to use a sieve when the screen is damaged to the point where it loses its tension and sags.
3. Check all screens for cleanness. This can be done by holding each screen up to the light and making sure that particles from previous screening tests are not stuck in the openings. Even on the finest screens, the blockage should be less than a few percent. Use a soft brass brush for cleaning screens coarser than 100 mesh, and use a nylon brush for sieves finer than 100 mesh. The ASTM procedures advise brushing the underside of the wire cloth with a circular motion, taking care not to exert too much pressure against the wire cloth. Tapping the frame of the sieve gently with a wooden stick or against the bench is also helpful. Take care not to batter the edges of the frames or pan since this will interfere with proper fitting and stacking of the screen deck. Embedded particles should never be forced out of the openings with a pick or needle. Ultrasonic cleaners specifically designed for the 8-in-diameter screens are effective when the manufacturer's directions are followed. These units can clean both coarse and fine mesh sieves, but fine mesh sieves can be severely damaged by other types of ultrasonic cleaners.
4. The weight of the feed sample required depends upon the diameter of the largest particles present in the sample. The general rules for this relationship are the same as those discussed in section 2.2.2. In addition, the amount of sample used for each screening operation should be limited so that no sieve in the series is overloaded. Overloading is generally defined as a crowding of oversize and near-mesh particles on the screen when the particles finer than one-half the sieve opening have passed through. Under these conditions, the oversize material will tend to wedge the near-mesh particles into the openings. The openings become blocked and useless until the wedged particles are removed. Overloading biases test results and can even cause tearing or distortion of the finer screens. If the representative sample size requires that large amounts of material must be screened, then the screening operation should be conducted in several smaller batches.

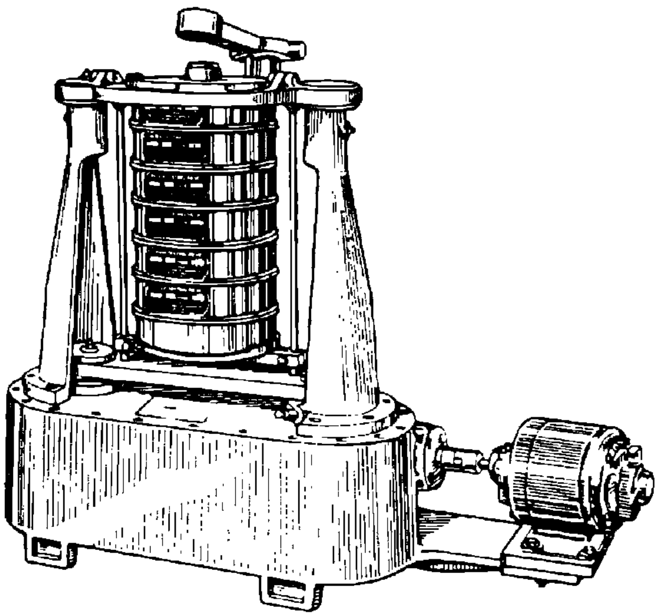
2.6.2.2 Dry Screening (8-in sieves)

Dry screening is usually applicable for samples containing less than 10% minus 200-mesh material. Nest the first six sieves of the desired screen series and fit a pan to the bottom sieve. Add the test material, which has been dried to constant weight at the desired temperature (normally 110 ± 5 °C) to the top screen and cover. Record the feed weight. The six-screen nest is suggested because most mechanical shakers such as the ROTAP unit can handle up to six screens (see figure 2.12). Clamp the nest into the mechanical shaker and shake for the required length of time. ASTM procedures define the screening time or end point as the time when additional periods of shaking fail to change the weight of material on any screen by more than 0.3%. Screening times normally vary from 3 to 30 min, but the exact time must be determined experimentally.

After the screening is complete, transfer the material on each screen to a tared pan, tapping and brushing the sieves to remove any lodged particles. If the undersize collected in the pan requires additional screening, then transfer it to the next stack of screens and repeat the above procedure.

Record the weights on a suitable form such as that shown in figure 2.13. The combined weight of all the fractions should equal the initial starting weight of the sample to within a few grams per kilogram. If the difference is much greater than this, then the source of error should be found and corrected and the test repeated.

Figure 2.12



Mechanical sieve shaker with tapper (ROTAP).

Figure 2.13

Sample:

Weight:

Date: Name: Screen Time:

SCREEN MESH		WEIGHT ON		CUMULATIVE PERCENT	
TYLER	U.S. NO	GRAMS	PERCENT	ON	PASSING
3					
4	4				
6	6				
8	8				
10	12				
14	16				
20	20				
28	30				
35	40				
48	50				
65	70				
100	100				
150	140				
200	200				
Pan					
TOTAL					

Screen analysis report form.

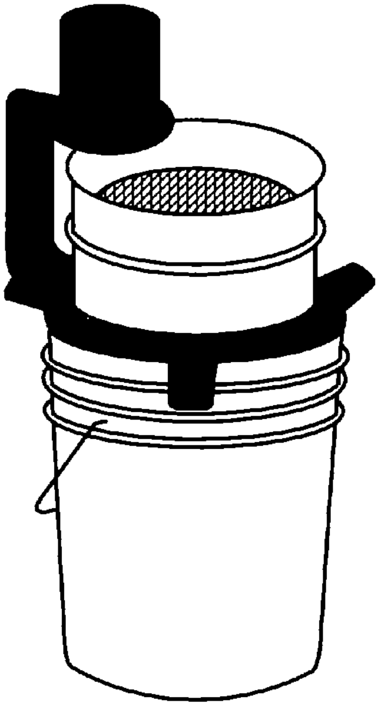
After each test is completed, all screens should be carefully examined for tears or other damage. If any damage is found, the damaged screens must be replaced and the test rerun.

2.6.2.3 Wet-Dry Screening (8-in screens)

Generally, wet-dry screening becomes desirable if the feed material contains more than 10% minus 200 mesh. Not only does the extremely fine material tend to cling to the coarser particles, but it also tends to cause plugging of the finer screens. Some materials such as leach residues containing extremely fine slimes may tend to agglomerate during drying, and dry screening would not give a true representation of the particle-size distribution.

For wet-dry screening, a weighed sample of the dried feed is placed on the finest sieve in the test series. For example, if a test using 65-, 100-, 150-, and 200-mesh screens is to be made, the sample would be placed on the 200-mesh sieve. This sieve is held in a mechanical shaker such as that shown in figure 2.14; the shaker is mounted over a bucket. The sample on the screen is then washed with a small jet of water until the slimes (minus 200-mesh fraction) have been almost completely washed through the screen. The visual appearance of the water on top of the material on the screen is a fair indication of the effectiveness of the washing. If it is clear, the sample has probably been washed enough. After washing is complete, the material on the screen is transferred into a pan and dried.

Figure 2.14



Mechanical shaker for wet screening. (Courtesy SEPOR, Inc.)

In most hydrometallurgical test work, the minus 200-mesh fraction collected in the bucket is recovered and saved for chemical analyses or other characterizations. The material in the bucket is filtered, dried, and weighed. Flocculation of the minus 200-mesh slurry before filtration can often significantly reduce the filtration time.

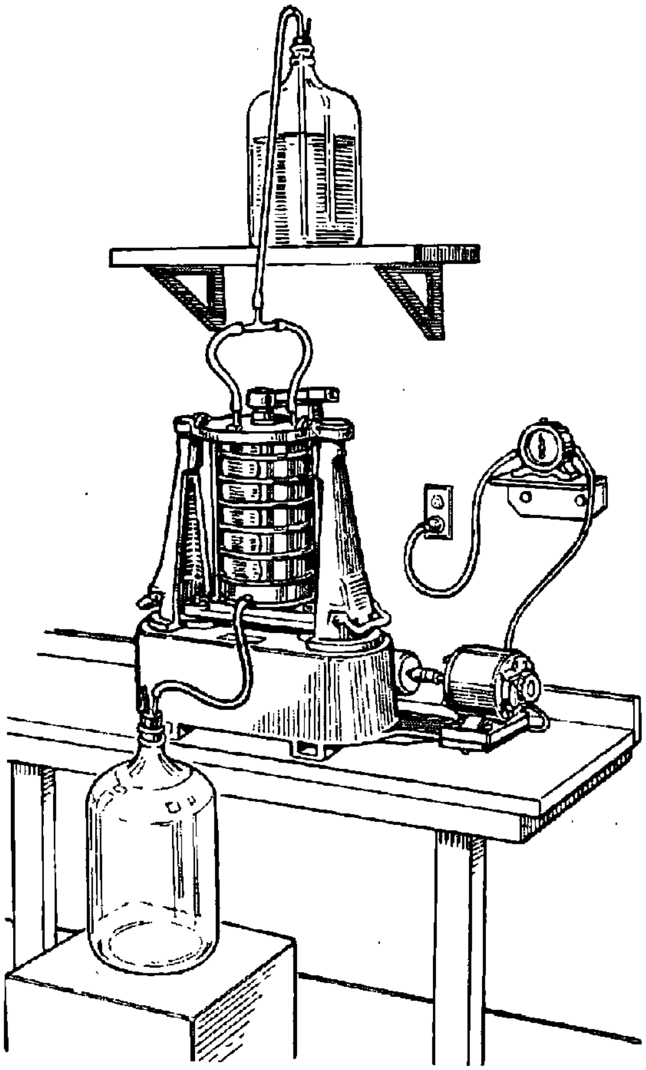
The dry plus 200-mesh fraction is weighed and then dry screened as described in section 2.6.2.2. Any minus 200-mesh material collected during the dry screening is combined with the minus 200-mesh fraction collected during the wet screening. All weights are recorded. Again, carefully check all screens for damage and rerun the test if any is found. If the sample being screened contains an appreciable amount of plus 14-mesh material, protecting the 200-mesh screen with a 14-mesh guard screen during the wet-screening operation is desirable. Figure 2.14 illustrates this arrangement.

2.6.2.4 Wet Screening (8-in screens)

Complete wet screening can be carried out on specially adapted mechanical shakers, such as that shown in figure 2.15. A controlled stream of water is fed onto the top screen, and the underflow from the finest screen is collected in a suitable container.

To start the test, the dried and weighed feed sample is slurried with water and washed onto the top screen of the chosen nest of sieves and the collection pan. The stack of screens is then clamped into the shaker. Normally, it is best to operate the shaker for a few seconds to a minute before the waterflow is started to ensure that most of the transfer liquid has passed through the stack of screens. A small wash waterflow is then started and continued for the desired time. If, after this startup procedure, little or no underflow is obtained, then it generally indicates blinding of one or more of the screens. This blinding can often be overcome by a little additional shaking time before turning on the waterflow or by gently tapping the sides of the screens in the stack.

Figure 2.15



Wet-screening apparatus (wet ROTAP).

Screening should be continued until the underflow is completely clear. This can be checked by catching a small sample in a glass beaker. The solution should be free of any cloudiness or undersize particles. If the undersize requires further sizing, the collected slurry should be transferred to the next stack of screens and the above procedure repeated.

The material collected on each screen should be washed from the screen and dried. It is often desirable to filter the material on a tared filter paper before drying. Also, in most hydrometallurgical investigations, the minus 200-mesh fraction is collected, filtered, dried, and saved for subsequent chemical analysis or other characterization. Record all weights on a suitable form.

Again, inspect all screens for damage, and rerun the test if any holes or tears are found. In wet screen analysis, it may be difficult to check the final total dry weight of the various fractions against the original starting weight. For example, this effect can occur when the sample contains water-soluble constituents. When water-soluble components are present, the degree of solubility must be determined and taken into account. If there is a material-balance divergence of more than a percent or so, then the complete procedure should be reviewed, checked for possible errors, and repeated if there are unanswered questions.

2.6.2.5 Data Reduction

After the weights have been recorded on a form such as that shown in figure 2.14, the percentages of material retained on or passing through each sieve are calculated. The percentage retained on each sieve is calculated by dividing the "total weight coarser" than that sieve by the total weight of all the screen fractions. The "total weight coarser" includes the material retained on that particular sieve plus the material on all coarser sieves.

The percentage passing each sieve is calculated by dividing the "total weight finer" than that sieve by the total weight of the test sample. The "total weight finer" includes all material passing through a given screen.

The cumulative percent retained (on) represents the total percentage of the test sample coarser than the aperture of that particular sieve. The cumulative percent passing represents the total percentage of the test sample that is finer than the aperture of that particular sieve. The total percent passing a given screen can be an important variable in hydrometallurgical processing; it often correlates with leaching and filtration rates. Figure 2.16 illustrates a completed laboratory screen analysis report. Figure 2.17 shows a semilog plot of the screen analysis results.

2.7 SAFETY

All the general safety practices discussed in chapter 1 apply to feed preparation operations. In particular, these include practices relating to safety glasses, safety shoes, other protective clothing, personal hygiene, housekeeping, and the consumption of food or drink in work areas. Additionally, special emphasis is required for procedures related to dust collection, guards on mechanical equipment, and noise protection.

Figure 2.16

Sample: Tails-Leach Test No. 121

Weight: 150.0 g

Date: January 24, 1992 Name: J. Doe Screen Time: 10 min

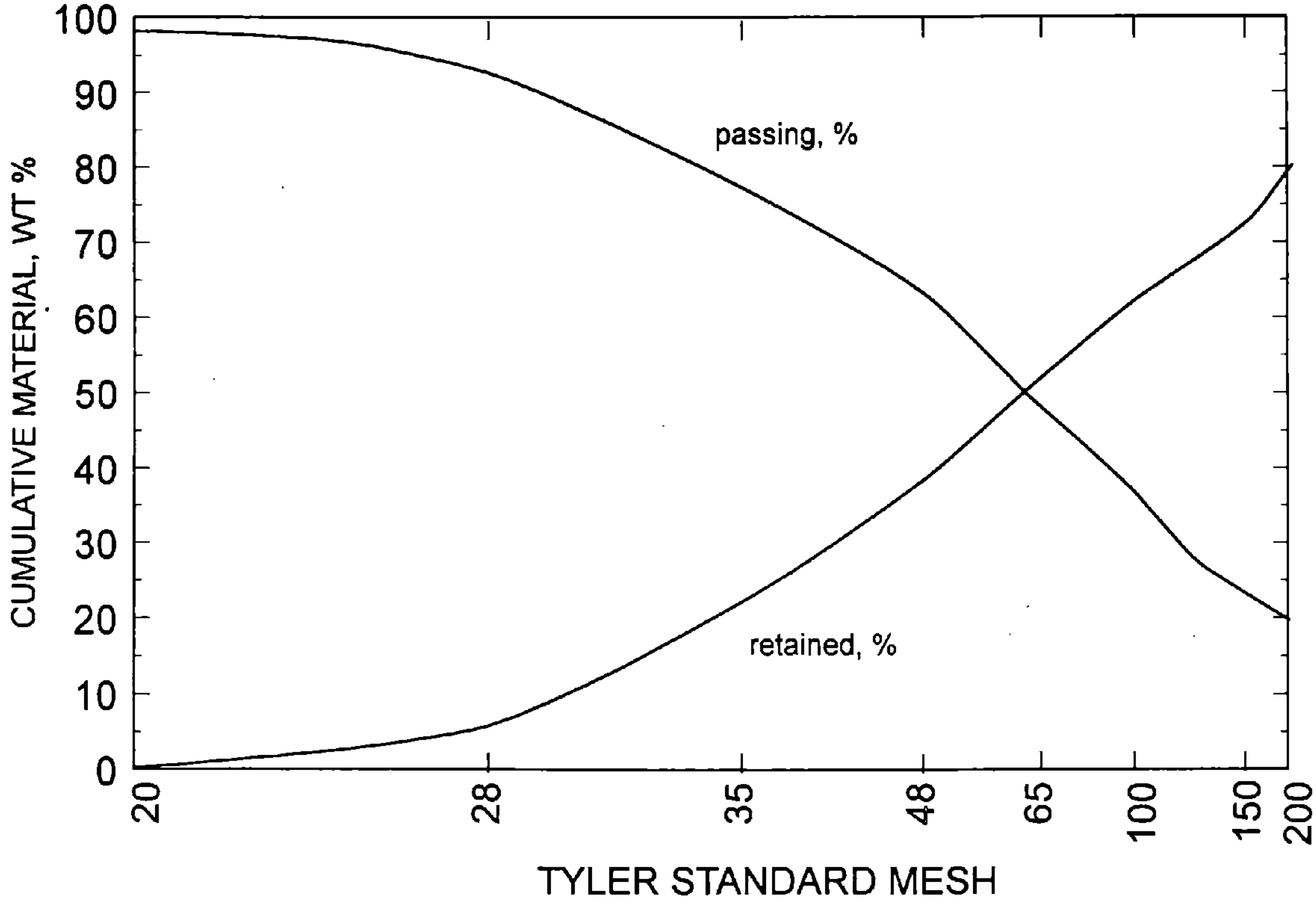
SCREEN MESH		WEIGHT ON		CUMULATIVE PERCENT	
TYLER	U.S. NO	GRAMS	PERCENT	ON	PASSING
3					
4	4				
6	6				
8	8				
10	12				
14	16				
20	20	0.6	0.4	0.4	99.6
28	30	7.8	5.2	5.6	94.4
35	40	25.8	17.1	22.7	77.3
48	50	22.8	15.3	38.0	62.0
65	70	18.0	12.0	50.0	50.0
100	100	18.0	12.0	62.0	38.0
150	140	16.5	11.0	73.0	27.0
200	200	10.5	7.0	80.0	20.0
Pan		30.0	20.0	100.0	
TOTAL		150.0	100.0		

Completed screen-analysis form.

Figure 2.17

Cumulative Direct Diagram of Screen Analysis on Sample of Tails-Leach Test No. 121

Name J. Doe Date Jan 24, 1992



Plot of screen-analysis results.

2.7.1 Dust Collection

Almost every phase of the feed sample preparation process can generate dust; it probably constitutes the major safety consideration associated with these operations. Until analyses and characterization studies have proved otherwise, it is prudent to assume that any given dust may contain one or more hazardous substances. For example, some gold ores may contain appreciable quantities of arsenic minerals, and a wide variety of toxic metals may be present in tailings samples. To the maximum degree possible, dust collection should be engineered into all sample preparation facilities. Exhaust hoods that capture the dust at its source can be designed for crushers, grinders, splitters, screening equipment, etc. Basically, a hood can be considered as an orifice through which the dust-laden air enters an exhaust system.

The literature generally defines the following three classes of hoods:

- *Local exhaust hoods*—These are relatively small structures enclosing or located close to the point of dust generation. Capture occurs before dispersion can take place.

- ***Side, downdraft, and overhead hoods***—These hoods are larger versions of the local exhaust hoods. They rely on larger exhaust volumes to prevent dust escape beyond the control zone.
- ***Booths or enclosures***—These designs isolate the dust generation source from the general workplace. An inward airflow through access or inspection openings prevents dust escapement. When booths or enclosures apply, experts consider them to be the most effective hood design.

The following references present detailed information on how to design, build, or buy dust collection systems: ACGIH (1992), Alden and Kane (1981), and Kane (1950 and 1951).

Alden and Kane (1981, p. 16) list the following general principles for the design of dust hoods:

1. Reduce the cause of dispersion as far as possible by modification of the process, machine, or material before designing hoods.
2. Place the hood as close as possible to the dust source, preferably enclosing it.
3. Locate and shape the hood so that the dust released from the source is either directed or ricocheted into the mouth of the collection pipe.
4. Cause the air to flow past the dust source and into the hood with a velocity at the point of dust origin greater than the escape velocity of the particles being generated.
5. Locate the hood so that the operator is never between the dust source and the hood.

The recommended indraft velocities listed in table 2.4 were developed by early investigators, but are still considered generally applicable. Since each installation, however, will have unique characteristics, design procedures such as those presented in the references above should be followed. This approach is needed to ensure that the ventilation system will perform adequately and economically.

Table 2.4.—Normal indraft velocities

Method of generation	Usual velocity, fpm	Typical applications
Released with low velocity.	100-200	Barrel filling, low-speed conveyor transfer points.
Active generation . .	200-500	Crushers, screens, high-speed conveyor transfer points.

Engineered dust collection is not usually feasible with feed preparation operations such as coning and quartering, fractional shoveling, and some splitting procedures. When conducting these operations, operators must use dust protection. Determining the degree and type of dust protection required can be complex, and therefore, the responsible safety officer or other knowledgeable source, such as an industrial hygienist familiar with OSHA regulations, should be contacted. For example, materials classified as toxic or hazardous (29 CFR 1910.1000) will have time-weighed exposure requirements and air sampling will probably be required. The type of dust protection needed will depend upon both the type of contaminant present and the degree of exposure. In some instances, the manufacturer or supplier of personal protection equipment can provide preliminary guidance.

2.7.2 Equipment Guards

All sample preparation machinery must be provided with guards that meet regulatory standards. These guards are designed to protect the operator and other employees in the work area from hazards associated with the machinery. Such hazards include nip points, rotating parts, flying chips, and the actual point of operation where work is performed upon the material being processed.

OSHA has published Machinery and Machine Guarding Standards (CFR, 29 CFR 1910.211-.222, 1991). Part 29 CFR 1910.211 defines the terms used throughout the standards, and 29 CFR 1910.212 discusses the general guarding requirements for all machines. Standards for belt guards and other power-transmission mechanisms are presented in 29 CFR 1910.219.

The careful design of guards is vital. An ineffective guard may be worse than none because it can give a false sense of security. In addition to mechanical guarding, emergency shutoff devices may be needed. Before using any machinery, the operator should inspect the equipment to ensure that the guards are in place and functioning.

2.7.3 Noise Protection

Noise is any undesired sound. At any level it can be distracting, and intense noise will produce hearing loss. Temporary hearing loss may occur after a short exposure to intense noise; if this exposure continues, then hearing loss can become permanent. Factors that affect the degree of temporary or permanent loss include the following:

- Overall sound level.
- Frequency distribution of the sound energy.
- Total duration of the exposure.
- Exposure continuity (i.e., periodic or continuous).
- Individual susceptibility to noise-induced hearing loss.

OSHA has published standards that consider these factors and specify mitigating measures (CFR, 29 CFR 1910.95, 1991). For example, the standards require that protection against the effects of noise exposure shall be provided when the sound levels exceed those shown in table 2.5. If feasible, administrative or engineering controls must be used to reduce sound levels to the permissible values. If such controls fail, personal protective equipment that reduces the sound levels to those shown in the table must be provided. Even simple ear plugs can provide adequate protection from most of the noise levels encountered in hydrometallurgical studies.

Table 2.5.—Permissible noise exposures

Duration, h/d	*Sound level (slow response), dBA*
8	90
6	92
4	95
3	97
2	100
1.5	102
1	105
0.5	110
0.25 or less	115

Procedures for calculating equivalent noise exposures under a variety of conditions are also presented in 29 CFR 1910.95 together with monitoring program requirements. The standards also define record keeping, training, and audiometric testing criteria.

Information on threshold limit values for noise has also been published by the American Conference of Governmental Industrial Hygienists (ACGIH, 1991). A general discussion of noise and its effects has been presented by Mahn (1991, pp. 157-161).

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CHAPTER 3.—LEACHING

3.1 INTRODUCTION

Hydrometallurgical and waste-treatment leaching experiments are designed to assess the effect of variables such as the following:

- Particle size.
- Temperature.
- Reagent additions.
- Slurry density.
- Degree of agitation.
- Pressure.
- Retention time.

The objective of most leaching studies is to minimize costs by optimizing the process variables to achieve extraction selectivity, maximum reactions rates, and minimum reagent additions. The laboratory equipment setup must be designed so that each of the critical variables can be evaluated. The following paragraphs review factors and conditions that can affect the leaching-system design and operation.

- *Sample requirements*—The amount of ore or other feed material required for a comprehensive, bench-scale experimental-leaching investigation can vary widely. The mineralogy and other compositional characteristics are almost always critical. The planning phase for any leaching study should include a mineralogical characterization of the ore or other leach feed. Even relatively simple microscopic techniques can provide useful information.

The minimum amount of material required for each individual leach test will depend on factors discussed in section 2.2.2. Particle size, grade, and homogeneity all play a role. For example, (based on table 2.1) each test on a low-grade, relatively uniform ore that will be leached at approximately minus 20 mesh should use about 500 g of feed material. For this material, a complete bench-scale leach-test program will probably require 25 to 50 kg of ore. For other feed materials, the information presented in table 2.1 and figure 2.1 can provide appropriate sample-weight guidelines. In any event, the variability between replicate tests should be investigated.

- *Particle size*—In general leaching requires only that the valuable mineral particle be exposed. Liberation such as that required for flotation is not necessary. Nevertheless, although finer grinding nearly always improves extraction, it can also increase reagent consumption due to side reactions and decrease the leaching selectivity. Therefore, the optimum grind usually represents a balance between these effects. Overgrinding can also increase pulp viscosities and reduce the settling and filtration rates in subsequent solids-liquid separations. In addition, overgrinding increases comminution costs. Table 3.1 presents a listing of typical leaching times as a function of size and table 3.2 lists typical agitation-leach feed sizings (Woodcock, 1985).

Table 3.1.—Typical leaching times as a function of particle size

Particles	*Time*
Waste dumps (minus 60 in)	10 years.
Heaps (minus 6-in ore)	1 year.
Minus 0.125-in ore (percolation)	2 to 14 days.
Minus 65-mesh ore (agitation)	2 to 24 days.
Minus 10 microns (agitation)	0.1 h.

Table 3.2.—Typical commercial agitation-leach feed sizings

Feed	*Size*
Bauxite	Minus 100 mesh.
Gold ores	80% minus 200 mesh.
Gold concentrates (sulfides)	Minus 325 mesh.
Ilmenite	Minus 200 mesh.
Nickel laterite	90% minus 200 mesh.
Nickel concentrates (sulfides)	Minus 200 mesh.
Uranium ores	Minus 10 mesh to minus 100 mesh.
Zinc calcines	Minus 200 mesh.

- *Temperature*—Temperature is an important ore-leaching variable. If the leaching process depends predominantly on chemical reactions, increased temperatures can significantly increase the reaction rate. When leaching is primarily diffusion dependent, the temperature effect becomes less dramatic because diffusion-controlled mass transfer in the liquid boundary layer has a relatively low temperature dependence (Forward and Peters, 1985, p. 13-11). It is not unusual, however, for both chemical and diffusion effects to play important roles. For example, when sulfides are being oxidized, an increase in temperature produces an exponential increase in the chemical reaction rate. Under these conditions, the slower diffusion rate becomes controlling. Elevated temperatures can sometimes increase the rate of undesirable side reactions. Temperature can also affect the solubility of substances. This effect is a key component of the Bayer alumina process. In general, the consequences of leaching temperature variations can become complex, and thorough testing is required. The researcher must design both the equipment setup and the experimental program so that relevant measurements can be obtained.

- ***Reagent additions***—Reagent additions typically constitute a major component of hydrometallurgical-leaching operation costs. The relationships among reagent concentrations, the amounts added, and other leaching variables are usually interdependent. Determining the optimum conditions for maximum extraction with minimum reagent consumptions requires experimentation. Designing the experimental system so that accurate measurement and control of reagent additions can be achieved is a critical step in the research planning process. Instrumental techniques such as pH, redox, conductivity, and ion-selective electrodes can provide reliable on-stream controls for many leaching systems. Redox control can be critical in systems where oxidation of a mineral with ionic oxidizers such as Fe^{3+} or ClO_4^- is required. For example, acid leaching of ores containing uraninite minerals requires oxidant additions sufficient to maintain oxidations potentials in the 400- to 450-mV range for satisfactory uranium extractions. Table 3.3 presents a summary of typical leaching conditions for a number of different hydrometallurgical systems (Woodcock, 1985).

The planning exercise must also include thorough consideration of methods for comprehensive feed and product analyses. Predesign consultation with analytical laboratory personnel almost always pays dividends.

- ***Slurry density***—The optimum slurry density for agitation leaching of most ores and similar materials usually lies close to the maximum possible that still permits satisfactory contact between the solid and liquid phases. This optimum depends on a range of interactions, such as the ore mineralogy, the degree of grinding, the leaching reagents and their concentration, the type of agitation being used, and the requirements of subsequent process operations. If the feed-preparation circuit uses wet grinding, the maximum slurry density possible may be dictated by the grinding-circuit characteristics. Column 5 in table 3.3 lists typical pulp-density concentrations for a variety of different ores or concentrates. When leaching high-clay ores, such as those found in some cyanidation circuits, the pulp viscosity may significantly inhibit the air dispersion required for oxidation. In general, however, high pulp densities do help to minimize the leaching circuit investment.

Table 3.3.—Summary of typical leaching-process conditions

Ore or concentrate	Sizing, mesh	Main leachant[1]	Other reagents	Pulp density, % solids	Temp, °C	Time
Antimony concentrate (tetrahedrite) . .	-100	25% Na_2S[2]	None	20	100	8 to 10 h.
Bauxite	-100	20-35% NaOH [2]	None	40	170	2 h.
Bismuth concentrate	-65	HCl	HNO_3	50	85	1.5 h.
Copper ore (oxide)	(3)-3/8	5% H_2SO_4	Fe^{3+} (4)	(5)	Amb.	5 days.
	-100	2% H_2SO_4	Fe^{3+} (4)	40	Amb.	2 h.
	(3)-0.5	10% NH_3	5% CO_2	(5)	Amb.	5 days.
Copper ore (sulfide)	(6)	H_2SO_4	Fe^{3+}, bacteria	(6)	Amb.	5 to 10 years.
Gold ore	-65	0.05% NaCN	O^2, $Ca(OH)_2$	50	Amb.	4 to 24 h.
Gold concentrate (sulfide)	-325	0.1% NaCN	O^2, $Ca(OH)_2$	40	Amb.	10 to 72 h.
Ilmenite	-200	90% H_2SO_4	Sb_2S_3	45	110	0.5 h.
Nickel laterite	-100	3% H_2SO_4	None	45	250	2 h.
Nickel laterite (reduced)	-100	6% NH_3	3.5% CO_2	20	Amb.	None.
Nickel concentrate (sulfide)	-200	15% NH_3	150 psig air	26	85	None.
Pyrite cinders	-65	7% HCl + NaCl	Cl_2	(5)	40	20 h.
Silver ore	-65	0.2% NaCN	O_2, $Ca(OH)_2$	45	Amb.	72 h.
Uranium ore	-100	0.5-5% H_2SO_4	Oxidant	45	Amb.	16 to 48 h.
	-100	5% Na_2CO_3	HCO_3-, air(7)	40	75	90 h.
Zinc calcine	-200	10% H_2SO_4(2)	None	12	50	3 h.

Amb. Ambient

[1] Concentrations shown apply mainly at the start of leaching.

[2] Contains recycled metal.

[3] Inch.

[4] Mainly needed if sulfides present.

[5] Percolation leach.

[6] Dump material.

[7] Other oxidants may be used.

- ***Degree of agitation***—When compared to the effects of other variables such as reagent concentrations and temperature, the leaching kinetics of ores and concentrates are relatively insensitive to the degree of agitation. In general, laboratory leaches require a degree of agitation that effectively disperses the leaching reagents and prevents the settlement of coarse particles. Energy inputs above that required to approach a uniform suspension may be of little benefit, and in some instances may promote particle attrition, which can complicate subsequent solids-liquid separations. Higher energy inputs may increase the initial reaction rate somewhat, but they usually have little or no effect on the reaction kinetics as the system approaches maximum extraction. Therefore, the time required to achieve near maximum extractions tends to be the same irrespective of the agitation energy input. These relationships hold because leaching is principally a topochemical phenomenon. Leaching kinetics are often controlled by diffusion of the leaching solution into the ore particles rather than by mass transfer at the surface; and, therefore, under these conditions, reaction rates are not significantly affected by the degree of agitation.

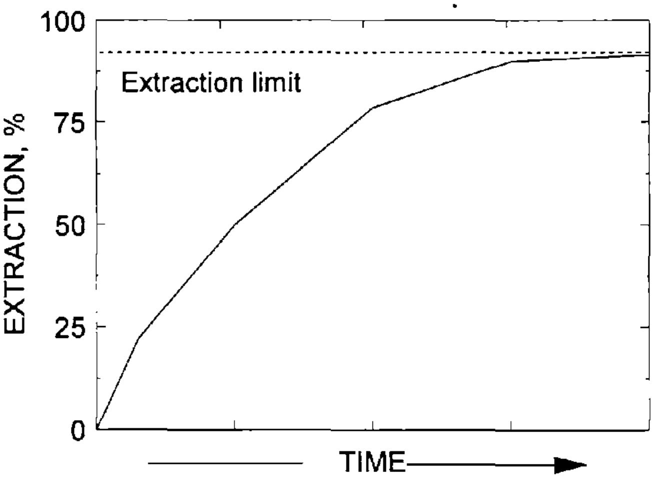
The degree of agitation can become critical, however, if gases are being dispersed into the pulp. This type of reaction system occurs when air is introduced into agitated cyanidation reactors or when oxygen is injected into pressurized sulfide-leaching autoclaves. Accurately predicting the process performance of gas-sparged hydrometallurgical reactors typically requires a combination of directly related pilot-scale data and experience (Oldshue and Kurgera, 1992). The pilot-plant tests must usually be conducted at a significant scale. In some instances even results obtained in 100-L reactors may be questionable (Gormley, 1992) (Tatterson , 1991).

- ***Pressure***—In most instances pressure leaching is used in hydrometallurgical operations for the following reasons:

1. To permit operating temperatures above 100 °C, which promote major increases in reaction rates.
2. To increase gas solubilities in the lixiviant, e.g., when using oxygen or air as an oxidizing agent for sulfides or refractory minerals.
3. A combination of reasons 1 and 2.

- ***Retention time***—Determining the required or optimum leach retention time for a particular ore or other material almost always requires laboratory leaching experiments. Figure 3.1 illustrates a typical curve that depicts extraction as a function of time. Characteristically, the curve shows a relatively fast initial rate followed by an asymptotically decreasing rate as the extraction approaches the maximum obtainable. The specific shape and location of the curve depends on a variety of factors such as particle size, particle distribution, matrix composition, porosity, temperature, reagent concentration, and other factors. The bench-scale experimental procedures and the equipment setup must be designed to measure and define the often complex relationships among these variables.

Figure 3.1



Typical relationship between percent extraction and time.

General references that relate to leaching theory, mass transfer, and functional applications include the following: Burkin (1955); Forward and Peters (1985); Hamm (1980); McCabe and Smith (1970); Miller (1974); Oldshue (1983); Rickles (1965); Schweitzer (1988); Treybal (1980); and Van Arsdale (1953).

3.2 LABORATORY LEACHING SETUPS AND SYSTEMS

3.2.1 Introduction

Most hydrometallurgical and waste-treatment leaching operations can be classified as chemical leaching. The valuable component transfers from the ore particle or other substrate into the extracting solvent as the result of a chemical reaction between the leaching agent and the solid. A variety of variables such as those discussed in section 3.1 can affect these reactions. Also, the reaction rate may change as leaching proceeds, and this change must be quantified.

The researcher should design each laboratory leaching setup or system to evaluate the anticipated effects of all potentially significant variables. It is not unusual to find that the initial leaching data indicate the original setup will require some modification. Although no single leaching-equipment arrangement will be applicable for all leaching systems, some generalizations do apply. The following descriptions and procedures can be considered as applicable starting points for various types of bench-scale batch- and continuous-leaching studies.

3.2.2 Batch Leaching

Batch leaching can include agitation leaching and column- or heap-leaching operations. Agitation leaching can be defined as any system in which both the solid and the liquid are in motion. During column or heap leaching, the ore bed remains static and the liquid moves through this static bed. One major difference between these two systems relates primarily to the size of the particles being leached. Column leaching is primarily applicable for relatively coarse particles.

3.2.2.1 Agitation Leaching

The most common form of agitation leaching involves setups in which the particles are suspended by some form of impeller. Bottle-rolling tests have also been used widely to study leaching systems such as the cyanidation of precious-metal ores. The following sections discuss laboratory-equipment arrangements and procedures that can be used or adapted for agitation-leaching experiments.

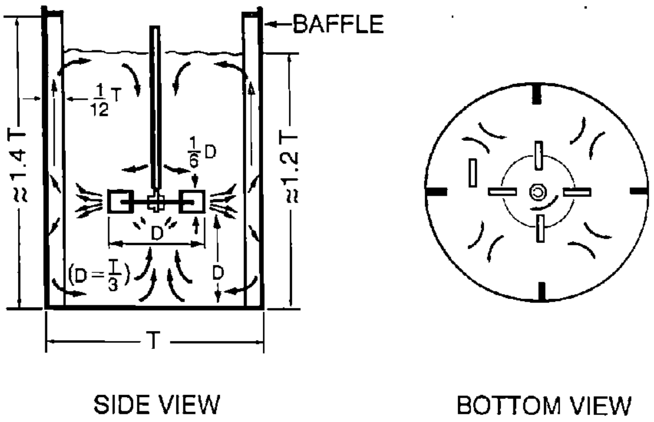
- *Impeller agitation*—Impeller-agitated leaching tests can be conducted in a variety of leaching vessels. The specific type of vessel used is usually determined by factors such as the required temperature control, the necessary degree of agitation, the pH and electromotive force (emf) measurements needed, reagent addition control, and sampling requirements.

Preliminary tests can usually be conducted in unbaffled beakers or similar containers using a central axially mounted agitator or possibly a magnetic-stirrer arrangement. Magnetic stirring, however, should be used with caution. If the pulp viscosity is appreciable or if the slurry contains relatively large or high-specific-gravity particles, the degree of mixing produced by magnetic stirrers may be questionable. Stirring with an axially mounted impeller in an unbaffled cylindrical vessel produces a vortex. Typically, the agitator speed must be limited because undesirable air entrainment may occur when the vortex reaches the impeller.

Baffled leaching vessels are applicable for nearly all ore or concentrate leaching experiments. Figure 3.2 depicts general guidelines for a baffled leaching-vessel configuration. The stirrer drive should be a variable-speed unit so that agitation effects can be evaluated. In small vessels (1,000 mL or less) pH probes, temperature sensors, etc., can provide some degree of baffling, but baffles such as those shown in figure 3.2 are better.

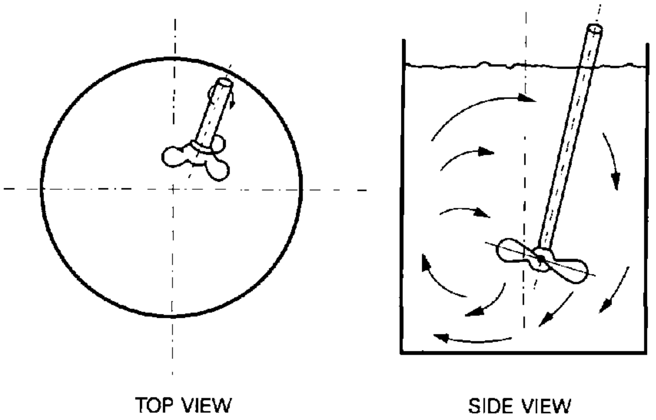
Satisfactory slurry agitation usually can also be achieved in unbaffled vessels by using an angular off-center axial-flow impeller configuration such as that shown in figure 3.3. The impeller is mounted approximately 15° from the vertical.

Figure 3.2



General guidelines for a baffled leaching-vessel configuration (equipped with either a single disk-type turbine or a single marine propeller).

Figure 3.3



Leaching-vessel configuration without baffles using a top-entering, off-center, marine-type propeller agitator.

A variety of heating methods, such as hotplates, heating mantels, and jacketed vessels, have been used to provide controlled leaching temperatures. Heating mantles provide good control of above-ambient leaching temperatures, and jacketed vessels can produce either heating or cooling functions. Controlling leaching temperatures within ± 1 or 2 °C is desirable for most leaching experiments. Manual temperature control using an electric hotplate or heating mantle connected to a variable transformer is satisfactory for relatively short leaches of 4 h or less. Automatic temperature control is recommended for longer leaches. A wide variety of both proportional and off-on temperature controllers are available. Proportional controllers normally provide the most precise control, but good control can also be achieved by combining a relatively simple off-on controller with a variable transformer. The variable transformer is adjusted so that the heating device is on approximately 90% of the time when maintaining the desired leaching temperature.

Most laboratory leaching experiments are conducted in relatively small vessels (2 L or less). This scale nearly always produces satisfactory extraction data, but if agitation power-input measurements are needed, larger scale testing is required. Some equipment manufacturers recommend that generating meaningful data for mixer performance requires a mixing vessel with at least a 40-L capacity. Therefore, the researcher should consult with a mixing-equipment manufacturer when mixer sizing and performance data are needed. It should be recognized, however, that consensus on agitator design does not always exist among vendors.

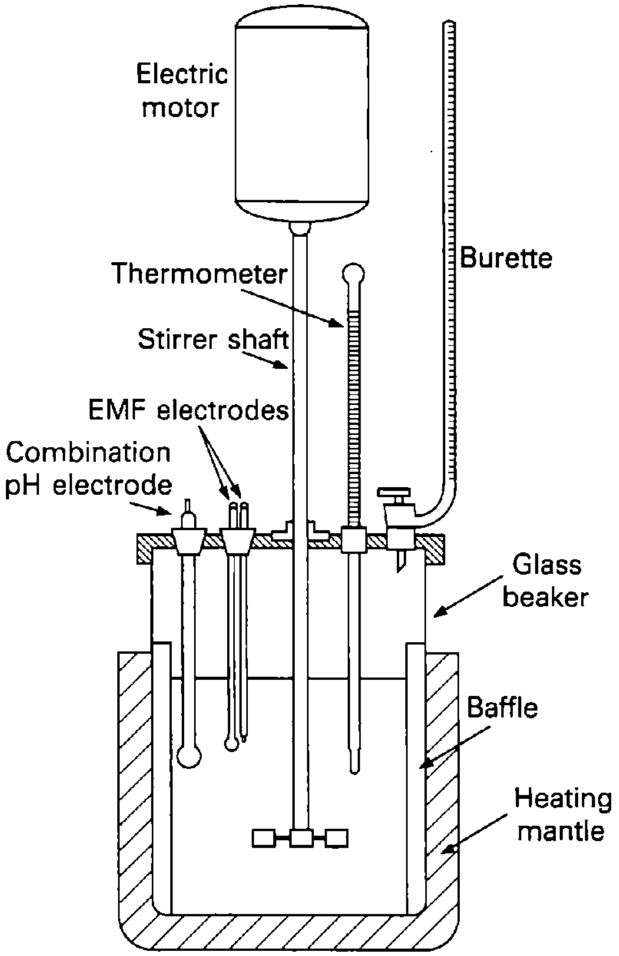
- *Acidic leaching*—Equipment arrangements similar to that shown in figure 3.4 have been used successfully for pH-controlled acid leaches on uranium ores, oxide copper ores, some solid wastes, and corresponding materials. This basic arrangement can be adapted to meet a wide variety of different requirements and conditions.

Baffled glass beakers are suitable leaching vessels for most experimental conditions. Dimensional relationships equivalent to that shown in figure 3.2 are recommended. Researchers have used a number of different baffle installations. For example, glass baffles can be fused directly to the beaker, or inserts that slip into the beaker can be fabricated from suitable materials. A common baffle arrangement consists of four baffles fastened to a pair of open hoops that can be compressed and then slipped into the beaker.

For most materials, a 1,000 mL Pyrex glassware beaker is a suitable leach vessel for 500-g test samples, and a 2,000-mL beaker is normally adequate for 1,000-g samples. In some instances, however, larger leaching vessels will be needed to provide the required head room. This situation will occur, for example, when leaching must be carried out on relatively dilute leach pulps. Many researchers have also used reaction kettles, such as that shown in figure 3.5, as leach vessels. The covers and bottoms, which have ground flanges, are clamped together for a tight seal. These units are particularly applicable for elevated-temperature leaches where a condenser is used to return any vaporized liquid to the leaching vessel.

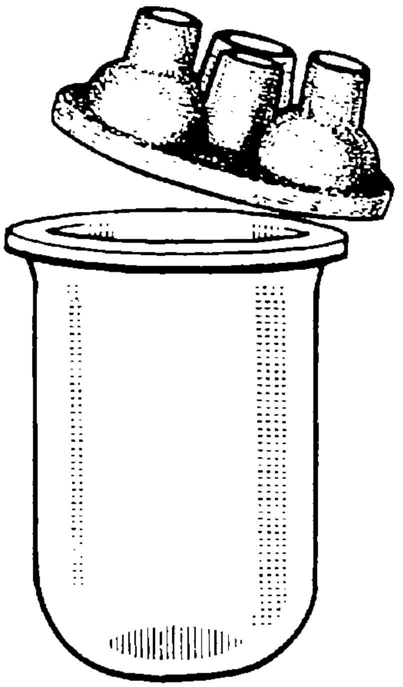
Agitation should be provided by a variable-speed agitator. In most instances a 0.1-hp unit will provide more than adequate stirring power, and a 0.05-hp unit will be satisfactory for many applications. For the standard leach-vessel configuration (figure 3.2), the 1,000-mL-beaker setup should use an impeller with approximately a 1.3-in diameter, and the 2,000-mL beaker will need a 1.6-in-diameter impeller. Impeller speeds in the range from 600 to 1,200 rpm will normally produce satisfactory particle suspension.

Figure 3.4



Apparatus for acid-leach tests.

Figure 3.5



Reaction-kettle glassware.

pH measurement—For most leaching experiments, standard combination electrodes provide adequate pH measurements. If contamination appears to be interfering with the measurements, a reference electrode with a junction that can readily be cleaned will be desirable. Reference electrodes are available that have a movable junction, which can readily be opened. This allows the filling solution to flow through the junction carrying away any contamination such as very fine ore particles or reaction products.

The pH electrodes should be calibrated against appropriate buffer solutions before each test. The buffer used should be as close as possible to the desired leaching pH. Recalibrating every 3 to 6 h during the leach test is also recommended. Any electrodes that show a slow response or drifting during the buffering operations should be cleaned or replaced; the reading should stabilize within 10 to 15 s after placement in the buffer solution. When cleaning or reconditioning a contaminated electrode, the manufacturer's instructions should be followed carefully. If a new electrode does not produce a stable reading within 10 s, the meter circuits may be defective. The manufacturer's directions for electrode care, buffer-solution preparation, and troubleshooting should be followed carefully. Generally accepted recommendations for electrode care include the following:

1. Unless otherwise specified by the manufacturer, electrodes should be stored in an acidic solution with a relatively low salt content such as a 1*M* (molar concentration) KCl solution adjusted to pH 4.0. Commercial storing solutions are also available. This procedure becomes particularly important if the electrodes are to be stored for longer than 2 weeks.
2. Electrodes should always be used in a vertical position.
3. Electrodes should be rinsed between samples with distilled or deionized water. Excess water should be removed by blotting the end of the electrode with a lint-free paper. The electrodes should never be wiped dry because this can cause spurious readings due to static charges that can transfer from the operator's body to the high-resistance glass bulb. The bulb acts like a charged capacitor, and the charge requires time to dissipate.

   If sufficient sample is available, rinsing the electrodes with a portion of the next sample is preferable. The waste rinse liquor is discarded. When this procedure is used, electrode blotting is not necessary.
4. When using refillable electrodes, the liquid level should be maintained at no less than two-thirds full. Unless otherwise specified by the manufacturer, the filling hole should be kept open during use.
5. A proper electrode holder should be used to provide support that will minimize the potential for damage when lowering the probe into solutions.

Nearly all buffers supplied in solution form contain preservatives that inhibit mold growth; and therefore, stock solutions have prolonged shelf life. Commercial buffer solutions usually have an expiration date printed on the label. Some buffer tablets or capsules do not contain preservatives, and the shelf life of stock solutions prepared from these tablets or capsules may be limited.

In general, the lower pH buffers are the most stable. For example, a working sample of 4.0-pH buffer that has been stabilized with a preservative can normally be safely used for at least 5 days if the solution is stored in a closed container such as a wide-mouth jar with a screw lid or in a beaker covered with a sheet of Parafilm plastic. A working sample of 10-pH buffer, however, may have a useful life of not more than 1 day. Nonstabilized buffer solutions may have even shorter working lives. Buffer suppliers recommend that buffer solutions be stored in sealed containers and kept in a cool location. For the most precise pH measurements, fresh buffer solution should be used for each calibration and then discarded.

In recent years, equipment manufacturers have produced pH meters with increasingly comprehensive and sophisticated capabilities. Memory circuits and automatic calculation functions are common. These developments emphasize and substantiate the importance of following the manufacturer's specific operating and troubleshooting instructions. In general the recommended procedures are adaptations of the following standardization and sample measurement steps (Westcott, 1978):

Standardization (single buffer).

1. Measure the temperature of the standard buffer solution. Set the pH-meter temperature compensator to the measured temperature.
2. Rinse the electrodes to be used with a few milliliters of buffer or distilled water. If water is used as the rinse, blot (do not wipe) the electrodes with a laboratory tissue to remove excess liquid. No blotting is necessary if a portion of the buffer is used as the rinse.
3. Place the electrodes in a fresh portion of the buffer and activate the meter. Allow the electrodes to equilibrate with the buffer before setting the meter readout to the standard pH value of the buffer for the measured temperature. Most chemistry handbooks list standard pH values versus temperature for the commonly used buffers.

Sample measurement.

1. Place the meter in standby, remove the electrodes from the buffer, and rinse with an aliquot of sample or distilled water. If a distilled water rinse is used, blot the electrodes.
2. Measure the sample temperature and set the pH-meter temperature controller to that value. (For the most accurate results, the buffer and the sample should have as nearly equal a pH as possible and should be at the same temperature.)
3. Place the rinsed electrodes in the sample and activate the meter. Allow the reading to stabilize before recording the pH value.

The following references contain detailed information on both pH theory and practical applications: ASTM (1957); Bates (1973); Galster (1991); and Westcott (1978). The Westcott reference, in particular, concentrates on solving problems and obtaining a high degree of accuracy in practical pH measurement.

Redox measurements—Some hydrometallurgical or waste-treatment operations require the measurement and control of oxidation-reduction-potentials (ORP). The leaching literature refers to these millivolt measurements using terms such as Redox, redox potential (Eh), emf, and ORP. All of these terms are used to designate the potential (in millivolt) developed by a metallic electrode when placed in a solution containing a species in two different oxidation states (e.g., ferric and ferrous ions). Natarajan and Iwasaki have studied the application of Redox measurements in hydrometallurgical systems (Natarajan and Iwasaki, 1970 and 1974).

Both the Pt Calomel and Pt (Ag and AgCl) electrode combinations have been used for Redox measurements in hydrometallurgical-leaching systems. The Pt Calomel combination has been the most widely used because the Ag and AgCl reference electrode is not generally suitable in the presence of sulfides, biologicals, and biochemicals. Nearly all bench-top pH meters provide millivolt readout features for making Redox measurements; the operating manuals give detailed hookup and operating instructions.

Redox measurements do not require standardization or calibration because, in effect, the potential measured is an absolute, specifically characteristic of the oxidation-reduction equilibrium. It is desirable, however, to check frequently for electrode poisoning or other operational problems. These checks can be made using solutions of known potential that are prepared by saturating buffer solutions with quinhydrone. The measured potential of these check solutions varies with both pH and temperature as shown in table 3.4.

Table 3.4.—ORP of quinhydrone solutions,[1] readings in millivolts

Temperature	20 °C	25 °C	30 °C
Reading in pH-4 buffer:			
Pt - calomel	+233	+218	+213
Ag - (Ag/AgCl)	+268	+263	+258
Reading in pH-7 buffer:			
Pt - calomel	+47	+41	+34
Ag - (Ag/AgCl)	+92	+86	+79

[1] Using European convention for the polarity of the electrochemical potentials.

The check test procedure is as follows:

1. Saturate the buffer with quinhydrone. Since quinhydrone has a relatively low solubility (approximately 4 g/L) only a few crystals will be needed to saturate 50 mL of buffer. Use a glass stirring rod. If all of the quinhydrone dissolves, add a few more crystals and stir. Repeat as necessary until a small amount of quinhydrone remains undissolved. The solution will have an amber color. A fresh check solution should be made up for each test because the mixture has a shelf life of only about 2 h.
2. Clean the platinum electrode. Chemical cleaning by immersion in chromic acid, aqua regia, or nitric acid has been used successfully, but mechanical cleaning is often preferable because it does not leave surface films that may

produce erratic readings. Mechanical cleaning can be accomplished by gently polishing the platinum surface with 600-grit wet silicon-carbide paper. Disk-type electrodes have also been cleaned successfully using levigated alumina on a metallurgical polishing wheel. After cleaning, the electrode should be rinsed with distilled water, blotted dry, and soaked in check solution for about 5 min before readings are made.

3. Rinse the electrodes with distilled water, blot dry, and place them in the check solution. Shift the meter to the millivolt-measurement mode and switch to the "measure" position. Allow the reading to stabilize. The measured potential will generally be within ±10 mV of the values listed in table 3.4. Record both the millivolt reading and the solution temperature. Noting the temperature is important because millivolt measurements are not temperature corrected. The pH meter's built-in temperature-compensation system is bypassed because it is only applicable for the hydrogen ion concentration as sensed by the pH electrode combination. The ORP versus temperature relationship is unique for each oxidation-reduction system.

Redox measurements use the following general procedure:

1. With meter in the millivolt mode, switch to the "standby" position. Rinse the electrodes with distilled water, blot dry, and place them in the test solution.
2. Switch the meter to the "measure" position and allow the reading to stabilize. Record both the millivolt reading and the temperature of the test solution.
3. Switch the meter to standby. Remove the electrodes from the test solution, rinse the electrodes with distilled water, blot dry, and store in a commercial storage solution or a 1*M* KCl solution adjusted to 4 pH.

When planning leaching experiments that will require Redox measurements, reviewing related literature references for clues to potential problems is advisable. Contacting electrode suppliers sometimes can also provide valuable suggestions for selecting suitable electrodes or solving operating problems.

Acid leach test procedure (H_2SO_4 leach uranium)—The following test scheme is typical of procedures that have been used successfully for constant-pH uranium-leaching experiments. Steps are outlined for a 1,000-g test at 50% solids (IAEA, 1990, p. 42).

- Place 1,000 mL of water in a 2,000-mL leaching vessel. Demineralized water is appropriate for nearly all initial studies. If, however, actual process water from a proposed mill site is available, at least confirmatory leaching experiments should be conducted using this water.
- Start the agitator, add the 1,000 g of dry ground ore, and bring the slurry to the desired leaching temperature. Controlling the temperature within ±1 °C or less is desirable.
- Adjust the pH to the target level (typically in the 0.5- to 1.5-pH range) by adding 1:1 H_2SO_4. Concentrated H_2SO_4 can also be used, but this makes temperature control more difficult. Normally the leaching time starts when the target pH is first reached. If the ore contains more than a few percent of carbonate minerals, it may be necessary to modify the acid-addition procedure to prevent excessive foaming. For example, foaming control has been achieved by first adjusting and holding the pH at about 3.0 for 15 to 30 min, and then lowering the pH to the target level. Occasionally researchers have found that the pH-adjustment operation for some ores is smoother if the water is adjusted to the target pH before the ore is added. When this technique is used, it may be necessary to add the ore slowly to minimize foaming problems.
- If needed, control the oxidation-reduction potential at the desired level by adding oxidants such as $NaClO_3$, MnO_2, or Caro's acid (Ring, 1985; and Secomb, 1985). The $NaClO_3$ can be conveniently added as a 200-g/L solution. Delaying the oxidant addition for about 30 min after the initial acid addition is often desirable. This procedure allows time for completion of the initial acid reactions with any sulfides present and may significantly reduce the oxidant requirements for some ores.
- Leach-extraction profiles can be followed by withdrawing 20- to 50-mL thief samples of the slurry at appropriate intervals. A wide variety of sampling devices have been used, but a 50-mL glass pipette with the tip removed and equipped with a suction bulb is usually satisfactory. For a 24-h leach, sampling at 0.5, 1.0, 2.0, 4.0, 8.0, and 24 h is usually suitable. It should be recognized, however, that sampling a stirred slurry, which contains a distribution of sizes and shapes, may produce erratic results. The composition of the solids component of duplicate thief samples may vary considerably. Sampling continuity depends on variables such as the fineness of grind, the mineral distribution, the particle size and shape distribution, pulp density, and the velocity patterns in the mixer. For these reasons, leach-extraction profiles are often based on solution analysis rather than on analysis of the solids in the thief samples. When the solution analysis approach is used, the thief sample is filtered immediately and the undiluted filtrate is submitted for analysis. The unwashed solids are discarded. The solution analyses together with the ore feed grade and the original solid-to-solution ratios are used to calculate the leach extractions at each sampling time intervals.

If all of the particles in the leach slurry are minus 100 mesh or finer, an alternative technique that involves analyzing both the liquid and solids fractions is often applicable. Under these conditions, the particle distribution in the agitated slurry is usually quite uniform. When this alternative approach is used, each 20- to 50-mL thief sample is filtered, and the filter cake is washed with a sequence of five 20 to 50 mL of acidified water (1.5 to 2.0 pH). Each of the washes in the sequence should be added before the cake on the filter starts to crack. If cracking does occur, the cracks should be closed with a spatula before the next wash is added. The total filtrate volume is measured. The washed solids are dried overnight at 105 °C and weighed. Both the liquid and the solids are submitted for analysis, and a material balance calculated. If the material balances for the series of time samples are not consistent, extractions based on the solution analysis technique are nearly always the most realistic.

For the most definitive results a separate leach test should be carried out for each leach time, particularly those near the optimum time indicated by the thief-sample approach. All samples from these individual leach tests should be saved, measured, and analyzed so that complete material balances can be made for each data point. If the material balances are not consistent, the tests should be repeated.

- Glass vessels equipped with type 316 stainless steel (316 SS) or Carpenter 20 alloy agitators and wetted-metal parts have proven satisfactory for most sulfuric acid leaching tests on uranium ores. Polypropylene and polyethylene agitators have also been used successfully. For other leaching systems, however, such as those in which halogens are present at elevated temperatures, other construction materials will probably be required. For these conditions, alloys such as Hasteloy C may be the only suitable metals. Often, laboratory supply houses and equipment manufacturers can offer guidance and recommendations for specific applications.

Alkaline solution leaching—Alkaline-leach solutions can be defined as those containing more hydroxyl than hydrogen ions, i.e., those having a pH above 7. The most commonly used alkaline lixiviants include NH_4OH, Na_2CO_3, Na_2CO_3-$NaHCO_3$, and NaOH solutions. A number of combination leach solutions that fall in this category have either been used or proposed. These include the alkaline cyanide lixiviants used for precious metal recovery, alkaline sodium ethylenediaminetetra-acetic acid (EDTA) solutions, and ammoniacal thiosulfate leach liquors.

Most of the criteria and equipment arrangements discussed in the previous section on acidic leaching also apply to alkaline leaching. A number of special factors, however, should be considered when planning alkaline-leaching experiments. These include the following:

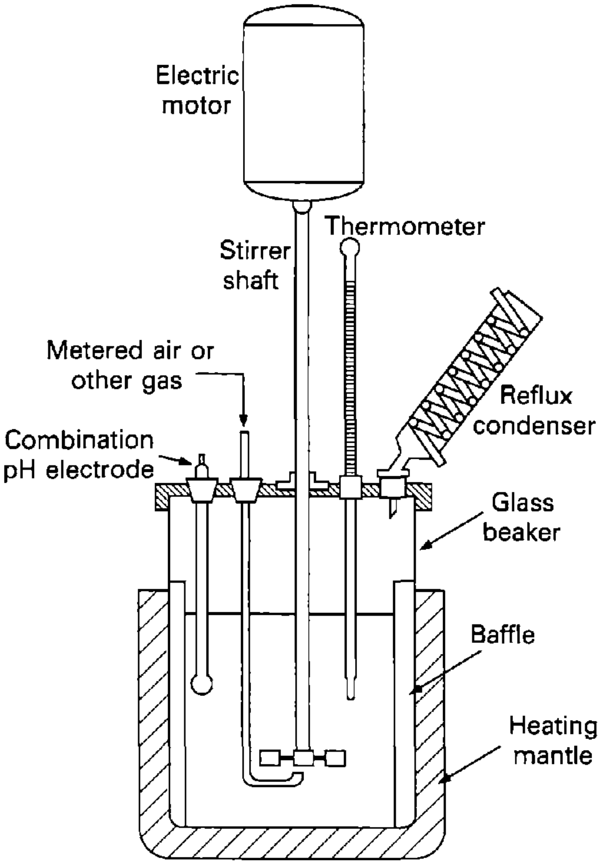
- *Materials of construction*—Pyrex-type glass has proven suitable for most atmospheric-pressure alkaline-leaching experiments. Even if some surface etching does occur, the effect on experimental data is minimal. Relatively strong caustic solutions, however, may require alternative construction materials. Each individual situation will require specific consideration. For example, type 316 SS offers excellent surface corrosion resistance to caustic solutions, but stress corrosion occurs at temperatures above 100 °C. This type of corrosion can become critical in pressure-leaching systems, which will be discussed in a subsequent section.
- *Temperature factors*—Typically alkaline leaches are carried out at above ambient temperatures for relatively long retention times. Therefore, to maintain constant pulp densities, it is nearly always desirable to use a closed leaching vessel and equip it with a condenser to return vaporized liquid to the vessel. The reaction-kettle glassware shown in figure 3.5 meets these requirements.
- *Pressure factors*—Pressure-leaching systems are sometimes required for alkaline leaches because temperatures above 100 °C may be needed to achieve adequate leaching rates. General guidelines for pressure-leach experiments will be discussed in a subsequent section.
- *Reagent additions*—Reagent additions to bench-scale alkaline leaches are typically made in the form of liquids or gases. When liquid reagents are used, it is usually desirable that the reagent be added as a relatively dilute solution because undesirable reactions may occur if concentrated reagents do not quickly disperse. Each situation, and the chemistry involved, must be considered individually. Gaseous reagents such as CO_2 and NH_3 are often best added as air and CO_2, and as air and NH_3 mixtures. Proper dispersion of gaseous reagents can be critical. For example, if air is being added below the impeller as an oxidant, the optimum addition rate will depend on factors such as the type of impeller, the impeller speed, and the leaching-vessel configuration. If the optimum rate is exceeded, the reactor will flood, dispersion will decrease, and mass transfer will become less efficient (Olderstein and others, 1989).
- *pH measurement*—The general guidelines on pH measurement presented in the previous section on acidic leaching also apply to alkaline leaching. In addition, factors such as the following should be emphasized:
- Strong alkaline solutions (pH 12 or greater) may impair the glass electrode response. The error in

alkaline solutions requires a positive correction factor for precision measurements. The researcher should make sure the glass electrode is suitable for the pH range being investigated. For example, an electrode classified as suitable for the 0- to 11-pH range may read a full 1.0 pH low at 13 pH when the solution being measured has a 1.0*M* Na^+ ion concentration. The reading for a 0- to 14-pH electrode under the same conditions would be low by only about 0.1 pH (Westcott, 1978, p. 49). The error also varies with temperature. Corrections recommended by the electrode manufacturer should be applied.

- The relatively short shelf life of high-pH buffers must be considered. As mentioned previously, a working sample of stabilized 10-pH buffer may have a useful shelf life of not more than 1 day because of CO_2 absorption from the air. The working life of nonstabilized buffer solutions may be even shorter.

Alkaline-leach test procedure No. 1 (carbonate leach—uranium)—The following test procedure describes a typical atmospheric alkaline-leach test on uranium ores. The procedure summarizes the steps for a 1,000-g carbonate-leach experiment at 50% solids. Figure 3.6 illustrates the generic configuration of an apparatus typically used for this type of test. Some alkaline-leaching experiments may also require the addition of other equipment such as a burette for adding reagent solutions.

Figure 3.6



Apparatus for alkaline-leach tests.

- Place 1,000 mL of the carbonate-bicarbonate leaching solution in a 2,000-mL leaching vessel. A typical carbonate-leaching solution might contain 30 g/L Na_2CO_3 and 15 g/L $NaHCO_3$.
- Secure the lid, start the agitator, and add the 1,000 g of the dry ground ore to the leach vessel through a suitable opening. In most instances, grinding the ore so that essentially all will pass through a 100-mesh screen is adequate.
- Start the waterflow to the condenser and heat the pulp to the desired temperature. For most atmospheric pressure leaches, the target temperature will be between 75 °C and 95 °C, but a few tests at lower temperatures should also be considered. Normally, the leach time starts when the pulp reaches the operating temperature.
- If the effect of oxidation is being investigated, start the controlled air flow or add chemical oxidants such as $KMnO_4$ or H_2O_2. The $KMnO_4$ oxidant has normally been added in the solid form, but solutions containing approximately 50 g/L of $KMnO_4$ have also been used. The H_2O_2 can usually be added as a 10% to 30% H_2O_2 solution.
- Leach-extraction profiles can be followed by withdrawing 25- to 50-mL thief samples of the leach slurry at appropriate intervals. Typical time sequences have included samples at 6, 12, 24, 48, 72, and 96 h. Since the grind for carbonate leaching is normally minus 100 mesh or finer, the particle-size distribution within a series of thief samples tends to be relatively uniform. Therefore, realistic leach-extraction profiles can be obtained by analysis of either the liquid or solid components of the thief samples.

If the solids-only analysis technique is used, the thief sample is filtered on a 5-cm-diameter Buchner funnel. Next, wash the filter cake with 25 to 50 mL of 5% Na_2CO_3 solution, and then add a sequence of three 25- to 50-mL water washes. Each wash in the sequence should be added before the filter cake starts to crack. If the cake does crack, the cracks should be closed with a spatula before the next wash is added. Dry and analyze the solids.

When the solution-only analysis approach is adopted, the thief sample is filtered immediately, and the undiluted filtrate submitted for analysis. The solution analyses together with the ore feed grade and the original solid-to-solution ratios are used to calculate the leach extractions at each sampling time interval.

Alternatively, both the liquid and solid fractions can be analyzed. This technique permits material balances at each time interval. When this approach is used, each 25- to 50-mL thief sample is filtered, the filter cake is first washed with 25 to 50 mL of 5% Na_2CO_3 solution, and then with three 25- to 50-mL water washes. The total filtrate volume is measured and the solution submitted for analysis. The washed solids are dried overnight at 105 °C, weighed, and prepared for analysis using procedures parallel to those described in section 2.4.6. If the alternative procedure produces consistent material balances, then either the simpler solution-only or solids-only analysis approach will most likely be adequate for subsequent experiments.

For the most definitive results, a separate leach test should be carried out for each leach time, particularly those near the optimum leach time indicated by the thief-sample approach. All samples are saved, measured, and analyzed so that complete material balances can be generated for each data point. If the material balances are not consistent, the cause should be identified and the tests repeated.

Alkaline leach test procedure No. 2 (cyanide leach—gold)—The following section discusses an agitation-leaching procedure that is generally applicable for cyanide-leach amenability tests at atmospheric pressure. Bottle-rolling tests, which are also commonly used, will be discussed in a subsequent section.

The equipment arrangement for the agitation-leaching procedure is essentially equivalent to that shown in figure 3.6. Additional openings should be provided for inserting a dissolved oxygen probe and also for introducing solid or liquid reagents or withdrawing samples. The reflux condenser helps to minimize evaporation losses but may not be necessary during leaches at room temperature.

The sodium cyanide reagent used in these leach tests is highly toxic; and, therefore, the relevant Material Safety Data Sheet (MSDS) should be thoroughly studied before using this chemical. For example, any contact with acids liberates extremely toxic and flammable HCN gas. The MSDS also cautions that toxic concentrations of HCN may form by the reaction of NaCN with CO_2 and moisture during prolonged contact with air in a closed system.

The NaCN determination stipulated in the following examples is carried out as follows:

Reagent preparation.

1. Rhodanine indicator—Dissolve 20 mg of p-dimethylamino-benzalrhodanine in 100 mL of acetone.
2. Sodium hydroxide solution (5%)—Dissolve 50 g of NaOH in distilled water and dilute to 1 L with distilled water.
3. Standard silver nitrate solution [0.0192*N* (normal solution)]—Crush approximately 5 g of $AgNO_3$ crystals and dry to constant weight at 40 °C. Dissolve 3.2647 g of the dried $AgNO_3$ in distilled water and dilute to 1 L with distilled water. Store in a brown bottle, preferably in a dark location.

Titration procedure.

1. Pipette a known volume of cyanide test solution into a 125-mL flask (1 mL for concentrations of 10 g/L or move up to 10 mL for low concentrations).
2. Dilute to 50 mL with distilled water.
3. Add 10 mL of the 5% NaOH solution.
4. Add 12 drops of the Rhodanine indicator solution.
5. Titrate with the $AgNO_3$ solution to a salmon-pink end point (color changes from canary yellow to salmon pink).
6. Free cyanide concentration:

$$\text{g/L [CN]}^- = \text{ml AgNO}_3\text{/ml of test solution,}$$

free NaCN concentration,

and
$$\text{g/L NaCN} = \text{g/L [CN]}^- \times 1.8846.$$

Leach-test example.

In the following example, a 1,000-g charge of micron-disseminated gold ore (i.e., free of visible particles of metallic gold), is leached at 50% solids. The 1,000-g ore charge has been wet ground to produce a product that is approximately 80% minus 200 mesh. The leaching pH will be 10.5, and the NaCN concentration will be 2.0 g/L. The leaching time will be 24 h, and air will be introduced to maintain a dissolved oxygen content of at least 5 ppm O_2 (assumed elevation = 1,520 m (5,000 ft) above sea level).

- Wash the entire 1,000-g sample of wet-ground ore from the grinding mill to the leaching vessel. This is usually carried out by using a coarse screen to catch the grinding balls as the slurry is being transferred. Next, add the amount of water required to attain the desired 50% solids slurry in the leaching vessel and start the agitator. Increase the agitator speed until no sanding-out occurs.

Alternatively, the entire ground-ore slurry can be filtered, and the filter cake charged to the leaching vessel.

- Adjust the slurry pH to 10 with reagent grade $Ca(OH)_2$, and add the required amount of NaCN to attain the desired 2-g/L concentration (2.04 g of 95% granular reagent grade NaCN). Check the pH, and add $Ca(OH)_2$ if necessary, to adjust the pH to 10.5. Record all reagent additions, pH values, etc., throughout the test.

- Insert the dissolved oxygen (DO) probe and measure the oxygen content of the leach solution. If the DO content is less than approximately 5 ppm (mg/L), start aeration and maintain an air flow sufficient to keep the DO content of the pulp above 5 ppm. The solubility of oxygen in a leach pulp is approximately 8 ppm at 25 °C and 1 atm, but this solubility must be corrected for altitude. For example, at an elevation of 1,520 m (5,000 ft), the solubility drops to a little less than 7 ppm at 25 °C. When the DO probe is removed from the leach slurry, rinse the probe into the leach vessel with a minimum of distilled water.

It is not uncommon to find that the DO content of the as-transferred pulp exceeds the 5.0-ppm criteria, and may remain above 5.0 ppm without any air addition throughout the leach. Also, even if an air addition is required, experience indicates that continuous monitoring of the DO content of the leach pulp may not be necessary.

- For a 24-h leach it is usually desirable to collect interval samples at 2, 4, and 8 h and a final sample at 24 h. The interval samples are often used only for measuring and controlling the cyanide concentration, but extraction profiles may also be desirable, particularly during the initial phases of a test program. Most often discrete leaches are used to develop the final extraction versus time profiles.

One method that is suitable for collecting the cyanide control samples involves the following steps. Measure and record the pH and DO concentrations. Stop the agitation and determine the weight of the leach slurry. This requires either that the leaching vessel can be detached or that the entire leaching system can be weighed. Allow the leach slurry to settle about 0.5 in, remove the desired aliquot of the clear supernatant liquor, and immediately titrate for residual free NaCN. Using this determination together with the liquor volume calculated from the slurry and feed-solids weights, calculate the residual free NaCN concentration. Start the agitation and reestablish the starting cyanide concentration by adding the required amount of solid NaCN. Check the pH, and if necessary add $Ca(OH)_2$ to adjust the pH to 10.5. Record all measurements and additions.

If both cyanide measurements and extraction-profile samples are desired, the following technique is usually applicable. Stop the agitator and determine the weight of the leach slurry. Restart the agitation and collect a 50-mL slurry sample with a pipet. Filter out the liquor using a pipette 9-cm Buchner funnel or an equivalent device. Determine the NaCN concentration of the undiluted leach liquor and return the unused leach liquor to the leach vessel. Reestablish the original NaCN concentration by adding the required amount of solid NaCN, and then readjust the slurry pH to 10.5 with lime. Wash the filter cake with at least three displacement washes of wash solution [deionized water adjusted to 11 pH with $Ca(OH)_2$], dry at 105 °C, and prepare the tailings residue for assay (see 2.4.6). The interval extraction is calculated based on head and tailings assays.

- When the total leach time (24 h in this example) has been completed, record the slurry pH, the DO content, and the slurry weight. Filter the slurry on an 18.5-cm Buchner funnel. To achieve reasonable filtration and washing rates, flocculation may be required for some pulps. Withdraw an aliquot of the undiluted filtrate for determination of the NaCN content. Wash the residue with at least three displacement portions of the 11-pH wash solution. Measure the total volume of filtrate plus washes and submit a sample for analysis. Dry the residue at 105 °C, weigh it, and prepare the material for assay (see 2.4.6). If the material balances are off by more than approximately ±10%, the test should be repeated and the reason for the discrepancy should be identified if possible.

Alkaline leach test procedure No. 3. (carbon-in-leach—gold)—The following procedure discusses a laboratory-scale method for conducting batch-type preliminary carbon-in-leach amenability tests on gold ores. In this type of leach, activated carbon is added to absorb gold and silver as they are solubilized by the cyanide-leach solution. This prevents adsorption of the precious metals by organic carbon or other "preg-robbing" components of the ore. The test method is equivalent to that described in Procedure No. 2 except that a measured amount of fresh activated carbon is added at the start of the leach. Other specific modifications and changes are discussed below:

- Typically, 6- by 16-mesh coconut shell carbon is used, and the carbon addition is about 3% of the solution weight. Preconditioning the carbon by attrition scrubbing prior to use is usually prudent. This can be accomplished by water scrubbing the carbon at 20% solids in a flotation machine for 15 min at 1,500 rpm. The scrubbed carbon is subsequently wet screened on 16-mesh U.S. (14-mesh Tyler), air dried, and stored in a closed container.
- When intermediate slurry samples are collected, the carbon is removed by screening before the pulp is filtered. The pulp should be poured through a 20-mesh or finer screen. Use the finest screen that does not collect any ore particles. Return the carbon to the leaching vessel. The remainder of the intermediate-sampling technique is the same as that described in Procedure No. 2.
- At the end of the leach period the slurry is screened to recover the carbon before the pulp is filtered. Again, pour the pulp through the finest screen size that does not collect any of the leached solids. The remainder of the process is the same as that for Procedure No. 2.

- If, after drying at 105 °C, the carbon product weighs less than 50 g, the entire carbon product should be ashed and fire assayed. When the weight of the carbon product exceeds 50 g, careful blending and splitting of the material may sometimes be satisfactory. In general, however, ashing and assaying the entire sample is recommended because all carbon particles may not have the same gold loading due to varying surface characteristics.
- ***Bottle-roll agitation***—Bottle-roll leaching has been used for various types of leaching tests, but it has been adopted primarily for preliminary cyanide-leaching tests. This technique has often been used to screen the effects of variables such as grind, cyanide concentration, and leach time.

Bottle-roll leach-test procedure (cyanide leach—gold)—The following discussion outlines a generic procedure for a bottle-roll leaching test on 500 g of gold ore that has been wet ground to 80% minus 200 mesh. Wet grinding is preferred (Hamilton, 1920), but for some materials such as oxidized ores, dry stage-grinding may also be acceptable. If there is any question, the two methods should be compared before an extensive test program is initiated. The NaCN concentration in this example will be 2.0 g/L, and the leaching pH will be maintained at 10.5. The leaching time will be 24 h.

- Transfer the 500 g of ground ore to a suitable leaching bottle and add water to attain the desired 50% solids slurry. The leaching bottle should be no more than one-third full. A 2.5- to 3.0-L bottle will be adequate for the 500-g leach. The mouth of the bottle should be large enough to accept a pH probe. Thoroughly mix the pulp, insert the pH probe, and while swirling the bottle in an upright position, adjust the pH to 10 by adding $Ca(OH)_2$. Record the amount of $Ca(OH)_2$ added and also the gross and tare weights of the leaching vessel.
- Add the amount of NaCN (1.02 g of granular 95% reagent-grade NaCN) required to achieve the desired NaCN concentration (2 g/L), and mix the slurry for about 5 min to ensure that the cyanide has dissolved. Check the slurry pH and add $Ca(OH)_2$ as necessary to adjust the pH to 10.5. When removing and washing the pH electrode, the washings should be collected in the leach bottle. A minimum amount of wash water should be used. Record the adjusted pH value and the amount of $Ca(OH)_2$ added.
- Place the bottle on a suitable set of rolls, which should be adjusted to roll the bottle at 15 to 20 rpm. The mouth of the bottle is left open to allow free air access to the pulp. Record the pulp temperature throughout the 24-h leach.
- Monitor and adjust the NaCN concentration at convenient time intervals. For a 24-h leach, checking and adjusting the NaCN concentration at 2-, 4-, and 8-h intervals is usually satisfactory. At each interval, remove the bottle from the rolls, weigh it, and measure both the pH and DO levels. Stand the bottle upright and allow the pulp to settle until there is approximately 0.5 in of clear supernatant liquor. Remove an appropriate aliquot of the clear liquor and immediately titrate for NaCN content. Calculate the residual NaCN content of the leach solution and add enough NaCN to reestablish the 2-g/L starting NaCN concentration. Swirl the bottle to assure that the NaCN addition has dissolved, check the pH, and add $Ca(OH)_2$ as needed to readjust the pH to 11. Rinse the electrodes in the leach bottle, using a minimum of wash water. Record all measurements and reagent additions. If an extraction profile is also desired, withdraw a suitable aliquot from the clear supernatant liquor and reserve it for subsequent analysis. Do not replace the sample volumes with fresh water.

When the 24-h leach time has been completed, measure and record the slurry pH, the DO content, and the net slurry weight. Filter the slurry in an 18.5-cm Buchner funnel. Flocculation may be required to achieve reasonable filtration rates for some pulps. Withdraw an aliquot of the undiluted filtrate and determine the free NaCN content. Wash the filter cake with at least three displacement portions of wash solution [deionized water adjusted to 10.5 pH with $Ca(OH)_2$]. Measure and record the total volume of filtrate plus washes and submit a sample for analysis. Dry the washed filter cake at 105 °C, weigh it, and prepare the material for assay (see 2.4.6). If the material balances are off by more than approximately ±10% the test should be repeated and the reason for the discrepancy should be identified if possible.

- ***Pressure leaching***—Pressure-leaching experiments carry inherent hazards, and special care should be taken when planning and implementing this type of test procedure. A job safety analysis (JSA) (see 1.2.5.3) is a must for pressure-leaching experiments, and a thorough JSA is particularly critical when new or previously unexplored variables are being investigated. Continuing contacts with equipment manufacturers and reagent suppliers can provide crucial information for the JSA and planning functions. Commercially produced laboratory reactors and pressure vessels are designed and manufactured to meet specified code requirements. To ensure safe operation, all pressurized equipment must be operated within the prescribed temperature and pressure limits. Meeting the specified code and other stipulated design requirements lies with the manufacturer; but when the equipment is being used, the basic safety responsibility rests with the user.

General design and operational criteria—In a general sense each pressure-leaching test program is unique and requires special attention. There are, however, generic questions that should be asked during the planning and JSA process. The following paragraphs and sections address key considerations. Equipment manufacturers, reagent suppliers, and the literature can often help with answers, but in some instances seeking specific expert advice is prudent. For example, reaction systems using pressurized oxygen can fall in this category.

Questions and considerations.

- *What vessel capacity will be needed?*—In general, the cold reactor should never be filled to more than 75% of its available free volume. In some instances the limit must be even lower. In all cases the available free space must be sufficient to accommodate the liquid expansion. For example, at 250 °C water occupies 1.25 times it volume at 25 °C. At 374 °C (the critical point), the volume multiplier is 3.13 (Keenan and Keyes, 1936).
- *What are the maximum temperatures and pressures required for the proposed experimental studies?*—Temperature and pressure requirements affect essentially all aspects of reactor design. These aspects include not only factors such as wall thickness and materials of construction, but also closure design, gasketing materials, and stirrer shaft glands. Close communication with the equipment manufacturer is critical, and the manufacturer's recommendations must not be violated.
- *What degree of stirring is required?*—Stirring can be particularly critical if gas dispersion is required. Many hydrometallurgical reactions require dispersion of air, oxygen, or other gases. Manufacturers can usually supply special gas-dispersion agitators.

Most reactor manufacturers can supply either packless magnetic-stirrer drives or various types of packed drives. The magnetic drives are more expensive, but for most hydrometallurgical applications they can offer relatively trouble-free operation even at pressures above 2,000 psi. Packed drives have provided satisfactory service for many pressure-leaching tests in the 400- to 600-psi range, but careful attention to maintenance is usually required. If gases are being introduced into the reactor, the operator must ensure that the stirrer drive system is compatible with the gas or gases being used. This requirement may become critical for systems where oxygen is being used. Organics can react violently in oxygen-enriched atmospheres. Therefore, for oxygen service, all internal surfaces must be cleaned using currently approved procedures (ASTM, 1988).

- *What materials of construction are needed?*—This requirement also dictates close communication with the manufacturer. Laboratory reactors can be supplied in a variety of different metals or alloys. In some instances removable glass or plastic liners may be applicable. Factors that must be considered when materials of construction are being selected include the physical strength, the temperature-strength characteristics, and the corrosion resistance. Corrosion resistance is often a critical consideration for hydrometallurgical reactions and also one of the most difficult to quantify because both the reactant and product characteristics must be defined. In addition to corrosion handbooks and metallurgical literature, helpful corrosion information can often be obtained from alloy producers and reactor manufacturers. The producers and manufacturers will usually answer questions and suggest applicable materials of construction but cannot guarantee that any particular alloy or metal will be fully resistant to a given corrosive environment. Predicting resistance to stress corrosion cracking, intergranular corrosion, and pitting for a particular application can be problematical. For example, although Type 316 SS resists surface corrosion by caustic solutions, stress corrosion cracking can occur at temperatures above 100 °C. This type of corrosion has probably been the most common cause of corrosion failure in stainless steel laboratory vessels (Parr Instrument Co., 1991, p. 9).

Other relatively subtle factors must also be considered. For example, although titanium reactors have been successfully used for many hydrometallurgical reactions involving sulfuric acid and oxygen, the danger of ignition is always present. Titanium will burn vigorously in the presence of oxygen at elevated temperatures and pressures (Parr Instrument Co., 1991, p. 10; and Krag, 1994).

Brittle fracture may also be a consideration for some forging alloys that have high nil-ductility temperatures (NDT). The NDT is the lower limit of ductility; below this temperature the metal exhibits brittle fracture. The reactor should not be pressurized until the reactor temperature is above the NDT. The NDT for plate is usually below 38 °C, but for some forging alloys the NDT may be as high as 120 °C (Curran, 1984). Even after the NDT has been exceeded, excessive heating or cooling rates can produce high thermal stresses. Checking the NDT for the metal or alloy being used is always prudent.

- *What type of valves, fittings, pressure gauges, etc., will be needed to initiate, control, and terminate each test?*—The valves, fittings, etc., required in the reactor head or body to start up, operate, and also terminate a given test must be thoroughly considered in the JSA. Special fittings may also be required if an internal cooling coil must be installed to control exothermic reactions. Special fittings may also be required for sampling devices or systems for charging solid or liquid reagents. Pressure gauges must always be rated higher than the maximum expected working pressure. For consistent pressure readings manufacturers generally recommend that the gauge should not be stressed beyond 70% of its full-scale reading. Also, if corrosive gases or vapors are present, installation of diaphragm or piston-type protective devices ahead of the pressure gage is recommended. If gases such as oxygen or air are being fed to the reactor from cylinders, pressure regulators will be required. Only regulators specifically rated for the particular application should be used. In general, two-stage regulators will produce significantly more stable pressure regulation than single-stage units.

- ***What type of overpressure protection should be installed on a reactor*?**—Protection against destructive pressures can be provided by rupture disks or in some cases by pressure-relief valves. Rupture disks are installed to protect both the operator and the equipment by releasing unexpected overpressures. When selecting a rupture disk, the entire reactor system should be considered, not just the reactor itself. The pressure rating of the rupture disk should always be less than that of the weakest component of the overall system. Also, to prevent premature failure, a disk should not be stressed beyond 70% of its rating during normal operations. Factors such as corrosion resistance and temperature-pressure characteristics of the rupture disk material should be discussed with the manufacturer or otherwise addressed. When installing a rupture disk, the manufacturer's directions should be followed carefully. An improperly installed rupture disk can fail at pressures much lower than its rated value.

A relief valve may be an appropriate safety device if the operating pressures are below 1,000 psi. Small diameter rupture disks, such as those found on many laboratory reactors, may be unreliable at pressures below 1,000 psi. Suitable extension piping should be installed to safely vent any toxic or flammable vapors that would be released if the rupture disk should burst. A collection vessel should also be installed to contain any liquids or solids that may discharge from the reactor when a rupture disk breaks. The cross section of the vent line should be several times larger than the rupture-disk diameter, and the change in size should be located as close to the rupture disk as possible. The discharge end of the extension piping should be securely anchored because force generated by the burst can tip over the reactor or even blow it off the bench. The extension piping will also help to dampen the loud noise generated when a rupture disk fails. Unless the operator is completely isolated from the reactor, ear protection is recommended.

- ***What external piping will be needed*?**—Some form of external piping is required for tests in which gases such as air, ammonia, hydrogen, or oxygen are being introduced into the reactor. Each installation should be designed to meet the handling requirements for the gas being used. Particular care is required for systems using oxygen because it can present serious fire hazards. The National Fire Protection Association (NFPA) manual "Fire Hazards in Oxygen-Enriched Atmospheres" presents a concise introductory discussion of oxygen, its hazards, and design guidelines (NFPA, 1990). The book also lists 100 references related to safety practices and design. Oxygen systems are unique because, although oxygen fires need an ignition source, the energy required can come from the compressed oxygen itself through adiabatic compression. Adiabatic compression is produced when oxygen at high pressure is rapidly introduced into a system initially at low pressure. This situation can occur in a piping system when a valve is opened quickly, and the high-velocity oxygen stream stops at a downstream barrier of some sort (Swagelok Co., 1991). The obstruction can be an elbow, a piping tee, a closed valve, or even a burr protruding into the gas stream. Under some conditions adiabatic compression may produce temperatures that exceed the autoignition point of metals such as titanium and even stainless steel. Organic contaminants and fine particles of many materials burn violently in pure oxygen, and careful cleaning practices (ASTM, 1988) are essential to prevent oxygen fires. Plastic materials, including the fluorocarbons (Teflon), should always be considered to be potentially reactive in oxygen-enriched systems. Designing and operating systems containing enriched oxygen can be complex; there is no single, simple approach. The first and most important rule for safety in the use of oxygen is Consult an Expert. Oxygen suppliers can often supply initial guidance in this area of expertise.

- ***What type of barricades and ventilation should be provided*?**—If there is any possibility that an out-of-control reaction may occur, the reactor should be operated behind a suitable barricade. When experimenting in new or unexplored areas, it is always desirable to assume that unexpected reactions may occur. Some explosive reactions can propagate with such speed that the reactor may fail before the rupture disk can release the excess pressure. Small reactors (e.g., 1-L and 2-L capacity) have often been operated on open benches or in hoods without additional protection, but remote operation behind suitable barricades is always prudent practice. This practice is particularly important when previously unexplored variables or reactions are being investigated. The design and thickness of any given barricade depends on the degree of protection that a JSA determines is necessary to protect the operator from flying fragments or other explosion hazards. These requirements can vary widely, and each barricade should be designed to protect against the specific and inherent hazards that may be present. Glass shields, even those reinforced with wire mesh, can provide splash protection, but only minimal protection from fragments. The following references present information on barricade design and safety practices related to high pressure technology: Comings, (1956); Industrial and Engineering Chemistry, (1961); Smith, (1964); and Steere, (1967). Additional references and guidance may also be available from reactor manufacturers and compressed-gas suppliers.

Adequate ventilation is also an important consideration, especially when working with toxic or flammable materials. As mentioned previously in the discussion of overpressure protection, ventilation can be particularly critical should a rupture disk burst. If the vent system is required to handle flammable gases or vapors, the system must meet both national and local explosion-proof code requirements. Provisions to dampen the noise and concussive force generated if and when a rupture disk bursts should also be engineered into the system.

- *What training should be provided?*—Safe operation requires that anyone using pressure-leaching equipment should receive appropriate training. Training procedures should be established to ensure that any person handling the equipment knows how to use it properly and how to respond to anomalous situations. All operators should be thoroughly familiar with the JSA, and written operating instructions are always desirable. When training and breaking in a new operator, hands-on guidance by an experienced operator should be provided for at least three or four tests. Also, MSDS should be studied for all reactant materials and possible reaction products before attempting to conduct any pressure-leaching operations.

- *What maintenance will be required?*—Pressure-leaching equipment requires thorough maintenance; all of the manufacturer's recommendations and instructions should be carefully studied and followed. Procedures should be established for periodic testing of the pressure vessel to be sure that the vessel remains structurally sound. If the user does not have pressure test facilities, the reactor should be returned to the manufacturer for hydraulic testing and any overhaul that may be needed. Testing is particularly critical if the user suspects that the vessel has been overstressed or damaged.

Continuing inspection of the reactor surfaces, valves, fittings, etc., for corrosion damage is critical and may require expert assistance. Corrosion damage can occur in several different forms including uniform attack of the metal surface, pitting, selective attack, cracking, and erosion. If the inspection procedure detects any significant corrosion damage, the reactor should be pressure tested before further use.

The manufacturer's recommendations for lubricating both straight and pipe threads should always be followed. Operations that involve the use of oxygen are particularly critical; oxygen-compatible lubricants should be selected in accordance with Guide G63 (ASTM, 1987). Oil should never be used on threads or fittings in any system that handles pressurized oxygen.

Efficient reactor operations require maintaining an adequate supply of spare parts. Reactor manufacturers can supply recommendations for minimum spare-parts requirements.

Spare-parts kits usually include components such as replacement gaskets, O-rings, shafts, bearings, rupture disks, packing gland parts, and possibly some special tools. Experience and consultation with the manufacturer may indicate that an additional supply of some spare parts may also be prudent.

- *What type of initial operating test should be conducted?*—Before starting the first experimental runs with reactants, a "water-only" test should be conducted to check the system for leaks and to observe the operational performance of the temperature controller. After a thorough study of the manufacturer's operating instructions, the reactor should be filled to no more than half full with water, sealed, and then brought up to approximately 150 °C. If no leaks are detected, and the temperature-control system operates properly, it is desirable to gradually increase the temperature to the maximum anticipated operating temperature while constantly monitoring the steam pressure being generated.

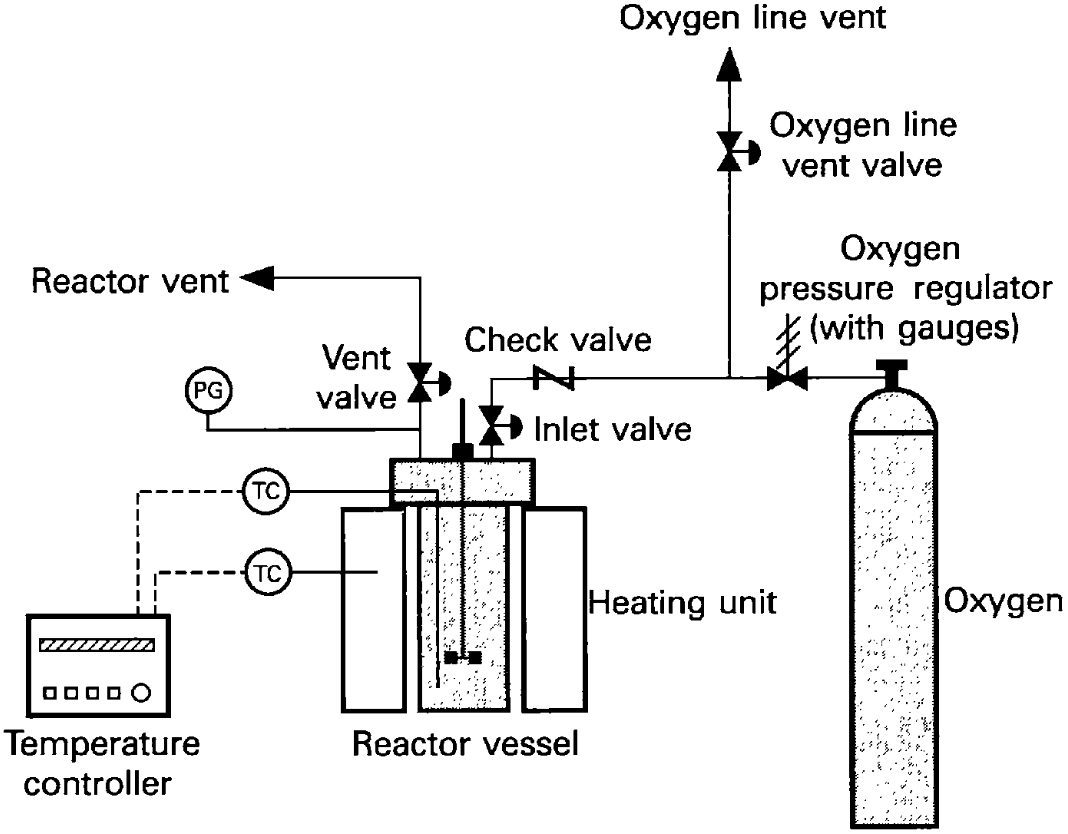
When an experimental program involves new or unfamiliar materials, it is always prudent to carry out preliminary experiments using small quantities of the reactants. If the reactions proceed smoothly, the amounts can be gradually increased. Any erratic behavior during the preliminary experiments indicates that further study and precautions are warranted.

Pressure-leach test procedure No. 1 (oxidation of a gold ore)—The following discussion describes the steps of a generic test procedure for aqueous pressure oxidation of a gold ore that contains approximately 5% sulfide minerals. The ore sample was wet ground to produce a product that was 80% minus 200 mesh. The leach was conducted at 45% solids. The desired leaching temperature was 180 °C, and the oxygen overpressure was 100 psi. The total pressure at temperature was 246 psi. The leaching time was 60 min.

The leach was conducted in a 2-L titanium reactor fitted with a serpentine-type internal cooling coil. Stirring was provided by a gas-entrainment-type impeller driven by a variable-speed packless magnetic drive. The stirring speed, which was established by observing the pulp behavior during tests at atmospheric pressure in a transparent vessel, was 1,100 rpm. If a gas-entrainment-type impeller is not available, satisfactory results can also be obtained with either propeller- or turbine-type impellers if a vortex is produced that will disperse oxygen into the slurry. The impeller speed required to produce a vortex can usually be established by tests in a transparent vessel at atmospheric pressure. If the reactor configuration is such that the pulp depth is significantly greater than the reactor diameter, a double impeller stirrer may be required. A schematic of the pressure-reaction apparatus is shown in figure 3.7. If a JSA determines that the chemical reactivity of the system is such that the operation must be conducted totally behind a barricade, all valves etc., must be fitted for remote control. The general test procedure is as follows:

- Transfer 1,666 g (approximately 1,200 mL) of the 45% solids ore slurry (750 g of ore and 916 g of water) to a clean reactor vessel. Whenever a reactor is used in oxygen service, the operator must always be sure that no oil or similar organic is present in any part of the system (ASTM, 1988).
- Install the reactor head and seal per the manufacturer's instructions. Place reactor in the heating unit and connect the oxygen and water-cooling lines. All valves are closed.
- Start the agitation, turn on the heating unit, and set the temperature controller for the desired 180 °C temperature. In some instances it may be desirable to gradually increase the temperature setting to prevent a significant temperature override. When the reactor temperature reaches slightly over 100 °C, open the reactor vent valve and bleed off the air that was trapped above the slurry in the reactor. Close the valve when a small but detectable stream of steam is flowing from the valve.

Figure 3.7



Pressure-reaction apparatus. (PG = pressure gauge; TC = thermocouple.)

- When the operating temperature has been reached, check to ensure that the reactor inlet valve and the oxygen vent-line valve are closed, and that the oxygen pressure regulator is in the full off position. Slowly open the valve on the oxygen tank, and gradually increase the tension on the oxygen regulator until the desired operating pressure (246 psi in this example) has been reached.
- Slowly open the inlet valve on the reactor and bring the reactor to the desired operating pressure. Check the reactor temperature. If the reaction is appreciably exothermic, as denoted by the start of a temperature spike, turn on the cooling-water flow. Ensure that the cooling-water discharge line is secured because the first flow through the system will likely be a surge of steam. Alternatively, it may be desirable to maintain a small flow of cooling water from startup. If a significant exothermic reaction takes place, the cooling-water flow can be increased gradually to prevent overshooting the desired operating temperature without encountering the steam surge. This procedure may also give better overall temperature control. In some instances, if the exothermic reaction is relatively mild, it may be possible to regulate the reactor temperature by using a controlled air flow through the cooling coil. It may also be desirable to minimize any temperature override by introducing the oxygen when the reactor temperature reaches a point 10 to 20 °C below the desired operating temperature.

In some instances better overall control of the experiment may be achieved by gradually increasing the overpressure as the temperature is increasing. This procedure requires some additional planning and attention, but a comparative evaluation of both procedures warrants consideration.

- When the reactor temperature has stabilized, maintain the oxygen pressure at the desired level by slowly adding oxygen through the reactor inlet valve. Continue adjusting the oxygen overpressure throughout the leaching period.
- At the end of the desired reaction time, turn off the heating unit. After checking to ensure that the reactor inlet valve is closed, turn off the oxygen-bottle valve and bleed the oxygen supply line through the oxygen vent-line valve. Cool the reactor to quench the oxidation reaction; this usually requires a temperature drop of at least 50 °C. If it has been necessary to operate the reactor behind a barricade, a sufficient temperature drop can normally be achieved by running a maximum water flow through the cooling coil. It is desirable to continue slurry agitation during the cooling operation. When the reactor temperature reaches about 95 °C, slowly open the reactor vent valve to bleed off the oxygen pressure in the reactor. To complete the cooling, disconnect all of the reactor lines and place the reactor in a suitable container of running water.

If operation behind a barricade has not been required, the reaction can also be quenched by disconnecting all reactor lines, removing the reactor from the heater, and placing it directly in a container of running water. Well-insulated gloves are required for this procedure. Protective clothing and equipment such as a face shield should be worn during this operation.

- Open the cooled reactor and transfer as much as possible of the pulp, without washing, to a 15-cm or 18.5-cm Buchner funnel. Flocculation may be required to achieve reasonable filtration rates for some pulps. Collect, measure, and save the undiluted filtrate. Determine the pH and redox potential of this solution. Next, transfer all of the remaining solids onto the filter and wash the filter cake with at least three displacement washes of acidified water. Measure the wash filtrate volume and save it separately. Dry the washed filter cake at 95 °C or less. Submit the solids and the two liquid samples for analysis. Typically the solids are analyzed for base-metal content, sulfide content, and gold content. The solutions are analyzed for base-metal content and sulfate content.

Pressure leach test procedure No. 2 (leach of cobalt concentrate)—The following procedure outlines a typical pressure oxidation leach on a cobalt rich flotation concentrate containing about 6.0% cobalt, 0.1% nickel, 2.0% copper, 10% arsenic, 35% iron, and 37% sulfur. The following test conditions apply:

- Reactor and size—2-L reactor as described in procedure No. 1.
- Feed grind—Concentrate wet ground to 60% minus 270 mesh.
- Leach slurry—10% solids.
- Agitator speed—1,100 rpm.
- Leach temperature—190 °C.
- Oxygen overpressure—100 psi (total pressure at temperature equals 382 psi).
- Leaching time—2 h.
- Clean the reactor and, since the reactor will be used in oxygen service, make sure that no oil is present in any part of the system.
- Transfer a sufficient amount of the wet-ground concentrate and deionized water to the clean reactor to produce a 10% solids slurry containing 133 g of concentrate and 1,200 mL water.
- The balance of the procedure parallels that described in procedure No. 1. Note that the 37% sulfur content will probably produce a stronger exothermic reaction. The solid and liquid samples are submitted for analyses.

3.2.2.2 Column Leaching

Historically, bench-scale column leaches have been used primarily to investigate the variables associated with various types of heap and vat leaches. These variables include factors such as particle size, reagent concentrations, oxidation requirements, leaching time, and the effects of agglomeration procedures and additives. General comments on the effect of these and other variables have been discussed in the following references McClelland, (1983); Seidel, (1963); Sullivan, (1931); and Van Arsdale, (1953). Most experimental studies have been associated with the recovery of copper, gold, and uranium from relatively low-grade ores. More recently the technique has found increasing application in waste-management research related to tailings disposal.

Researchers have used a variety of techniques and procedures. Even though no specific equipment arrangements or test procedures have been generally accepted as standard, a number of broad concepts do apply. These include the following considerations:

- *Column size*—The column size is primarily dependent on the maximum particle size of the material being leached. General experience indicates that the inside diameter of the column should be at least 4 to 6 times the diameter of the maximum particle size. Also, the bed depth in the column should be at least 10 times the column diameter. Even if the maximum particle size is less than 0.5 in, it is preferable that the leach column have an inside diameter of at least 3 in.
- *Column features*—Constructing the column from materials such as glass pipe or a transparent acrylic plastic is desirable. This type of column permits direct observation of phenomena such as color changes or wave fronts that may occur during the leaching operation. Other preferable features include provisions for trickle- and pond-leaching operation, single pass or recirculation operation, temperature control, and unattended operation as described below:

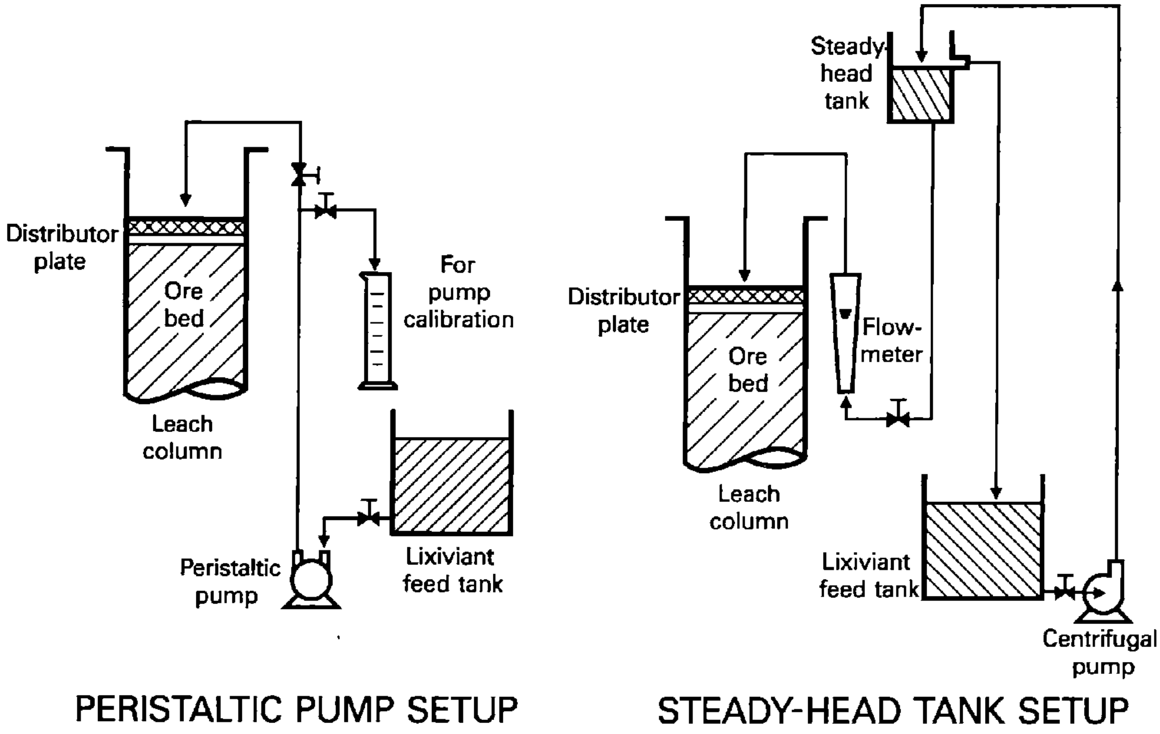
- *Trickle and pond leaching*—It is often desirable to set up the leaching column so that it can be operated in either the trickle- or the pond-leaching mode. Trickle leaching refers, in general, to all leach procedures in which the leaching solution is distributed on the surface of the ore bed. The rate of addition is such that all of the liquid percolates into the bed and there is no appreciable accumulation on the surface of the bed. Drip- and spray-leaching procedures use the same principle. Pond leaching entails adding the leaching solution at a rate that exceeds the zero-head percolation rate and a pond builds up on the surface of the bed. The percolation rate depends on factors such as the characteristics of the ore bed and the depth of the pond. Both gold and copper heap-leaching operations have commonly used trickle leaching. The pond-leach technique has most often found practice in uranium heap leaching and the vat leaching of oxidized copper ores.

Laboratory-scale trickle-leach systems have used pump and steady-head setups such as those shown in figure 3.8. Various types of distributor plates such as a perforated plastic disk with holes on 0.5-in centers or alternatively several layers of plastic screen material or burlap have been used. Arrangements similar to that shown in figure 3.9 have proven satisfactory for pond-leach-type column leaches.

- *Single pass or recirculation*—It is often desirable to consider designing the column system so that it can operate with either single-pass or recirculating flow. In some instances recirculation can increase the reaction rate. In particular, this increase can occur when the presence of iron ions promotes oxidation rates (e.g., in copper ores when sulfides are present or in uranium ores when the uranium is present in the +4 valence state).
- *Temperature control*—Although the temperature can usually not be controlled in commercial heap-leaching operations, investigating the effect of temperature on extraction rates may still be important. Chemical reactions can significantly increase the temperature inside a large heap. Temperature control in laboratory columns can be achieved by using jacketed columns or by insulating the column and warming the feed solutions.
- *Unattended operation*—Since column-leach experiments nearly always operate on an around-the-clock basis, the systems should be designed to operate in a fail-safe mode. For example, if bed plugging might possibly occur during unattended operation, the design should include provisions for shutting down the system and for containing any spill. This provision becomes particularly critical if hazardous solutions such as cyanide are being used.
- *Agglomeration*—Agglomeration can significantly increase the percolation rate of leach solutions through some materials such as gold ores that have appreciable clay contents. Portland cement and other additives have proven to be effective binders (Chamberlain, 1984; and McClelland, 1983). A typical procedure involves the following steps McClelland, (1982):

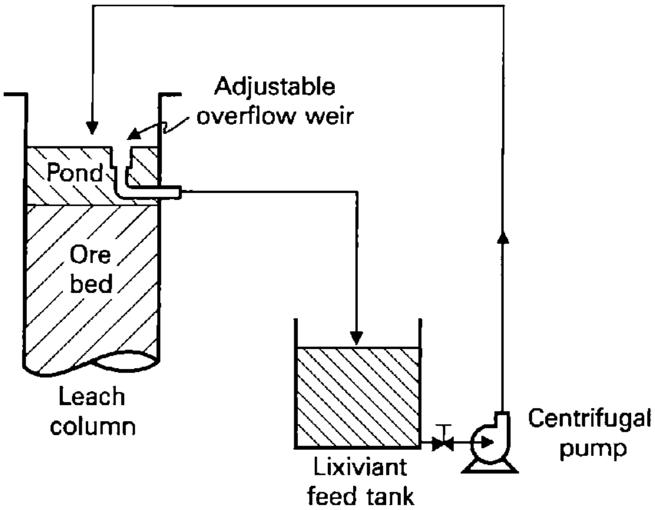
- The gold ore is crushed to 80% minus 0.375 in and mixed with portland cement (at 5 to 10 lb per st of ore).
- This dry mixture is then wetted with water or a cyanide solution and agglomerated by mechanical tumbling. Both disk type and drum-type pelletizers have been used. Figure 3.10 illustrates a disk type pelletizer. The agglomerates typically contain 8% to 16% moisture.

Figure 3.8



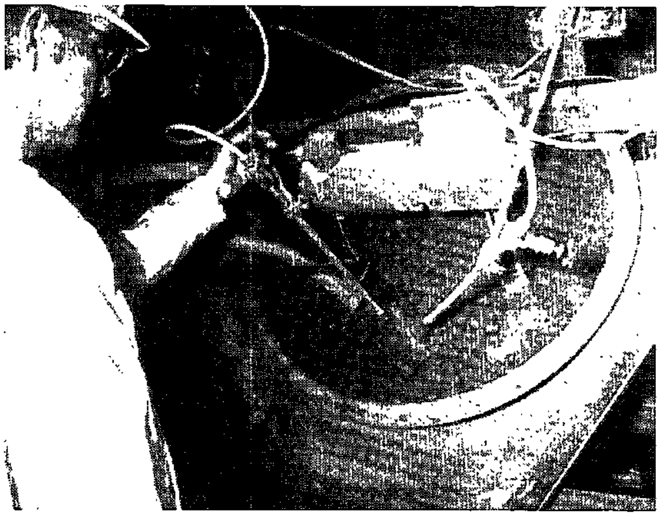
"Trickle-leach" lixiviant-feed arrangements.

Figure 3.9



"Pond-leach" lixiviant-feed arrangement.

Figure 3.10



Disk-type pelletizer.

- The agglomerated feed is carefully bedded into the column, the column is capped, and the agglomerates cured for up to 72 h before introducing the leach solution.

Agglomeration has also been used when vat leaching sandstone uranium ores (Mashbir, 1964). The ore was crushed to minus 1 in or finer and fed to a rubber-lined balling drum where water and then sulfuric acid were sprayed onto the bed of tumbling ore. The water addition was equivalent to approximately 5% of the ore weight, and the sulfuric acid addition was equivalent to that required for effective agitation leaching of the uranium ore. The agglomerated material was bedded into vats and leached with water.

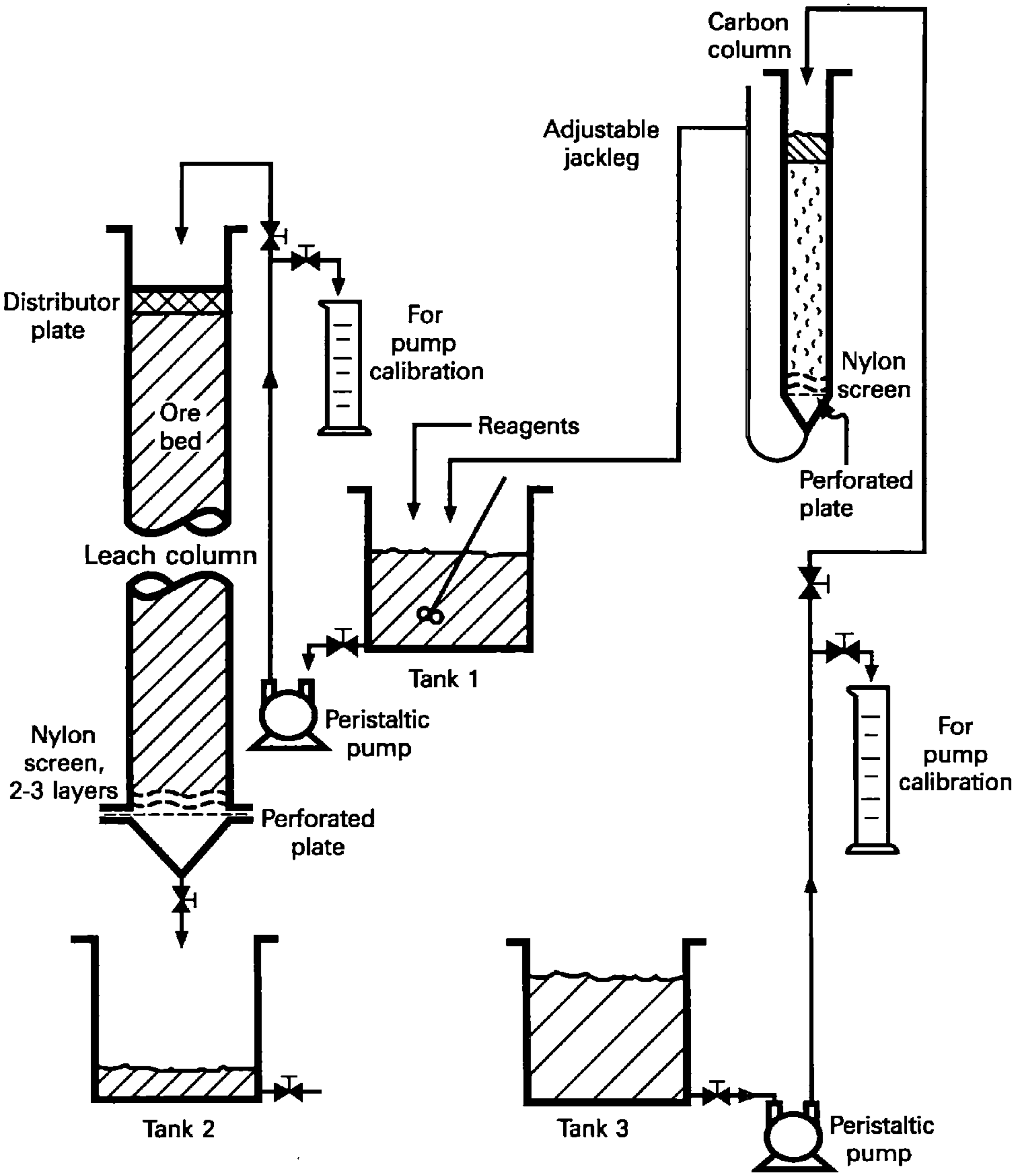
- *Preliminary tests*—Before starting column-leaching tests on a new ore, it is almost always desirable to conduct preliminary agitation-leaching tests to develop a feel for reagent consumptions and maximum extractions. Bottle-rolling tests on coarse ground ore (minus 10 mesh) are usually applicable for both gold ores and other materials.

Column-leach test procedure No. 1 (cyanide leach of gold ore)—A variety of column-leaching test procedures have been used to investigate the variables associated with cyanide leaching of oxidized gold ores. The following procedure is typical of those procedures that produce results that closely approximate the effects observed during industrial-scale heap-leaching operations. The equipment arrangement, which is illustrated in figure 3.11, consists of a leach column operated in closed circuit with a carbon-adsorption column. The leaching column is 6 in. in diameter by approximately 6-ft long and is fabricated from a clear plastic material. The carbon-adsorption column is 2-in. in diameter by 14-in long and is charged with approximately 100 g of fresh 6- by 16-mesh coconut-shell carbon. The adsorption column is fitted with an adjustable wier (jackleg) so that the liquid-level head in the column can be adjusted to produce the desired flow rate through the column. The liquid level in the column is controlled by raising or lowering the position of the jackleg overflow.

The setup illustrated uses adjustable peristaltic pumps with delivery capacities of 5 to 10 mL/min. The various tanks are sized so that each of these containers can hold a 24-h output from the leaching column (normally 10 to 15 L). The retainer-plate system illustrated in figure 3.10 consists of a perforated plate (0.25 in holes on 1-in centers) that is covered with two or three layers of 35-mesh nylon screen. Other retainer systems have used burlap in place of the screen material or coarse gravel contained in a closed screen basket or burlap bag. Beds of loose gravel have also been used, but separating the gravel from the leach residue may present problems. The illustrated retainer-plate system in the carbon column also consists of a perforated plate and several layers of nylon screen. The general test procedure consists of the following steps:

- After the ore is crushed to the desired size and sampled, it is loaded into the column and covered with a distributor plate such as that described in the previous section on column features. The column should be loaded carefully to minimize compaction of the ore bed and particle segregation. This can be accomplished by lowering increments of ore into the column to gradually build up the ore bed. Filling a 6-in-inside-diameter (ID) column will require about 16 to 18 lb of ore per foot of bed depth.
- Load the adsorption column with 100 g of 6- by 16-mesh activated coconut-shell carbon.
- About 10 to 15 L of saturated lime water will be required to condition the ore bed. This solution can be prepared by adding 2.5 g of commercial hydrated lime per liter of water and stirring for 2 to 3 h. Filter the solution and determine the CaO content (typically by an oxalic acid titration). Transfer the line water to the tank No. 1 position and pump the solution onto the top of the ore bed at a rate of about 5 mL/min until the column effluent shows a pH or 10.5 to 11.5. In some instances it may be necessary to resaturate the effluent with hydrated lime and continue the conditioning treatment before the desired effluent pH is achieved.
- After the ore conditioning is completed add NaCN to the combined effluent to produce a leaching solution containing the desired starting NaCN concentration. To offset the initial NaCN consumption rate, the starting NaCN concentration will often have to be appreciably higher than the desired steady-state cyanide concentration. For example, if a steady-state cyanide concentration of 0.5 g/L NaCN is desired, a starting NaCN concentration of at least 1.0 g/L NaCN may be necessary. Transfer the starting solution to the tank No. 1 position and continue pumping at the 5 mL/min or other desired rate.
- Collect the column effluent in tank No. 2 for 24 h, measure, and assay for gold content.
- Transfer tank No. 2 to the tank No. 3 position and replace tank No. 2. Continue pumping to the leaching column.
- Pump the contents of tank No. 3 to the carbon column with pump No. 2 using at least the same flow rate as pump No. 1. The carbon column underflow discharges to the tank No. 1 position. Continue this sequence of operations until the ore-column effluent drops to the desired gold concentration.
- At least once every 24 h, determine cyanide concentration, pH, and gold content of the carbon-column effluent. Add reagents as required to adjust the pH of the leaching solution to 10.5 and the cyanide concentration to the desired steady state-level. If the carbon-column effluent shows a measurable gold concentration (i.e., > 0.1 mg/L), change the carbon.

Figure 3.11



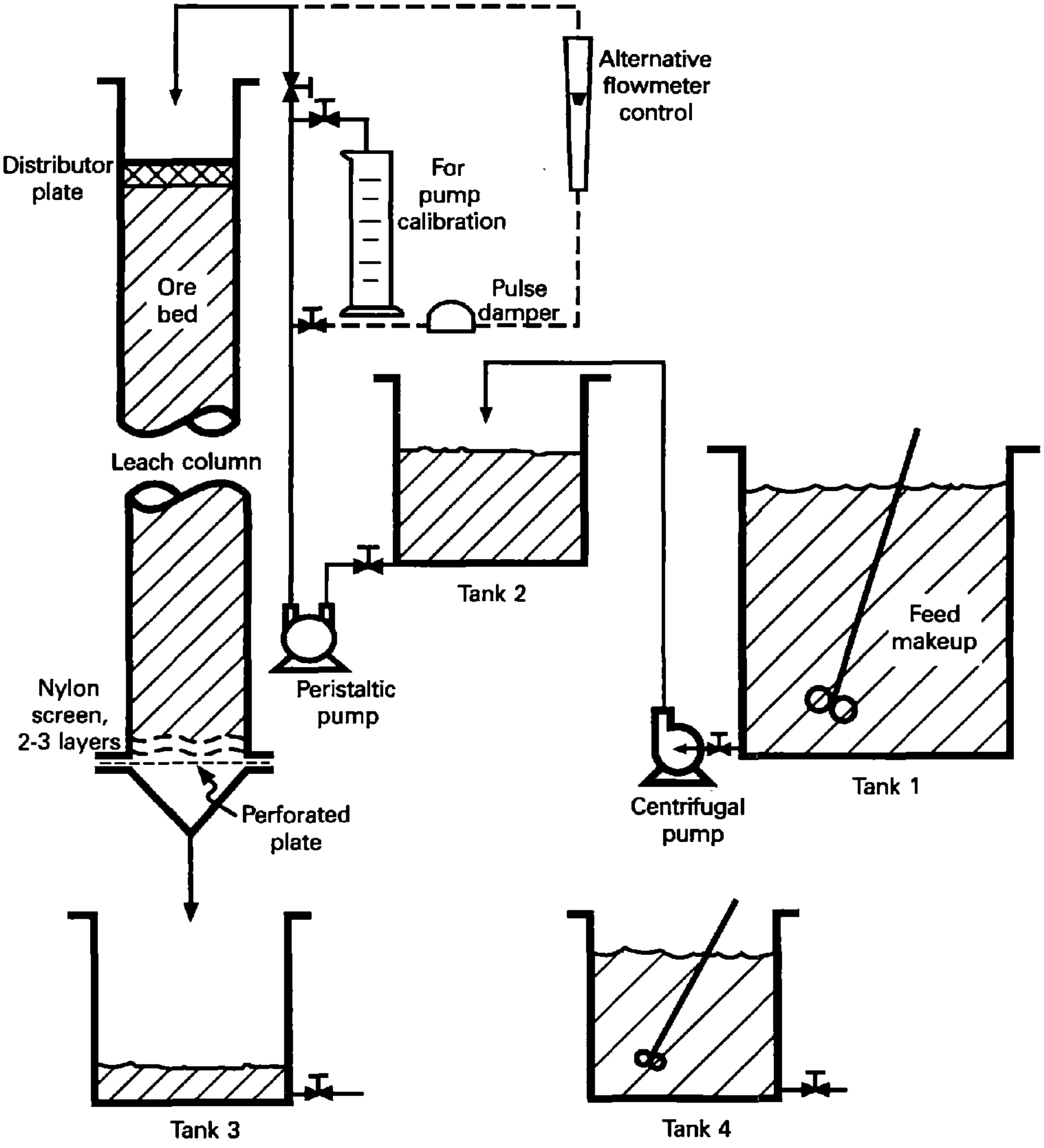
Column arrangement for gold-ore leaching.

- At the end of the leaching period, start the washing operation. The leach solution in tank No. 1 is replaced with water. The wash water is pumped onto the surface of the ore bed at the same rate as that used for the leaching solution. The minimum amount of wash water used should be equivalent to at least 20% of the ore weight in the column. All of the column effluent collected during the washing operation should be measured, analyzed, and then pumped through the carbon column.
- Any residual cyanide remaining in the washed ore bed is destroyed by treating the bed with a 0.1% calcium hypochlorite wash solution. A volume of solution about equal to the volume of wash water used is pumped onto the bed surface and allowed to percolate through the bed. The resulting effluent solution can be discarded.
- After the hypochlorite treatment, the leach residue can be discharged from the column, dried, sampled, and assayed.
- After all of the final solutions have been sampled and assayed, the solutions should be treated to destroy the cyanide content before being discarded. This can be accomplished by adding 10 g of calcium hypochlorite per gram of NaCN present in the solutions and agitating the solutions vigorously for at least 1 h.
- Calculated head assays and gold recoveries are usually determined based on the leach-test products, i.e., the amount of gold absorbed by the carbon and the gold remaining in the washed residue. This approach is used because if any metallics are present in the ore, a representative feed sample of minus 0.75-in ore would weigh at least 1,000 lb (see table 2.1). Both volumetric and weight determinations have been used to measure the quantity of leach-column effluent collected during each 24-h sampling period. In general, weight measurements are usually more precise and accurate than volumetric measurements. If, however, the solutions are analyzed by atomic absorption spectrophotometry and the results are expressed in milligram per liter, a correction for solution specific gravity may be required when weight measurements are used. Also, the amount of gold present in the carbon should be compared to the total gold content of the combined leach-column effluents. If these two values do not compare within approximately ±10%, repeating the test and determining the reason for the discrepancy is recommended.

Column-leach test procedure No. 2 (column leach of copper ore—The following discussion outlines a typical test procedure for a single-pass acid leach on an oxidized copper ore. Figure 3.12 illustrates the general arrangement of the column-leaching system. Nearly all of the general considerations of column size, column features, etc., discussed in the opening section of 3.2.2.2 can apply to this column setup. The leaching column has an inside diameter of 6-in and is approximately 6.5 ft tall. Fabricating the column from a transparent material such as acrylic plastic or glass is desirable. If possible, size the feed makeup tank (tank No. 1) so that only one or two batches of leaching solution will be required for the entire test. For example, if the column feed rate is 4 mL/min, a 55-gal plastic lined drum will hold a 30-day supply of feed solution. Tanks No. 2, No. 3, and No. 4 are sized so that each will hold 24 h of column feed or output. The system shown in figure 3.12 uses a small centrifugal pump to transfer feed solution from tank No. 1 to tank No. 2. The column feed rate is controlled using an adjustable peristaltic pump with a 2 to 20 mL/min capacity. Figure 3.12 illustrates two alternatives for measuring the column feed rate: (1) The pump speed is adjusted to provide the desired output as determined by periodic measurements using a graduated cylinder, or (2) A pulse damper is installed in the feed line ahead of a flowmeter, and the pump speed is adjusted to provide the desired output. The column system uses a distributor plate or wick to insure uniform solution distribution onto the bed surface. Perforated plates, several layers of plastic screen, burlap, or glass wool have all been used successfully. The retainer plate at the bottom of the column consists of a perforated plate (0.25-in holes on 1-in centers) covered with two or three layers of 35-mesh nylon screen. Other retainer systems such as those described in column-leach test procedure No. 1 have also proven successful. The general test procedure for the column leach of copper ore consists of the following steps:

- Assuming that the bulk density of the oxidized copper ore is 90 lb/ft^3, approximately 100 lb of ore will be required to produce a 6-ft bed depth in the 6-in column. The ore is crushed to the desired size, blended, and bedded into the column. Bedding is usually best accomplished by lowering increments of ore into the column to gradually build up the bed. The distributor plate or wick system is placed on top of the ore bed. Record the bed height.
- Make up the desired H_2SO_4 acid-leach solution (usually 2 to 20 g/L H_2SO_4) in tank No. 1. Determine the H_2SO_4 content (typically by titration with a standard base) and the pH. Transfer a 24-h supply of leach solution to tank No. 2 and record the volume or weight of the solution. If weight measurements are used, also record the specific gravity of the solution.
- Start feeding the leach solution to the top of the column at the desired feed rate. The initial rate is usually about 0.3 (gal/min)/ft^2 (approximately 4 mL/min for a 6-in column). If the feed solution starts to pond on top of the bed, decrease the flow rate.

Figure 3.12



Column arrangement for copper-ore leaching (single pass, trickle leach).

- Collect the column effluent in tank No. 3 for 24 h. Move tank No. 3 to the tank No. 4 position and replace tank No. 3. Measure the volume or weight of column effluent in tank No. 3 and calculate the average feed rate. Adjust the rate if necessary. Also, if the bed height has changed, record the new height.
- Refill tank No. 2 with fresh feed solution, measure and record the volume or weight, and continue pumping to the column.
- Mix the contents of tank No. 3 thoroughly and sample the contents. Determine the H_2SO_4 content, the pH, and the redox potential of the sample and submit a portion for copper, iron, and other desired analyses. It is usually desirable to cumulate all of the product solutions produced during the leach test for composite measurement and analysis. The solutions may also be needed for further testing such as solvent extraction or cementation studies. If the leach-product solution is not retained, neutralize or otherwise treat the solution as required to meet discharge requirements.
- Continue the above sequence of operations until the desired leaching time or copper extraction has been achieved. The end point of the leaching period is usually determined by preparing a running metallurgical balance that shows the relationship between copper extraction and leaching time. When the desired end point has been reached, stop feeding the leach solution, move tank No. 3 to the tank No. 4 position, and replace tank No. 3 with a clean, fresh vessel. Measure and sample the contents of the tank in the tank No. 4 position as usual. Allow the column to drain into the fresh tank in the tank No. 3 position (usually 8 to 12 h is sufficient), measure, and sample as usual.
- After measuring the leach feed solution remaining in tank No. 2, transfer the solution back to tank No. 1, wash tank No. 2, and fill it with water or an alternative wash solution. Start feeding the wash solution to the column at the same flow rate used for the leach solution. Collect, measure, and analyze the wash product solutions daily. Also measure and record the pH of the wash- product solution at regular intervals. Stop the wash-water feed when the underflow from the column reaches a pH of 4.0. Allow the column to drain, combine all of the washes, measure the total volume or weight, mix thoroughly, sample, and analyze as usual.
- Discharge the washed residue from the column, measure the wet weight of the residue, and dry the residue at 100 °C to a constant weight. Sample the dried residue using procedures equivalent to those discussed in chapter 2 and submit for copper, iron, and other desired analyses.
- Comparative metallurgical balances are prepared using both the daily-solution and composite-solution quantities and analyses. In general, the measured copper content in the feed ore and that in the products should agree within about ±5%. If the balance is appreciably different, repeating the test and determining the reason for the discrepancy is prudent practice.

3.2.2.3 Trace Element Mobility Procedures

In recent years, regulatory criteria have lead to the study and development of standardized procedures for determining the mobility and release of both inorganic and organic components from various types of wastes. These standard procedures include the following methods:

- Extraction procedure (EP) toxicity test—(U.S. 40 CFR 261, 1980). [An agitation leach using 0.5N acetic acid to maintain the extraction slurry pH at 5.0 ±0.2]. (This test has now been replaced by the following procedure.)
- Toxicity characteristic leaching procedure (TCLP)—(U.S. 40 CFR 261, 1990). [An agitation leach using either a sodium acetate buffer (pH 4.93 ±0.05) or a dilute acetic acid solution (pH 2.88 ± 0.05).]
- Standard test method for shake extraction of solid waste with water, ASTM Method 3987—(ASTM, 1992b). [Uses a reagent water extraction fluid to simulate leaching by ground water or rainfall.]
- California waste-extraction test (WET)—(California EPA, 1991). [An agitation leach using a 0.2*M* sodium citrate extraction fluid (pH 5.0 ±0.1).]
- Canadian leachate extraction procedure—[Canadian Standards Association (CSA), 1987]. [An agitation leach using a 0.5*N* acetic acid solution to maintain the extraction slurry pH at 5.0 ±0.2.]
- Standard test method for sequential batch extraction of waste with water, ASTM Method 4793—(ASTM, 1992a). [An agitation leach using water as the extraction fluid.]
- Standard test method for leaching solid waste in a column apparatus, ASTM Method 4874—(ASTM, 1989). [Uses aqueous leaching solutions such as distilled water. The solutions move through the bed of waste material in a saturated upflow mode.]

Periodically, nearly all of these procedures have received some modification; therefore, before starting any test program, the latest regulations and procedure modifications should be consulted. At the present time no "standard" test methods have been developed that can be used to predict the trace-element release from geological materials, tailings, or other waste materials such as those containing sulfide minerals or compounds. There are, however, several "nonstandard" tests, such as the Humidity Cell procedure and Selective Dissolution methods that have been reported in the literature. In general these techniques attempt to simulate environments that can be encountered when mineral processing wastes are present.

Currently standardization of these procedures is under investigation.

Even though the TCLP is not a standardized test for geological materials, tailings containing sulfides, etc., it is typically applied on these materials to develop comparative base-line data because it has legal recognition.

The following three procedures present introductory discussions of the TCLP, Humidity Cell, and Sequential Selective Dissolution procedures that have application to mineral processing wastes.

- ***Trace element mobility procedure No. 1 (TCLP on "100% solids")***—The Method 1311 TCLP was developed by the U.S. Environmental Protection Agency to simulate the leaching that an industrial waste will undergo when deposited in a sanitary landfill containing about 5% industrial waste and 95% municipal refuse. This batch test is based on the premise that the acidic sodium acetate leaching solutions used will simulate the composition and characteristics of the leaching fluid generated by decomposition of the refuse in the landfill. The TCLP procedure, which was formally adopted in 1990 (U.S. 40 CFR 261, 1990; and U.S. 40 CFR 261, 1991), replaced the extraction-procedure toxicity test that had been used prior to that time. The new procedure provides for the determination of both inorganic and organic analytes present in the solid, liquid, and multiphasic components of the waste being tested. Although the TCLP test does not simulate the environments associated with acid mine drainage or the seepage from tailings that contain iron sulfides, it is a recognized standard procedure that can serve as a regulatory point of reference. The following is an abbreviated outline of the Method 1311 TCLP procedure as applied to a "100% solids" sample of hydrometallurgical tailings. Method 1311 defines "100% solids" as a material that will yield no liquid when subjected to pressure filtration at pressures up to 50 psi. This abbreviated procedure description is intended only to give a general feel for the steps of the method. Before conducting actual tests, the researcher should refer to a complete copy of the most recent revision of the TCLP procedure.
- The first step in the extraction procedure is a preliminary leach to determine which of the following extractant solutions should be used.

<u>Extraction fluid No. 1</u>.

1. Add 5.7 mL of glacial acetic acid to 500 mL of deionized water.
2. Add 64.3 mL of 1*N* NaOH.
3. Dilute to 1 L.

<u>Extraction fluid No. 2</u>.

1. Dilute 5.7 mL of glacial acetic acid to 1 L.

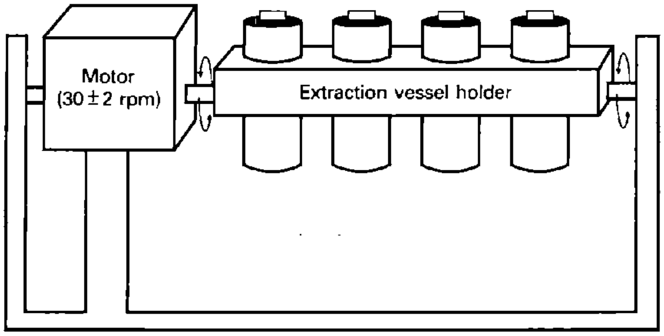
- Cut out a small subsample of the waste material to be tested and reduce it (if necessary) to a particle size of minus 1 mm or finer.
- Place 5 g of this material in a 500-mL beaker and add 95.5 mL of deionized water.
- Cover the beaker with a watch glass and stir for 5 min with a magnetic stirrer.
- Measure the pH. If the pH is <5.0, use extraction fluid No. 1 for the subsequent TCLP.
- If the pH is >5.0, add 3.5 mL of 1*N* HCl, slurry briefly, cover with a watch glass, heat to 50 °C, hold at 50 °C for 10 min, and then let it cool to room temperature.
- Measure the pH. If the pH is <5.0 use extraction fluid No. 1 for the subsequent TCLP. If the pH is >5.0, use extraction fluid No. 2.
- The minimum amount of sample for the TCLP test is 100 g.
- The amount of extraction fluid to be added is determined as follows:

$$\text{weight of fluid} = [(20) \times (\text{percent solids}) \times (\text{weight of waste})]/100.$$

(Therefore, 100 g of 100% solids waste will require 2,000 g of extraction fluid.)

- Transfer the extraction fluid to the extraction vessel (a borosilicate glass or polytetrafluoroethylene bottle), add the waste material, and seal the bottle tightly. Using Teflon nonstick tape on the bottle threads is recommended. The bottle should be of such size that there is headspace above the slurry liquid level.
- Secure the bottle in a rotary agitation device capable of rotating the extraction vessel in an end-over-end fashion. (see figure 3.13).

Figure 3.13



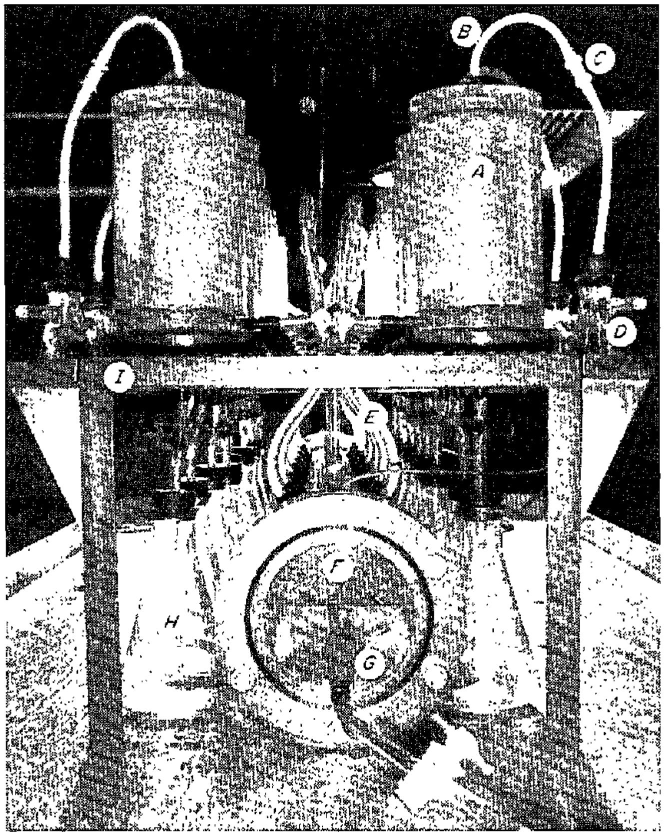
Rotary-agitation apparatus.

- Rotate the extraction vessel at 28 to 30 rpm for 16 to 20 h. The temperature should be maintained at 23 °C ±2 °C during the extraction process.
- After the agitation period has been completed, the slurry should be filtered in a pressure filter using a borosilicate glass-fiber filter (0.6 to 0.8 μm). Prior to the filtration the glass fiber filter should be washed once with 1N HNO_3 and rinsed three times with deionized water (minimum of 1 L per wash). Slowly increase the pressure in 10 psi increments to a maximum of 50 psi. Maintain the 50 psi pressure until no additional filtrate is forced out within a 2 min period.
- Immediately measure the pH of the filtrate, take a small aliquot of the filtrate, and add nitric acid. If a precipitate does not form, acidify the analytical sample to <2 pH with nitric acid and submit for analysis. If a precipitate does form, do not acidify the analytical sample, and analyze it as soon as possible. All aliquots should be stored at 4 °C until analyzed.
- ***Trace-element mobility procedure No. 2 (humidity-cell technique)***—The humidity-cell test is an accelerated weathering method that aims to simulate the geological weathering process of mining and mineral processing wastes. This kinetic procedure, which was originally developed to investigate factors affecting acid mine drainage associated with coal mining operations (Caruccio, 1968), can be used to study conditions such as the weathering of iron sulfides in an aerobic, unsaturated environment. The test procedure has not yet been standardized, but at the present time an ASTM committee is in the process of developing a standard.

The test protocol consists of placing the test sample in a humidity cell that provides for control of the flow rate and humidity of the air that is passed through a bed of the sample Lawrence (1990); Sobek and others (1978); Sullivan and Yelton (1988); and White and Jeffers (1990). Figures 3.14 and 3.15 illustrate an array containing 16 individual 4-in humidity cells White and Jeffers (1994). The complete test includes 20 or more weekly cycles, each of which involve the following generic operations.

- The tare weight of each humidity cell is determined so that net-weight measurements can be determined throughout the test period.
- Prepare a filter bed in each cell by bedding a weighed amount (approximately 20 g in a 4-in ID cell) of a relatively inert material such as quartz wool on the perforated-screen bottom of the cell.
- Carefully bed the test sample on the filter medium. A typical sample might be 1,000 g of mine waste rock that has been dried at 50 °C and crushed to minus 0.25 in.
- Conduct a baseline leach by placing 500 mL of deionized water, e.g., Type 2 [ASTM Specification D-1193 (ASTM, 1992)], in a separatory funnel and dripping the water onto the 1000 g bed of waste in the humidity cell. The drip rate should be adjusted so that the waste sample is thoroughly wetted but not flooded. When the effluent drip stops, determine the net-effluent weight and the net weight of the humidity-cell contents. The effluent is sampled and saved for analysis. The scope and extent of the analytical determinations in general will be determined by the type of waste material being tested and the appropriate regulatory requirements. Typical analytical measurements have included pH, conductivity, redox potential, Cl^-, SO_4^{2-}, aluminum, arsenic, barium, calcium, cadmium, cobalt, copper, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel, lead, selenium, silicon, strontium, zinc, and also total acidity or alkalinity.

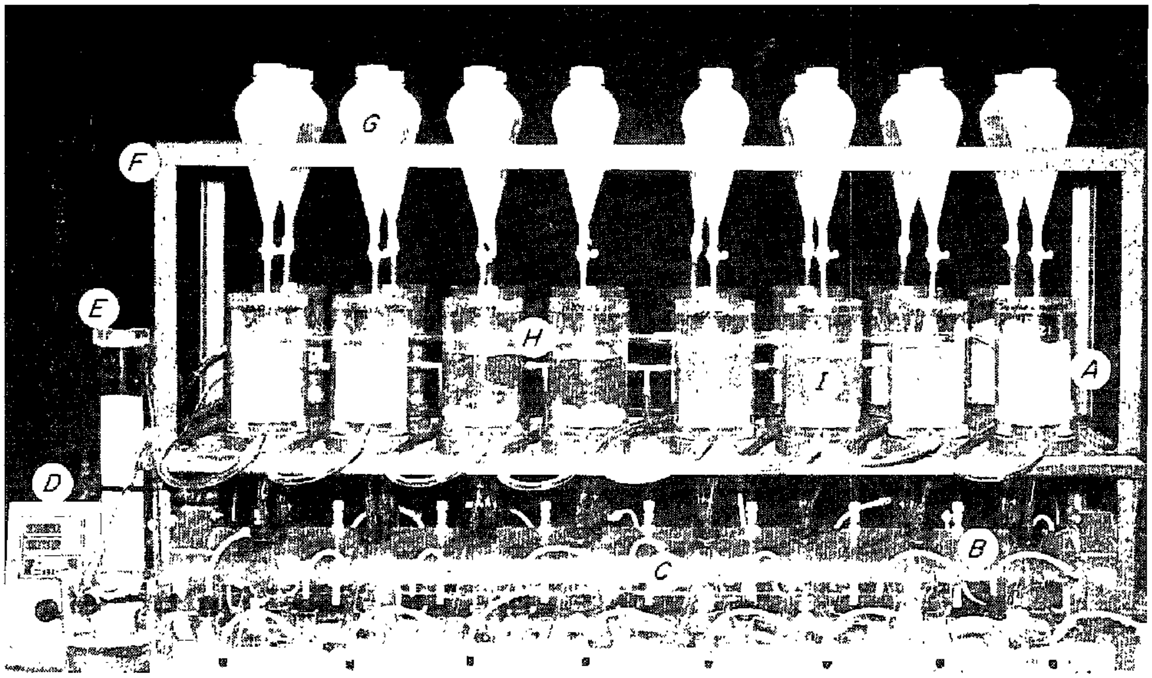
Figure 3.14



Humidity-cell arrangement (side view of 16-cell array). A, 4-in humidity cell with lid; B, air exit port; C, quick disconnect; D, 50-mL air exit port bubbler; E, wet-air lines to humidity cells; F, humidifier; G, humidifier immersion heater; H, 500-mL Erlenmeyer collection flask; I, humidity cell table.

- Some researchers have omitted the baseline or "0-time" leach and proceeded directly to the following dry-wet air cycle. Carry out the 3-day dry-air cycle by routing the

Figure 3.15



Humidity-cell arrangement (front view of 16-cell array with separatory funnel rack). A, 16-cell array; B, humidifier; C, gas disperser (fritted cylinder); D, humidifier temperature controller; E, desiccant column; F, separatory funnel rack; G, 500-mL separatory funnel; H, dry-air manifold; I, 4-in humidity cell.

air through a desiccant column [see figure 3.15 (*E*)] and then passing dry air upflow through the bed in each cell at a controlled rate of approximately 1 L/min.

- Next, the wet-air cycle is conducted by passing air humidified to 100% relative humidity at 30 ±2 °C for 3 days. The air-flow rate is again controlled at approximately 1 L/min for each cell.
- After the wet-air cycles are complete, the bed of waste material is leached with 500 mL of the deionized water. The net residue weight and the effluent weight are determined, and a sample of the effluent, which is designated at the "week-one leach," is saved for analysis.
- The weekly cycle, which consists of 3 days of dry-air contact followed by 3 days of wet-air contact and then the leach with deionized water, is continued for at least 20 weeks. Some procedures recommend adding a culture of *Thiobascillus ferrooxidans* and *Thiobascillus thiooxidans* during week 15 of the test to increase acid production. If, however, the waste material contains sulfides, these bacteria will usually be present naturally, and further additions may produce only minimal effects. Detailed records should be kept of all dates, times, measurements, and observations throughout the test.

Since the humidity-cell technique may become a standardized procedure with regulatory implications in the future, the researcher should consult the most recent U.S. EPA or ASTM literature for procedural information before initiating a test program.

- ***Trace-element mobility procedure No.3 (sequential selective dissolution)***—The sequential-selective-dissolution procedure was developed to approximate the relative extraction rates of easily exchangeable, adsorbed, organic-bound, carbonate, and sulfide trace-element forms from various waste materials (Lund and others, 1980; Sposito and others, 1982; and Stover and others, 1976). The general procedure described by Stover and others uses small (about 2 g) samples of the finely pulverized waste material being studied. The tests are conducted in triplicate. Each 2-g sample is sequentially contacted with a series of reagents of increasing chemical reactivity. Each sequential contact uses 25 g of the given reagent solution. The extractions are made by shaking the solids-solution mixture in a 50-mL Oak-Ridge-type polypropylene centrifuge tube, which has a screw cap closure. Following each extraction step, the mixture is centrifuged at 10,000 rpm for 10 min; the supernatant solution is decanted and reserved for analysis. The following reagent sequence was used by Stover and others (1976):

1. To extract exchangeable forms, the sample is contacted with a 0.5*M* potassium nitrate solution for 16 h.
2. To extract adsorbed forms, the residue from the first extraction is contacted with deionized water for 2 h.
3. To extract the organic forms, the residue from the second extraction is contacted with a 0.5*M* solution of sodium hydroxide for 16 h.
4. To extract the carbonate forms, the residue from the third extraction is contacted with a 0.05*M* EDTA solution for 6 h.
5. To extract the sulfide forms, the residue from the fourth extraction is contacted with a 4*M* nitric acid solution for 16 h at 80 °C.

The relative extraction of an element in each extraction step is calculated by dividing the amount of that element found in a given extract product by the amount of that element found in the original 2-g sample. Test results can be used to make qualitative predictions of the trace-element release sequence. Data developed from tests on two oil-shale samples from the eastern United States suggest that those elements that reside in the soluble and adsorbed phases of a given material will be solubilized rapidly during leaching. Those elements that reside in the carbonate and sulfide phases will be released during iron sulfide oxidation (Sullivan and Yelton, 1988).

3.2.3 Continuous Leaching

Bench-scale continuous leaching investigations are most often conducted to confirm results obtained during batch-leaching experiments. Since each continuous-leaching setup must be specifically tailored to the system being investigated, recommendations for specific setups, equivalent to those outlined in the previous sections on batch leaching, are not typically applicable. Designing and operating these systems can become complex. Consulting the literature related to similar commercial-scale operations can provide valuable guidelines for the type and degree of control that will be required to obtain meaningful data. There are, however, a number of generalizations that should be considered when setting up a laboratory-scale continuous-leaching apparatus. These generic criteria include the following:

- ***Reactor criteria***—The reactor configuration and degree of agitation guidelines discussed in section 3.2.2.1 are also generally applicable to the agitation requirements for continuous-leaching circuits. Controlled feeding of finely ground dry ore to a bench-scale leaching system can usually be accomplished by using calibrated variable-speed screw-type feeders. In some instances it may be desirable to add the ore feed in slurry form using some type of variable-speed positive-displacement pump. If possible, reagents should be fed in liquid form. Both peristaltic pumps and flowmeter arrangements such as those previously shown in figures 3.8, 3.11, and 3.12 have proven satisfactory. Dry reagents can usually be added using small screw-type feeders.

- ***Short circuiting***—Since retention time is an important variable in nearly all leaching operations, the potential for short circuiting in a continuous-leaching system must be considered. Short-circuiting refers to the fact that the retention time for some particles in a continuous system can be shorter than the average retention time in the leaching vessel. This condition is a natural characteristic of any well mixed tank that is operating in a continuous-flow mode. The overall effect, however, can be essentially eliminated by using a multiple-tank leaching system. The statistical evaluation developed by MacMullen and Weber is applicable for predicting the history of particle flow in a hydrometallurgical-leaching system (MacMullen and Weber, 1935). Table 3.5 illustrates the relationship between the short-circuiting effect and the number of tanks in a continuous-flow leaching system (Oldshue, 1983, p. 134). For example, only 3% of the particles fed to a well mixed 5-tank cocurrent leach system would short circuit, while 30% of the particles fed to a single-stage leach with the same total volume would pass through the tank in less than the average retention time. The term "well mixed" implies that the suspension of all particles is uniform throughout each leach tank. Particle suspension that is less than uniform suspension can alter the short-circuiting phenomenon. Comparing the particle-size versus leach-extraction relationships obtained during both batch-leaching and continuous-leaching experiments is nearly always desirable.

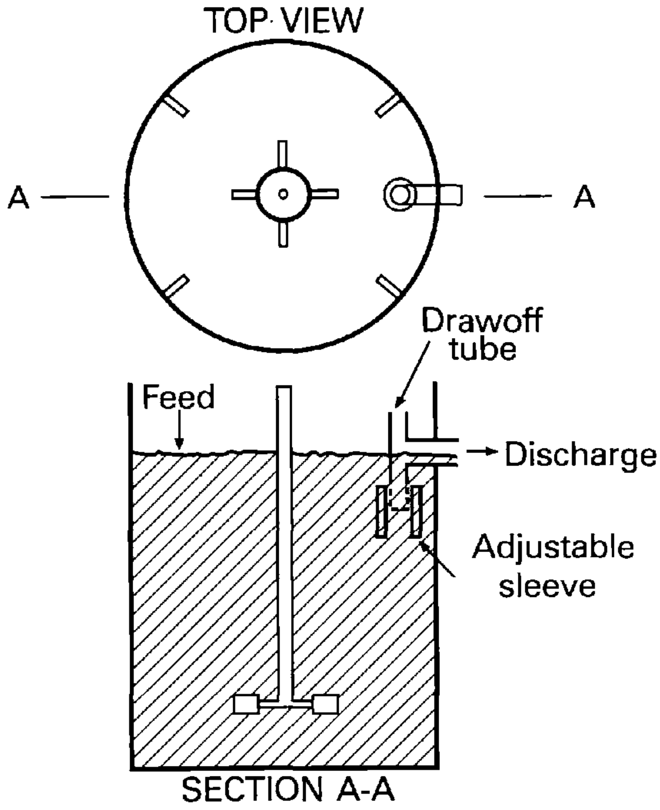
Table 3.5—Relationship between number of tanks and short-circuiting, percent

Number of stages	Too short	Correct time	Too long
1	30	65	5
2	15	83	2
3	9	90	1
5	3	97	0
10	1	99	0
20	0	100	0

- ***Feed and draw-off considerations***—For steady-state operation, the physical composition of the feed and exit streams of each leach reactor must be essentially the same.

Since most metallurgical-leach feed pulps are the product of fine grinding and fall in the hindered settling category (i.e., having settling rates of less than approximately 1 ft/min), meeting this objective is realistic. Even under these conditions, however, some form of baffled draw-off point is desirable because maintaining a uniform suspension in the top several percent of the leach-tank volume may be questionable. This relationship can be particularly critical if any particles in the slurry exhibit free settling velocities approaching 6 ft/min (Oldshue, 1963, p. 26). Under these conditions, the draw-off point in the leach tank must be lowered so that steady-state conditions can be maintained. This requirement can usually be achieved by placing a draw-off tube in the leaching vessel (figure 3.16). The pulp up-flow velocity in this draw-off tube must be high enough to keep all particles in suspension. In some small-scale continuous-leaching systems achieving the required up-flow velocity may require installing an airlift-type device in the draw-off tube. If steady-state operation is not maintained and the coarse particles are not continuously removed, the leach reactor may sand up.

Figure 3.16



Leaching reactor with drawoff tube.

3.3 SAFETY

3.3.1 Introduction

When setting up and conducting any type of leaching experiment, the primary guideline must be to work defensively at all times. The researcher should build methods for control, security, and escape into each experimental setup. Safety rules cannot be completely codified, especially for research. Therefore, each operation must be evaluated for its intrinsic dangers. Job Safety Analysis techniques, such as those outlined in section 1.2.5.3 of chapter 1, present a step-wise procedure for preparing this evaluation. The researcher has a professional, moral, and legal responsibility for both knowing and following the safety rules and practices applicable to the experimental work being conducted.

Leaching safety considerations relate primarily to hazards such as corrosive or toxic agents and explosive characteristics. Other chemical-research hazards such as liquid flammability, pyrophoric substances, and vacuum system implosions, which can be critical when working with organic reactions, are not usually encountered during hydrometallurgical-leaching-system experiments. Each of the previous sections in this chapter contains recommendations for safety practices associated with the particular operation discussed. The following sections contain some additional recommendations and suggestions.

3.3.2 Corrosive or Toxic Agents

The MSDS should be a key reference that are always consulted when designing leaching experiments and the associated equipment setups. It is important that all reaction components including the feed material, the leaching reagents, and the reaction products be considered. The mineral acid and caustic alkaline solutions used in many hydrometallurgical-leaching systems can be extremely corrosive. Therefore, both personal protective equipment and collection systems for spills are important. Fail-safe designs and spill collection are particularly critical when unattended operations such as column leaches or overnight bottle-rolling tests are being conducted. If there is any possibility that toxic gases, vapors, or dusts may be present, the experiments should be carried out in an effectively operating hood. Again, as mentioned in the opening sentence, operating defensively is always prudent practice.

3.3.3 Explosive Characteristics

The explosive hazards associated with hydrometallurgical-leaching practices relate primarily to pressure-leaching operations. The previous sections on Pressure Leaching contain recommendations for specific aspects of pressure-leaching equipment setups and operations. These recommendations consider factors such as vessel capacity, maximum temperatures and pressures, stirring requirements, materials of construction, valves and fittings, overpressure protection, external piping, barricades, ventilation, maintenance, and the initial operating tests. Hazards associated with pressurized-oxygen systems were also discussed. In addition, caution should be exercised with any oxygen-enriched system, even those at atmospheric pressure. An oxygen-enriched atmosphere (OEA) is usually defined as one in which (1) the concentration of oxygen exceeds 21% by volume, (2) the oxygen partial pressure exceeds 160 torr (millimeter of mercury), or (3) both. The degree of fire hazard of an OEA varies with the concentration of oxygen present, the total pressure, and the diluent gas (NFPA, 1990). For example, it is possible that an oxygen piping-system leak in a confined autoclave bay could significantly increase the oxygen concentration and produce an OEA in which organic materials might burn at explosive or near explosive rates. Compressed air is also an OEA, and the fire hazard of combustible materials present becomes greater because of the increased oxygen partial pressure. For example, as air is compressed from atmospheric pressure to 60 psi, the partial pressure of the contained oxygen increases from 160 torr to ≈ 800 torr even though the amount of oxygen present has not changed (NFPA, 1990). All pressurized systems have inherent hazards, but the presence of OEA significantly increases the potential for fires and explosions.

3.3.4 Other Considerations

Other safety considerations associated with laboratory leaching experiments include the following:

- All equipment setups should be neat. Any leaching arrangement that is not balanced, fixed, and aesthetically pleasing is probably dangerous.
- Provisions for controls to offset the effect of anomalous conditions such as rapid temperature changes, chemical spills, fire, explosion, and fumes should be an intrinsic component of the research planning process. These considerations become increasingly critical when high reagent concentrations or pressurized leaching are used.
- When an unknown reaction is being investigated, it is always prudent to run the first tests on a small scale. Even if the initial small-scale tests are uneventful, remain alert because the amount of reactants present can sometimes influence the effective reaction rate when factors such as heat transfer are controlling.
- Do not add a reagent faster than it is being consumed. This is particularly important when the reactions have induction periods. This can occur when surface coatings must be removed before the reaction proceeds well. An oxidation process should be carefully monitored because these reactions often do not proceed at reasonable rates unless the temperature is held within relatively narrow limits.
- Operational and waste-disposal practices should follow all regulatory requirements such as those discussed in Chapter 1. This includes not only waste solutions and leach residues but byproducts and unused reagents as well.

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CHAPTER 4.—SOLIDS-LIQUID SEPARATION

4.1 INTRODUCTION

Solids-liquid separation is an integral component of nearly all hydrometallurgical operations, and it can be one of the most expensive elements of a flowsheet. For example, in some uranium ore processing operations, the countercurrent washing circuit accounts for nearly 40% of the total capital expenditure. Therefore, projecting solids-liquid separation requirements assumes critical importance, even during the initial phases of a hydrometallurgical research project.

The context of the following procedures and discussions presumes that the researcher has studied the general literature related to the investigation but has limited experience in specific experimental techniques. The aim is to provide a starting point for personnel who have or are receiving professional training. Understanding the unit operations and equipment involved in solids-liquid separations is particularly important because the correlations used for data reduction are primarily empirical and are based on industrial experience.

Solids-liquid separations in hydrometallurgical processes have the following primary objectives:

- To recover a valuable leach liquor and to wash the solid residue before disposal.
- To recover a valuable precipitate or other solid (the liquor being discarded).
- To separate and recover both the solid and liquid components when both contain valuable constituents.

In waste management operations, neither the solid nor the liquid may have intrinsic value; the most probable direct objective of these solids-liquid separations is to prevent water pollution.

Factors that influence all solids-liquid separations include the following:

- *Particle size and size distribution*—Finer particles generally have slower settling and filtration rates. Thickener discharges also tend to be more dilute and filter cakes contain more moisture when the percentage of fine particles increases. Therefore, processing operations should avoid overgrinding or excessive attrition. Experimental studies must identify the optimum particle size that is consistent with overall plant operation and recovery.
- *Solids concentration*—Required equipment sizes and costs usually decrease with increased feed slurry concentrations because the volume of both slurry and liquid that must be handled decreases. This holds true for both thickening and filtration operations. Some pulps, however, can exhibit an optimum feed density; thickener capacities will decrease both above and below this optimum.
- *Particle shape and surface characteristics*—The optimum condition is generally a spherical particle with zero porosity. As either of these factors degrades from the desired state, operational difficulties increase. Surface chemistry also influences the required flocculant type and dosage.
- *Pretreatment*—Pretreatments such as flocculation, heating and cooling, etc., can affect both the rate and mode of solids-liquid separations. For example, even though flocs may settle considerably faster than the fastest of the individual particles, the final compaction density may be lower because large amounts of water may be entrapped within the voids of the flocs.
- *Liquid viscosity*—When the liquid viscosity increases, both settling and filtration rates decrease. In severe climates, slurry temperatures become particularly important because the viscosity of water increases significantly as temperatures approach freezing.

While other factors can also influence solids-liquid separations, the above represent those of primary common influence. In addition, potential variations in the chemical or mineral composition of the feed pulps must always be considered. Ores from different areas of the same mine can exhibit significantly different solids-liquid separation characteristics. This variability, along with the effect of changing process conditions, must be evaluated during all studies of hydrometallurgical process development.

Laboratory-scale solids-liquid separation tests have been developed to evaluate the effects of these and other variables; the procedures derive from a combination of theory and experience.

Solids-liquid separations in most hydrometallurgical operations are based on gravity sedimentation and/or filtration; some operations have used centrifuging.

When the primary purpose of a *gravity sedimentation* operation is to recover the solids in a concentrated slurry, the process is called "thickening." If the principal objective is to clarify the liquid, the term "clarification" is used. In hydrometallurgical circuits, correctly sized and designed thickeners often accomplish both clarification and thickening. Waste management applications usually emphasize clarification requirements. Both of these processes require a density difference between the solids and the suspending liquid.

Filtration employs pressure or vacuum to drive the liquid through a porous medium that supports and retains the solids. Because the particles are constrained and the liquid is free to flow under the force of a differential pressure, a density difference between the solid and the liquid is not necessary.

In *centrifugal processes*, the separating forces, which are generated by rotational energy, increase the sedimentation effect. Size differences become less critical, and the sedimentation effect extends to finer particle sizes.

A wide gap continues to exist between theory and practice in solids-liquid separation. This gap arises because reliable quantitative relationships have not been established between primary properties such as particle size, distribution, and flocculation and derived secondary properties such as settling flux and filtration cake resistance. Unless large-scale data and experience exist for a comparable slurry, reliable equipment selection and sizing must rely on laboratory- or pilot-scale tests. The feed slurries used for these tests must duplicate the anticipated production slurries as closely as possible. The following sections discuss laboratory procedures for conducting solids-liquid separation tests to determine parameters for thickening, clarification, and filtration requirements.

General references that discuss both solids-liquid separation theory and application have been published by Carman (1956), Dahlstrom (1985b), Emmett (1984), Jacobs (1984), Poole and Doyle (1968), Svarovsky (1981, 1985), and Wesely (1985).

4.2 THICKENING TESTS

4.2.1 Introduction

Thickening, as practiced in hydrometallurgical processing, can be defined as removing a portion of the liquid from a slurry by allowing the solids to settle under the influence of gravity. The terms "thickening" and "clarification" have sometimes been used interchangeably, but "thickening" is more specifically defined as the process of separating the solids into a concentrated slurry. The term "clarification" is most applicable when the primary objective is to clarify the liquid; the water industry is the largest user of gravity clarifiers. Since the development of effective flocculants, many hydrometallurgical thickeners function as both thickeners and clarifiers.

4.2.2 Flocculation

Sedimentation aids such as lime and alum have been used in industrial plants since the early part of the 19th century. Subsequently, glues, starches, and other naturally occurring organic polymers gradually found increasing use in mineral processing operations. When synthetic water-soluble polymers were introduced in the early 1950's, solids-liquid separations in hydrometallurgical flowsheets entered a new area. These products significantly increased both the effectiveness and flexibility of thickening and filtration operations.

Selection of a flocculant depends on optimizing the cost-to-performance relationships between capital and operating expenses. Although the synthetic flocculants are relatively expensive, savings resulting from reduced capital costs may readily exceed flocculant costs. For most hydrometallurgical operations these cost comparisons are based on data developed during laboratory-scale testing.

The effect of any specific flocculant depends on a number of variables, which can include the following:

- *The mineralogical composition of the feed slurry*—For example, clay-like minerals are often the most difficult to flocculate and settle.
- *Particle size of the mineral constituents*—Finer particles usually require more flocculant.
- *pH of the liquid*—Changing the pH can affect either flocculation or dispersion of the feed pulp.
- *Temperature of the pulp*—Higher temperatures generally improve flocculant effectiveness. Therefore, all flocculation and settling tests must be conducted at the expected operating temperature.
- *Feed pulp density*—The percentage of solids in the feed pulp can influence both the degree and type of flocculation, but an increase in the solids content may not require a proportional increase in the flocculant dosage.
- *Soluble salts effects*—The presence of soluble salts can either aid or retard flocculation.

4.2.2.1 Preparing Flocculant Solutions

Literally hundreds of flocculants are available, and experience plays a major role in selecting a flocculant for any specific solids-liquid separation. Literature references related to similar processing operations can often supply valuable leads. Product data and other information available from flocculant manufacturers are particularly valuable. The flocculant producers shown in the 1991 E&MJ International Directory of Mining (Engineering and Mining Journal, 1990) are as follows:

Allied Colloids, Inc., Suffolk, VA.
American Cyanamid Co., Wayne, NJ.
Betz Laboratories, Inc., Trevose, PA.
Calgon Corp., Pittsburgh, PA.
ChemLink, Inc. (Industrial/Petroleum Chemicals Div.), Newton Square, PA.
Chemserve Steinhall (Pty.) Ltd., Meyerton, Transvaal, South Africa.
Drew Industrial Division (Ashland Chemical, Inc., subsidiary of Ashland Oil, Inc.), Boonton, NJ.
Henkel Corp., Tucson, AZ.
Henkel Corp., Mineral Industry Division, Tucson, AZ

Henkel KGaA, Mining Chemical Division, Dusseldorf, Germany
Hoechst Aktiengesellschaft, Frankfurt am Main, Germany.
Metallgesellschaft AG, Frankfurt am Main, Germany.
Minerec Mining Chemicals, Tucson, AZ.
Nalco Chemical Co., Naperville, IL.
PQ Corp., Valley Forge, PA.
Stauffer Chemical Co. (subsidiary of Chesebrough-Ponds Inc., BasicChemicals Division), Westport, CT.
Tennessee Chemical Co., Atlanta, GA.
Union Carbide Corp. (Specialty Chemicals Division), Danbury, CT.
Witco Corp., New York, NY.

Halverson and Panzer (1980) presented a general review of flocculants along with an extensive bibliography of references.

Unless specific experience is available, it is nearly always desirable to test typical reagents from each of the following three basic types: cationic, anionic, and non-ionic. Flocculants are usually added as dilute solutions, and preparation of the flocculant solutions should follow the manufacturers' recommendations. If specific recommendations are not available, the following procedure may be used to prepare a 0.1% solution of the flocculant:

1. Weigh out 0.50 g of dry flocculant on a suitable analytical balance (readability, 0.001 g).
2. Place 500 mL of water in a 1,000-mL beaker.
3. Agitate the water with a laboratory mixer to create a vortex.
4. Feed the premeasured 0.50 g of flocculant into the edge of the vortex at a rate that produces a dispersed mixture with no lumps.
5. Continue to stir until all the solid flocculant is in solution. This will usually take 60 to 90 min, but for some flocculants up to 3 h may be required.
6. Prepare the flocculant solutions fresh each day, as usually recommended by the manufacturers for best results. In any event, use the solutions within 2 or 3 days after preparation.

One milliliter of the resulting 0.1% solution contains 0.001 g of flocculant. Therefore, adding 10 mL of this flocculant solution to a slurry containing 200 g of solids per liter is equivalent to a 0.05-kg/t (0.1-lb/st) flocculant addition.

The same general procedure can be used to prepare flocculant solutions from reagents supplied in liquid form except that only a few minutes of agitation will be necessary. Flocculants supplied in an emulsified form usually require 20 to 30 min of stirring to ensure complete dissolution.

Gentle stirring should be used when flocculant solutions are being prepared. A high degree of shear will often reduce the subsequent flocculation efficiency. Also, interactions may occur between the degree of shear and the polymer dilution. In general, the more dilute the polymer solution, the greater the shear effect.

4.2.2.2 Preliminary Flocculation Tests

Preliminary scoping tests to evaluate the relative effectiveness of cationic, anionic, and non-ionic flocculants on a slurry may be conducted using the following procedure:

1. Pour 200-mL samples of representative slurry into each of four 250-mL beakers (one sample is a blank).
2. While stirring each pulp with a small spatula, add the respective flocculant dropwise from a small syringe until a flocculent appearance is produced. To achieve a significant settling rate, you may need to use a few additional drops of reagent. Most flocculant manufacturers recommend that the flocculant concentration not exceed 0.1%, and even lower concentrations are preferable. Flocculant additions during these tests usually range from 0.005 to 0.1 kg/t (0.01 to 0.2 lb/st) of dry solids. When hand-stirring the pulp with the small spatula, take care to reproduce the degree of stirring (shear) as closely as possible in the three beakers.
3. If all three flocculants produce about the same result, make relative rate-of-descent measurements. For example, the time required for the interface to settle 1 in can be used as a basis for comparison.
4. Select a reagent based on these rate-of-descent results together with the amount of reagent added and the unit reagent costs.

Sometimes effective flocculation may require a two-step procedure. For example, a cationic reagent followed by an anionic reagent may produce significantly improved flocculation. The reverse addition sequence should also be tried. Likewise, the addition of an inorganic reagent such as lime, alum, or ferric chloride followed by flocculation with a polymer may be effective. If sufficient pulp is available, comparative flocculation tests may also be made using 1-L graduated cylinders fitted with a plunger to mix the pulp. A suitable plunger consists of a stainless steel disk 2 in. in diameter and 1/16 in thick, welded to a stainless steel handle 24 in long and 3/16 in. in diameter. The disk contains sixteen 1/4-in holes drilled in a symmetrical pattern. The following procedure is used:

1. Place 1 L of representative pulp in the graduated cylinder and mix thoroughly. Mix the pulp over a period of about 5 or 6 s by six vigorous up-and-down strokes of the plunger between the bottom of the cylinder and the

800-mL mark. This procedure prevents the entrapment of air, which impairs reproducibility of results.

2. Add the desired amount of 0.1% flocculant solution, which has been previously diluted to 50 mL with water or clear supernatant.

3. Mix the flocculant solution into the pulp using six strokes of the plunger as described in step 1. To achieve consistency and reproducibility, keep the mixing technique uniform throughout the test series.

4. Record the settling rate as a function of time. The timing may be started when the interface level passes the 1,000-mL mark. Record the position of the interface at suitable time intervals or when the boundary layer passes each 10-, 50-, or 100-mL mark on the cylinder. In many instances, four tests can be run simultaneously.

Test results are usually evaluated by comparing the initial settling rate for each flocculant tested. The effect of reagent addition variations for a given flocculant is illustrated by plotting the initial settling rate versus the flocculant dosage.

Results from either the beaker or cylinder tests can be used to design the settling test experiments that are conducted to determine settling area requirements and to predict thickener underflow densities.

Tiller and others (1974) discussed the coagulation and flocculation of slurries. Their summary article on the pretreatment of slurries also examined the strengths and weaknesses of various testing procedures and presented a list of significant references.

Scheiner (1990) reviewed optimization of the overall flocculation sequence. The paper examined the complex interactions that can occur among variables such as the type of polymer, polymer concentration, mineral composition, particle size, mixing, and the use of flocculant combinations.

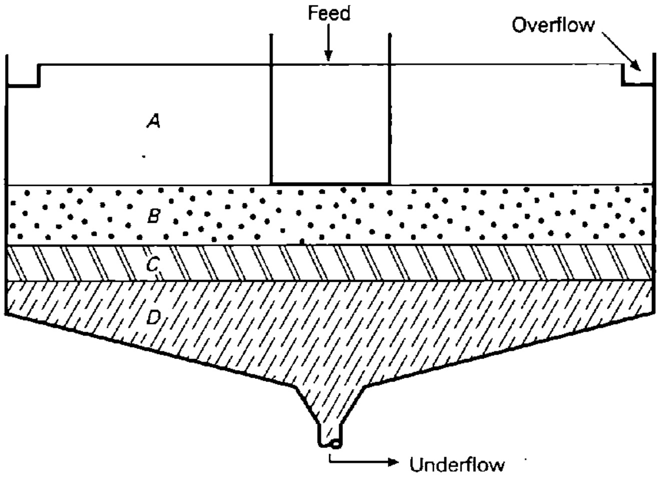
Other references that contain applicable information on flocculation theory and practice include the following: Chandler (1989), Hughes (1981), Ives (1981), Purchas, (1971), and Svarovsky (1985)

4.2.3 Conventional Thickeners

The feed pulp enters a conventional thickener through a central feed well, which disperses the feed gently into the thickener. The clear liquor leaves the tank at the periphery, and the thickened pulp discharges at the bottom. The flow patterns within a thickener can be complex, but in general, the solids-liquid concentrations in conventional thickener operation can be categorized into the following four zones, which are shown in figure 4.1:

The clear solution zone (*A*).
The mass subsidence or free settling zone (*B*).
The hindered settling or transition zone (*C*).
The compression or compaction zone (*D*).

Figure 4.1



Characteristic zones in an operating thickener. A, Clear solution zone; B, mass subsidence or free settling zone; C, hindered settling or transition zone; D, compression or compaction zone.

In any given thickener operation, not all of these zones may be present; but the thickener must be sized and designed to accommodate every regime that does occur. Laboratory procedures that can produce the required design data include the Kynch method, the Coe and Clevenger method, and the second-order and long-tube techniques discussed in the following sections.

4.2.3.1 Kynch Method

The Kynch method has become the most widely used hydrometallurgical settling test procedure. It applies to nearly all flocculated or unflocculated mineral processing pulps that settle with a sharp interface between the settled solids and the clear supernatant liquor. The basis for the procedure is a mathematical analysis of batch sedimentation developed by Kynch (1952). Talmage and Fitch (1955) extended Kynch's batch settling analysis to continuous operations. Their method predicts settling area requirements by developing a settling curve from batch tests and then applying the Kynch analysis procedure. The settling curve, which is a plot of interface height versus time, can be developed as follows for each dosage of flocculant tested:

Settling Test Procedure

1. Select a 1-L or 2-L graduated cylinder. A 2-L cylinder is preferred, but a 1-L cylinder may be used if the available pulp volume is limited. The 2-L cylinder minimizes wall effects. Measure the tare weight of the cylinder, and calibrate the cylinder in feet per milliliter. The following procedure is based on using a 2-L cylinder.

2. Add the thoroughly mixed pulp sample to the 2-L cylinder, up to the 1,950-mL mark. The balance will be made up by the flocculant solution, clear supernatant solution, and/or water.

3. The flocculant dosage will be based on the previous exploratory flocculant tests, such as those described in section 4.2.2.2. Place the desired amount of flocculant solution (preferably as a 0.1% solution) in a 400-mL beaker. If the volume is less than 50 mL, add clear supernatant solution or water to bring the volume up to about 50 mL.

4. Fill the flocculation device, such as that shown in figure 4.2, with the flocculant solution from the 400-mL beaker. This device is a syringe and tube arrangement used to distribute the flocculant evenly throughout the pulp in the cylinder. Next, thoroughly mix the pulp in the cylinder with a plunger such as that described in section 4.2.2.2, or use a No. 12 rubber stopper on the end of a stiff wire such as that shown in figure 4.2 Insert the flocculation device into the slurry in the cylinder and inject a portion of the flocculant solution continuously into the pulp as the device is lowered to the bottom and then lifted to just below the surface. Repeat this procedure three or four times over a total period of about 10 to 15 s.

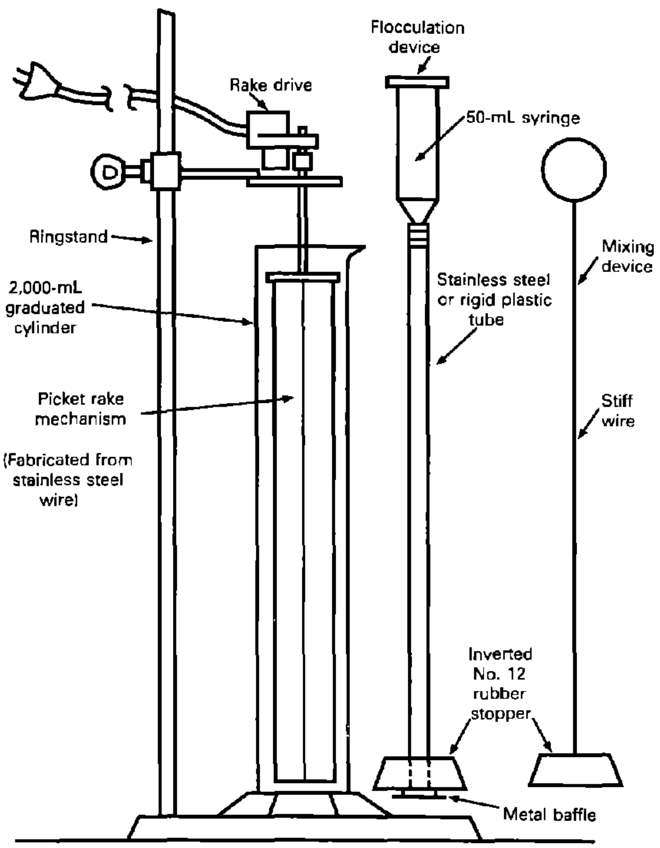
5. Remove the flocculation device and insert a picket-rake mechanism such as that shown in figure 4.2; the rakes should rotate at about 6 to 10 rph. Start the timer when the interface height passes the 2,000-mL mark, and continue recording the interface height until no further significant sedimentation occurs. This may require from less than 1 h for some ore pulps up to nearly 80 h for hydroxide or metallic sulfide precipitates. It is desirable to record the time at which the pulp height passes each 100- to 200-mL level during the initial straight-line portion of the settling curve. More closely spaced readings (at approximately 50 mL) should be taken as the pulp enters the hindered settling zone. After the pulp enters the compaction or compression zone, less frequent readings are required. For some pulps, a gentle tapping vibration of the cylinder may be needed to produce a horizontal interface. Record all measurements and other information on a form such as that shown in figure 4.3.

6. After the final compaction density is reached, carefully remove the raking mechanism in a manner that will produce minimum disruption of the settled slurry. Weigh the cylinder plus its contents to ±1.0 g. This measurement will be used to determine the weight and percent solids of the feed slurry.

7. Carefully siphon off all of the clear supernatant liquor. Determine the specific gravity of this solution. The measurement should be made at the temperature at which the settling test was conducted.

8. Record the volume of the remaining decanted pulp, and also determine the weight of the cylinder and its contents. These measurements are used to determine the specific gravity of the solids.

Figure 4.2



Thickening test apparatus.

9. Determine the dry weight of the solids present. If the liquid present in the settled slurry contains only a minimal amount of dissolved salts, wash the entire slurry into a pan and dry it at approximately 100 °C. If appreciable dissolved salts are present, filter and wash the solids before drying.

Data Reduction[1]

A variety of different procedures have been proposed and used for determining thickener area requirements from batch settling test data. The following procedure is based on an unpublished method developed over a period of years by the EIMCO Process Equipment Co., Salt Lake City, UT. The analysis is based on the equation shown below:

$$\text{Depth-corrected unit area} = \frac{t_u}{C_oH_o} \times \left(\frac{h}{H}\right)^n .$$

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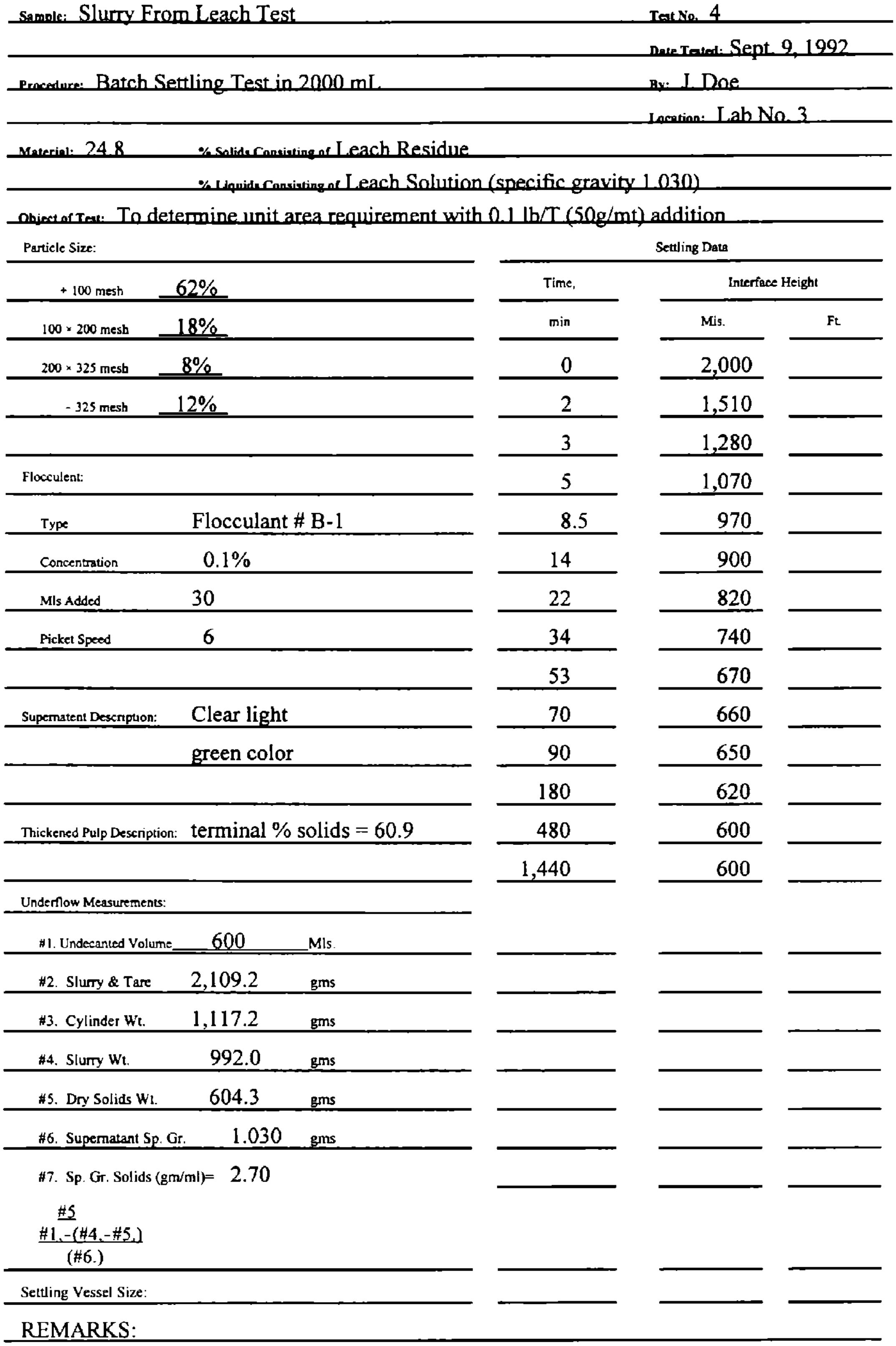
[1] Symbols used in the following equations are those used by Kynch (1952) and supplemented by EIMCO.

Figure 4.3



Sample: Slurry From Leach Test — Test No. 4

Date Tested: Sept. 9, 1992

Procedure: Batch Settling Test in 2000 mL — By: J. Doe

Location: Lab No. 3

Material: 24.8 % Solids Consisting of Leach Residue

% Liquids Consisting of Leach Solution (specific gravity 1.030)

Object of Test: To determine unit area requirement with 0.1 lb/T (50g/mt) addition

Particle Size:		Settling Data		
+ 100 mesh	62%	Time,	Interface Height	
100 × 200 mesh	18%	min	Mls.	Ft.
200 × 325 mesh	8%	0	2,000	
- 325 mesh	12%	2	1,510	
		3	1,280	
Flocculent:		5	1,070	
Type	Flocculant # B-1	8.5	970	
Concentration	0.1%	14	900	
Mls Added	30	22	820	
Picket Speed	6	34	740	
		53	670	
Supernatent Description:	Clear light	70	660	
	green color	90	650	
		180	620	
Thickened Pulp Description:	terminal % solids = 60.9	480	600	
		1,440	600	
Underflow Measurements:				
#1. Undecanted Volume	600 Mls.			
#2. Slurry & Tare	2,109.2 gms			
#3. Cylinder Wt.	1,117.2 gms			
#4. Slurry Wt.	992.0 gms			
#5. Dry Solids Wt.	604.3 gms			
#6. Supernatant Sp. Gr.	1.030 gms			
#7. Sp. Gr. Solids (gm/ml)= $\frac{\#5}{\#1.-\frac{(\#4.-\#5.)}{(\#6.)}}$	2.70			
Settling Vessel Size:				

REMARKS:

Settling test form.

The relationship includes both the conventional Kynch function:

$$\frac{t_u}{C_o H_o},$$

and a depth correction factor:

$$\left(\frac{h}{H}\right)^n.$$

The symbols used in the above equation are defined in the following numerical analyses, which use the settling test data presented in figure 4.3.

1. The measured pulp interface height is plotted as a function of time (curve A-E in figure 4.4).
2. The desired underflow concentration is selected, and the pulp height (H_u) corresponding to this concentration is calculated:

$$H_u = \frac{C_o\, H_o}{C_u},$$

where H_u = underflow pulp height, mL,

C_o = initial pulp concentration, g of dry solids per liter of pulp (604.3/2 = 302.15 g/L),

H_o = initial pulp depth (2,000 mL),

and C_u = desired underflow concentration, g of dry solids per liter.

If the desired underflow concentration, C_u, is known, H_u can be calculated directly from the above equation. If only the desired percent solids is known, H_u can be calculated by solving the equation shown below for H_u:

$$\frac{\text{Desired percent solids}}{100} = \frac{W}{W + D\left(H_u - \frac{W}{G}\right)},$$

where W = weight of dry solids (604.3 g from figure 4.3),

D = specific gravity of the solution (1.03, figure 4.3),

G = specific gravity of the dry solids (2.7, figure 4.3),

and H_u = underflow pulp height, mL.

For example, if desired underflow percent solids equals 55%, then:

$$\frac{55}{100} = \frac{604.3}{604.3 + 1.03\left(H_u - \frac{604.3}{2.7}\right)};$$

$$H_u = 704 \text{ mL}$$

3. Line H_u-H_u' is drawn to intersect the settling curve A-E at time t_u (the time for the pulp to settle to H_u).
4. The uncorrected unit area can now be calculated:

$$\text{Uncorrected unit area} = \frac{t_u}{C_o\, H_o},$$

where t_u = settling time at intersection of curve A-E and line H_u-H_u' (0.0292 days),

C_o = initial pulp concentration (0.30215 t/m^3),

H_o = initial pulp height (0.405 m).

Therefore:

$$\text{Uncorrected unit area} = \frac{0.0292}{0.30215 \times 0.405}$$

$$= 0.2386\ (\text{m}^2/\text{t})/\text{d}\ [2.32(\text{ft}^2/\text{st})/\text{d}].$$

5. The depth correction factor derives from empirical relationships established by correlating data obtained from cylinder tests with results observed during experiments on full-scale thickeners. The correction also assumes that the thickener will operate with an average pulp depth in compression of 1 m. The depth correction factor is calculated as follows:

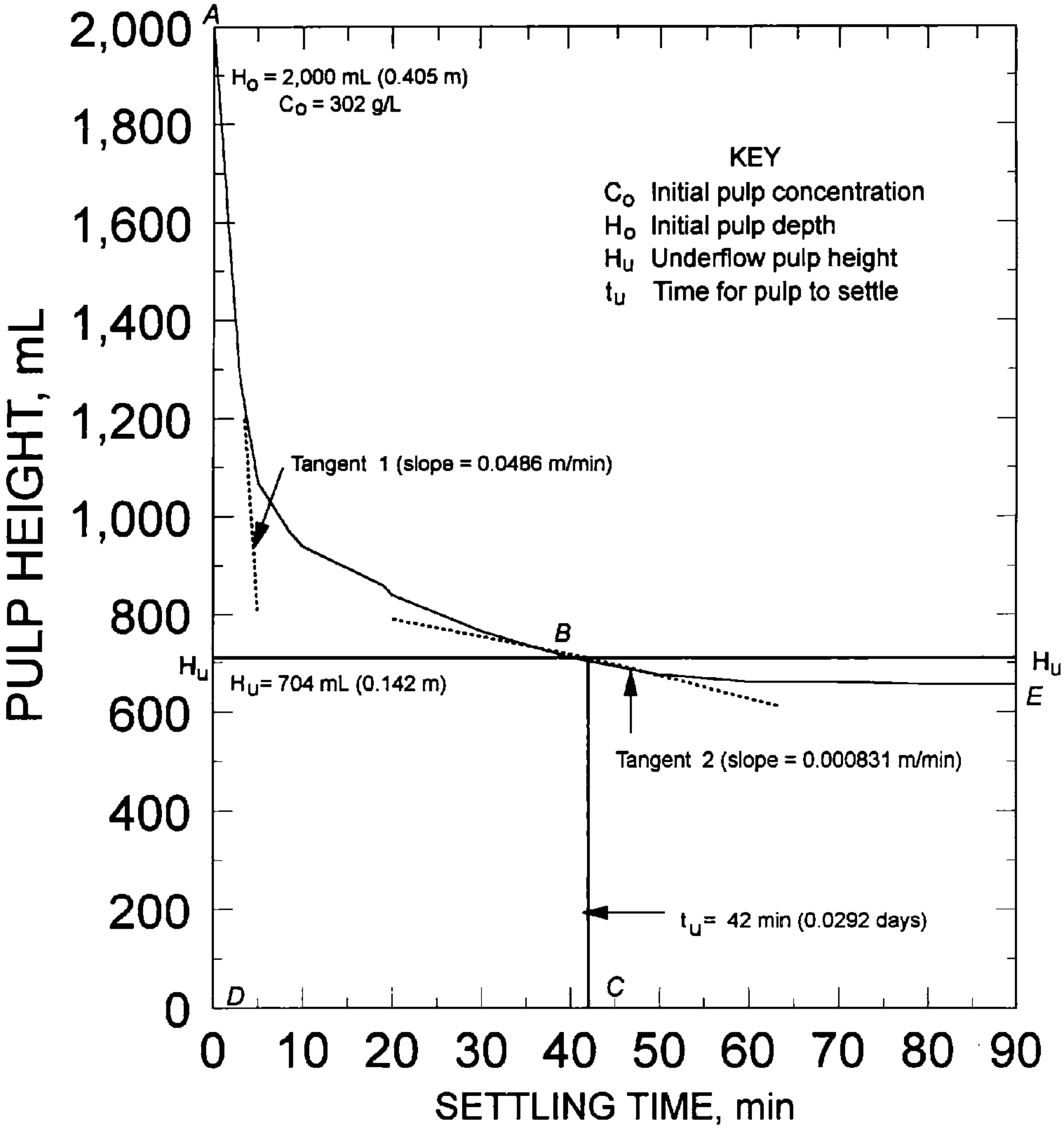
$$\text{Depth correction factor} = \left(\frac{h}{H}\right)^n,$$

where H = 1 m (average pulp height in compression zone),

and h = A/t_u,

where A = area below settling curve (area *A-B-C-D* in figure 4.4)(0.00526 m•d),

Figure 4.4



Batch settling test curve.

and t_u = settling time required to reach the desired underflow density (0.0292 days).

Therefore:

$$h = \frac{0.00526}{0.0292} = 0.180 \text{ m}.$$

The exponent n is derived from relationships shown in figure 4.4 as follows:

The settling rate at t_u (0.000831 m/min) is divided by the initial settling rate (0.0486 m/min), and the ratio is expressed as a percentage, i.e:

$$\text{Settling rate ratio} = \frac{\text{slope of tangent 2}}{\text{slope of tangent 1}} \times 100,$$

$$= \frac{0.000831}{0.0486} \times 100 = 1.7\%.$$

Therefore, from figure 4.5, which derives from empirical relationships established by correlating data obtained during experiments on full-scale industrial thickeners, n = 0.46.

Thus:

$$\text{Depth correction factor} = \left[\frac{0.180}{1}\right]^{0.46} = 0.454.$$

If H is very small or near its maximum, the depth correction factor can be too low. If the depth correction factor is below 0.25, use a value of 0.25 for the correction factor. Similarly, do not use values of H greater than 1.0 unless actual operational data justify a greater depth in the calculation.

6. Therefore:

$$\text{Depth corrected unit area} = \frac{t_u}{C_0H_0} \times \left[\frac{h}{H}\right]^n$$

$$= \frac{0.0292}{0.302 \times 0.405} \times \left[\frac{0.180}{1}\right]^{0.46}$$

$$= 0.109 \ (\text{m}^2/\text{t})/\text{d}$$

$$[1.06 \ (\text{ft}^2/\text{st})/\text{d}].$$

7. A design safety factor of 1.2 to 1.5 is normally used.

If a design safety factor of 1.3 is used, then:

Depth-corrected unit area (with safety factor)

$$= 0.142 \ (\text{m}^2/\text{t})/\text{d} \ [1.39 \ (\text{ft}^2/\text{st})/\text{d}].$$

Other procedures proposed for determining Kynch unit area requirements from settling test data include those described by Barnea (1977), Fitch (1971, 1975), Hasset (1965), Keane (1979), Moncrief (1964), Roberts (1949), Scott (1967), Tarrer and others (1974), Wilhelm and Naide (1981), and Yoshioka (1957).

4.2.3.2 Coe and Clevenger Method

The Coe and Clevenger method consists of a series of settling tests in which the initial pulp settling rate is measured at different starting pulp concentrations. The procedure is based on the following premises: (1) the settling rate is a function of solids concentration, and (2) there is a critical controlling concentration. The settling rate at this critical concentration determines the required thickener size (Coe and Clevenger, 1916). To be applicable, the pulp must settle with a visible interface.

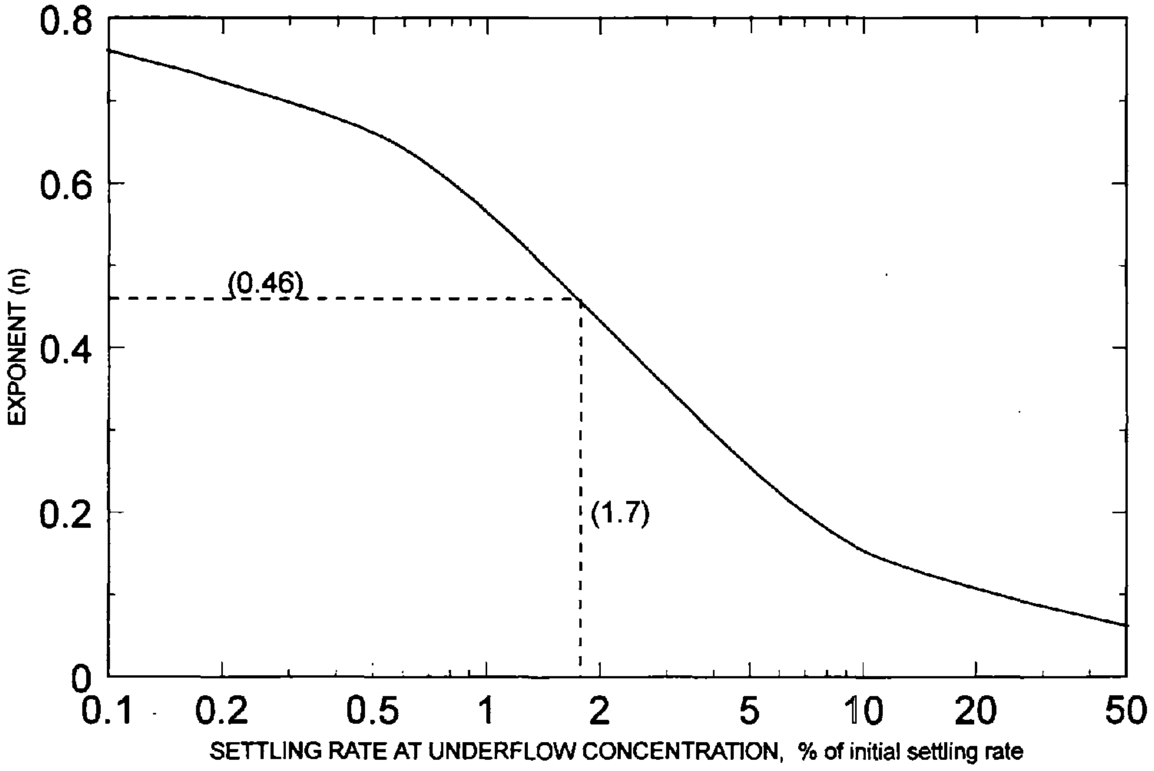
Although the Coe and Clevenger method has been widely used, it has definite limitations and in general should be used only for pulps that do not require flocculation. This limitation arises because the solids concentration of a pulp almost always influences flocculation. Also, repulping usually damages or even destroys the original flocs, and even if they reform, the flocs will exhibit different characteristics. The Kynch method described in section 4.2.3.1 should be used for hydrometallurgical pulps that have been flocculated.

Test Procedure

A convenient method for conducting a Coe and Clevenger type of settling test is as follows:

1. Determine the tare weight of a 2-L or a 1-L cylinder. (A 2-L cylinder is preferred.)
2. Fill the cylinder to the 2-L mark with the test slurry and determine the total weight of pulp plus cylinder.
3. Thoroughly mix the pulp and start the timer.
4. Record the pulp height at 2-min intervals or, alternatively, at the time the pulp interface passes through successive 20-mL intervals.
5. Continue to record the pulp height for 8 to 10 intervals.
6. Allow the pulp to settle until 200 mL of the clear supernatant solution can be withdrawn.
7. Weigh and record the weight of the remaining 1,800 mL of pulp plus cylinder.

Figure 4.5



Depth correction curve.

8. Repeat steps 3 through 6.
9. Weigh and record the weight of the remaining 1,600 mL of pulp plus cylinder.
10. Repeat steps 3 through 6.
11. Weigh and record the weight of the remaining 1,400 mL of pulp plus cylinder.
12. Repeat steps 3 through 6.
13. Weigh and record the weight of the remaining 1,200 mL of pulp plus cylinder. This completes the recommended number of incremental settling measurements on this 2-L sample.
14. Determine the final compaction density by continuing the settling for an extended period (preferably 24 h). It is preferable to use a picket rake mechanism, such as that shown in figure 4.2, during the extended settling period. If a mechanical raking mechanism is not available, periodic gentle hand stirring with a spatula or rake will be helpful.
15. At the end of the 24-h settling period, record the pulp level, decant the supernatant liquid, weigh and record the weight of the remaining pulp plus cylinder.
16. Determine the dry weight of the solids present. If the solution present in the settled slurry contains only a minimal amount of dissolved salts, wash the entire slurry into a pan and dry at approximately 100 °C. If appreciable salts are present, filter and wash the solids before drying.
17. Determine the specific gravity of the supernatant solution.

Modified Procedure

If sufficient feed pulp is available, the following modified test procedure may be desirable:

1. Split the original feed pulp sample into three fractions: one 2-L fraction, one 4-L fraction, and one 8-L fraction. Keep the 2-L sample as is. Allow the 4-L and 8-L samples to settle until enough supernatant solution can be withdrawn to bring the pulp volume to 2 L.
2. Conduct settling tests on each of the three samples as outlined in steps 1 through 17 above.

Data Reduction[2]

The following sequence of calculation can be used to correlate the Coe and Clevenger test data. The procedure

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[2] Symbols used in the following equations are those used by Coe and Clevenger (1916), and supplemented by EIMCO.

feed pulp dilution; it is repeated for each feed pulp concentration tested.

First, the solution decant volume K is determined, using the following equation:

$$K = \left[\frac{\text{total milliliters decanted}}{\text{initial sample volume}}\right] \times \text{initial sample volume.}$$

For example, if 2,000 mL has been decanted to 1,400 mL, then:

$$K = \left(\frac{2{,}000 - 1{,}400}{2{,}000}\right) \times 2{,}000 = 600 \text{ mL.}$$

Next, the pulp dilution factor F (weight ratio of liquid to solids in the specific feed pulp tested) is calculated, using the following equation:

$$F = \frac{g_L - K(\text{Sp.Gr.}_L)}{g_s},$$

where g_L = grams of liquid in 2,000 mL of original sample.

Sp.Gr._L = specific gravity of liquid,

and g_s = grams of dry solids in 2,000 mL of original sample.

Then, the unit area is calculated, using the following equation:[3]

$$A = \frac{1.333 \times (F - D)}{(R)(\text{Sp.Gr.}_L)},$$

where A = unit area, $(\text{ft}^2/\text{st})/\text{d}$,

D = weight ratio of liquid to solids at the desired underflow density,

F = weight ratio of liquid to solids for rate R (see equation for F above),

R = settling rate at dilution F, ft/h,

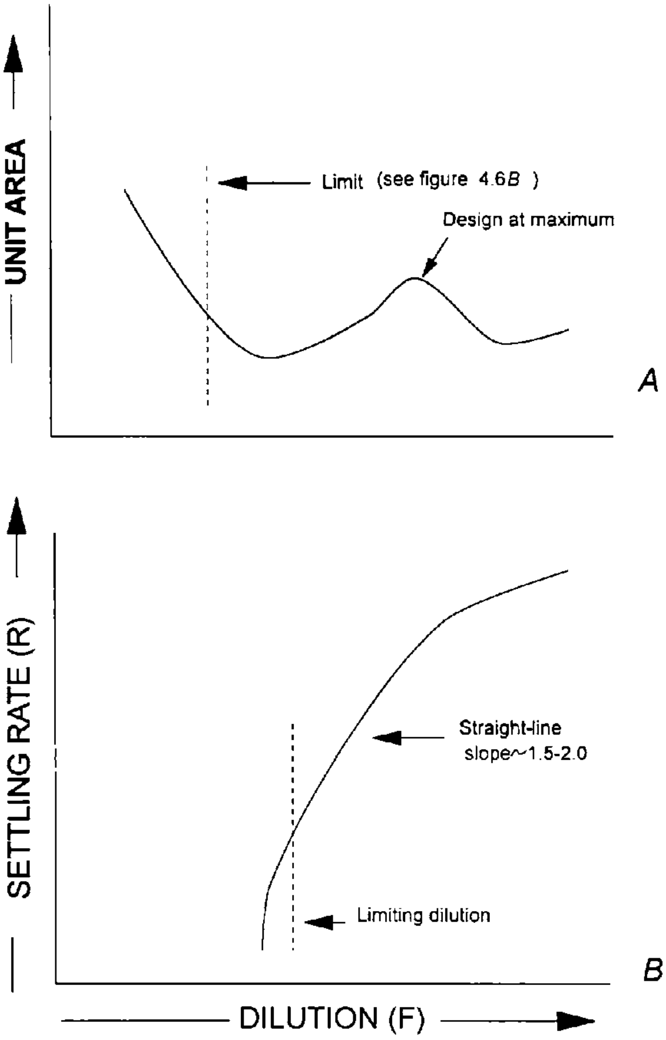
and Sp.Gr._L = specific gravity of liquid.

The required thickener size is then based on the largest unit area determined between the feed and desired underflow concentrations. Figure 4.6*A* illustrates a typical plot of the calculated unit areas versus the respective F values on plain coordinate graph paper. Also, the unit area chosen should be above the limiting dilution. This dilution represents the "thickest free-settling pulp," i.e., the pulp that is in the hindered settling (straight-line) phase but not in compression. To determine this point, R versus F is plotted on log-log paper. As shown on figure 4.6*B*, a straight line with a slope of 1.5 to 2.0 will result in the hindered settling range. The dilution (F) at which the straight line breaks indicates the pulp density below which the Coe and Clevenger evaluation should not be used.

4.2.3.3 Second-Order and Long-Tube Tests

Second-order and long-tube tests are used primarily to determine the clarification requirements for dilute pulps

Figure 4.6



Coe and Clevenger plots. A, Unit area plot; B, log-log plot showing test limitation.

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[3] Detailed information on the derivation of this equation is presented in the original reference (Coe and Clevenger, 1916).

that do not settle with a distinct interface. These requirements usually involve meeting some type of predetermined clarity specification. Clarification applies principally to water treatment applications but may also pertain to waste treatment or water recovery operations. In many, if not most, hydrometallurgical operations, thickening requirements often exceed clarification requirements. When this occurs, thickening requirements determine the necessary thickener or clarifier size.

With dispersed particulate systems that do not flocculate, the clarifier overflow rate determines product solution clarity. However, when the feed pulp contains particles that flocculate either by themselves or through the addition of flocculants, particle detention time usually becomes the controlling variable. The so-called second-order test is used to determine the clarification requirements that are controlled by detention time for pulps that *do flocculate.* The long-tube test procedure is applicable for pulps that *do not flocculate,* and the overflow rate is controlling.

Second-Order Test Procedure

The second-order test determines the concentration of solids in the overflow as a function of detention time. The test acquired its name because the rate at which particles flocculate is defined by a second-order reaction (Fiedler and Fitch, 1959). This equation, the integrated form of which is shown below, relates the number of particles flocculating and therefore settling to the number of unflocculated particles present at any given time (Oliver, 1963):

$$K(t - t_o) = \frac{1}{C} - \frac{1}{C_o},$$

where K = rate constant,

t = time,

t_o = time at start of flocculation reaction,

C = concentration of flocculable solids at time t,

and C_o = concentration of flocculable solids at time t_o.

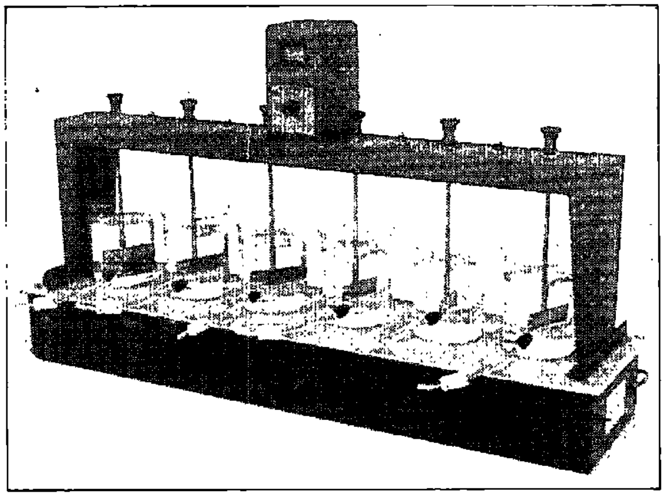
If observations indicate that either natural or induced flocculation is occurring, the following procedures may be used to determine the detention time requirements.

With Flocculating Bank

If a flocculating bank or standard "jar test apparatus," such as that manufactured by the Phipps-Bird Co., is available, the following procedure is recommended:

1. Set up the flocculating bank. The standard unit consists of the following components: (1) a six-stirrer mechanism driven by a single variable-speed motor, (2) six 1,500-mL beakers each equipped with a side-mounted sample tap, and (3) six agitators (see figure 4.7) Some models of the jar test apparatus are fitted with a flocculating disk on each agitator to simulate the action of mechanical flocculation. The flocculating disks are approximately 3.5 in. in diameter and float on the surface of the pulp as they are rotated by the stirrer mechanism.
2. Carefully mix about 7 L of the feed pulp to obtain a homogeneous suspension without seriously disrupting any existing floc structure. Take a 100-mL feed sample for determination of the solids content.
3. Quickly fill each of the beakers to the 1,000-mL level, start the stirrer mechanism (approximately 12 to 14 rpm), and note the time. Note: If additional flocculant is to be added, the following procedure is usually satisfactory: Add the diluted flocculant solution simultaneously to all six beakers with a suitably sized rack that holds six 50-mL test tubes. Agitate the pulp for about 60 s at approximately 100 rpm. Reduce the stirring speed to the 12- to 14-rpm range, and note the time.
4. Take one "overflow" sample from each beaker during the following 90 min. Suggested sampling times are 5, 10, 15, 30, 60, and 90 min. For example, to minimize the time error as much as possible, take the initial sample through the sample tap from beaker 6 at 5 min. Take the next sample from beaker 5 at 10 min, etc. Start removing each sample about 10 s before the designated sample time. Discard the first 10 to 20 mL that comes out of the sample tap and then collect a 100-mL sample in a 100-mL volumetric flask.
5. Filter the feed sample and each of the overflow samples on separate tared Gooch crucibles, dry at 100 °C,

Figure 4.7



Six-unit jar test apparatus.

and weigh on an analytical balance to the fourth decimal place. If the specific gravity of the clarified liquor is 1.0, this technique produces suspended solids measurements directly in parts per million.

Without Flocculating Bank

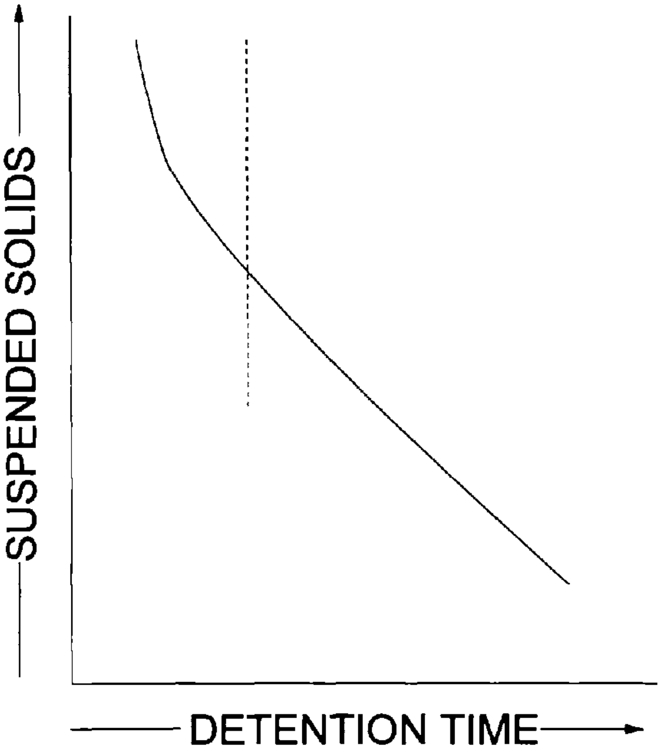
If a flocculating bank or jar test apparatus is not available, the following method may be substituted:

1. Conduct the test using one or more 2-L graduated cylinders or other transparent container with a depth of at least 12 in.
2. If one 2-L cylinder is used, carefully mix the pulp to obtain homogeneous suspension without seriously disrupting the floc structure and take a 100-mL head sample. Quickly transfer 2,000 mL of the homogeneous pulp to the cylinder. Note the time.
3. During the next 90 to 120 min, remove six 100-mL overflow samples from the cylinder at timed intervals. A typical set of sampling times is 5, 10, 15, 30, 60, and 90 min. A 100-mL pipette with the tip bent into a U-shape is a convenient device for collecting the samples. Take samples about 3 in below the liquid level that exists at each timed interval.
4. Filter the feed sample and each of the overflow samples on separate tared Gooch crucibles, dry at 100 °C, and weigh on an analytical balance to the fourth decimal place. If the specific gravity of the clarified liquor is 1.0, this technique produces suspended solids measurements directly in parts per million.

Data Reduction

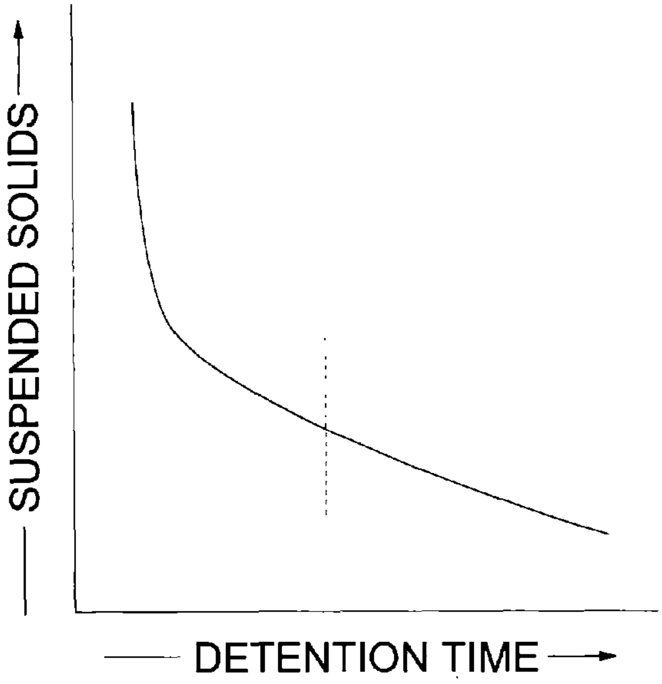
The precision of the suspended solids data obtained can be illustrated by plotting the suspended solids values in parts per million against sampling time on log-log paper as shown in figure 4.8. After about 10 to 15 min of settling, the plot should produce a straight line. A linear plot of the same values on plain coordinate paper produces a curve such as shown in figure 4.9. The "knee" in this curve indicates a point of diminishing returns. The settling time that produces the desired overflow clarity is determined from these graphs. Dividing this time by the "detention efficiency" (obtained from the manufacturer for a specific type of equipment) gives the required detention time for a commercial-scale unit. Detention efficiencies for cylindrical tanks range from about 0.25 to 0.60 and are usually a function of the diameter-to-depth ratio. Figure 4.10 illustrates approximate detention efficiencies for diameter-to-depth ratios up to about 12:1. For preliminary evaluations, a rule-of-thumb detention efficiency of 0.33 may be used.

Figure 4.8



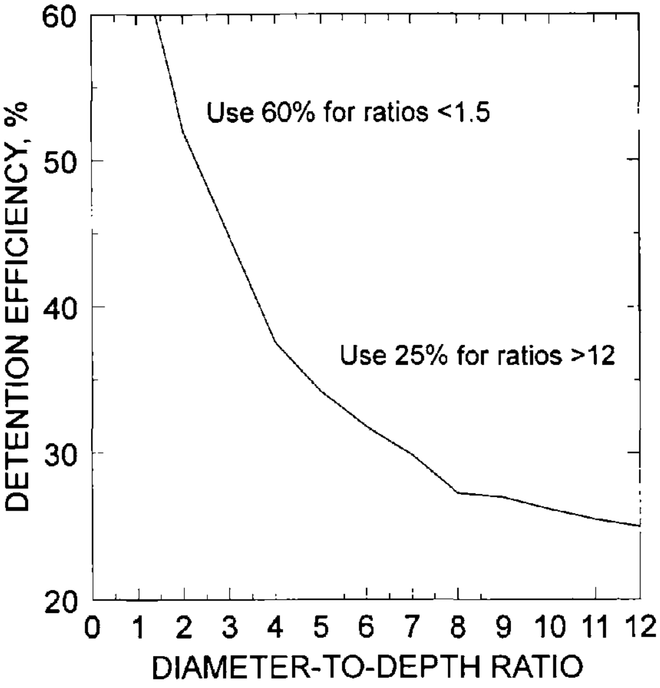
Log-log plot of suspended solids content versus detention time.

Figure 4.9



Linear plot of suspended solids content versus detention time.

Figure 4.10



Approximate detention efficiency for cylindrical tanks.

Long-Tube Test Procedure

The long-tube test is used for clarification applications where particles *do not* flocculate. When this condition exists, the overflow rates determine clarifier sizing, and clarifier detention time is not a decisive design factor. This static test simulates dynamic overflow rates by collecting a series of samples at different depths after a given settling period. Tests are conducted at each of three or more time intervals that simulate overflow rates believed applicable for the material being tested.

Standard Procedure

The standard long-tube procedure requires (1) special apparatus, (2) a relatively complicated procedure, and (3) calculation correction factors. To a significant degree, realistic interpretation of experimental results depends on the experience of the individual evaluating the test data. Therefore, contacting equipment manufacturers for their specific recommendations is recommended. Only a general description of the long-tube method is presented here.

The long-tube test uses a length of plastic, glass, or metal tubing 6 to 15 ft in length and no less than 2.5 -in. in diameter. (The EIMCO Co. literature[4] suggests that a 3-in-diameter by 8-ft-long clear plastic tube is usually appropriate). The tube is fitted with 0.25-in sample ports spaced at 1-ft intervals. The pulp sample is thoroughly mixed, and the tube is filled. Samples (100 mL) are withdrawn from each of the spaced taps after the chosen time interval. The suspended solids content of each sample is determined, and the overflow or rise rates are calculated by dividing the sampling depth by the time interval used. Typically, this value together with the tube diameter is used to calculate and express the overflow rate in terms of gallons per minute per square foot. The test is repeated at two to five additional sampling times (typical times are 15 min, 30 min, 1 h, and 2 h).

Simplified Procedure

A simplified procedure may also be used to generate relevant data for laboratory-scale hydrometallurgical evaluations. This procedure uses a smaller tube, such as a 2-L graduated cylinder. For each data point the cylinder is filled with the test pulp, and after the selected settling time, a single sample is siphoned from one measured depth, preferably at about the 1-L level. The test is repeated using from three to five different settling times corresponding to the range of overflow rates believed practical for the specific application. This relatively simple procedure produces less accurate data than the standard test, but requires no special equipment and can be performed in the field.

Data Reduction

When the suspended solids concentrations for each measurement are plotted against the calculated overflow rates, all of the data should correlate on a single curve such as that shown in figure 4.11, if the overflow rate is controlling. If the plot shows a family of curves similar to those illustrated in figure 4.12, this relationship indicates that detention time is controlling, and the second-order procedure should be used to determine the required detention time.

A scaleup factor must be applied to the overflow rate determinations. Because the factor depends on clarifier configuration, size, and inlet design, contacting manufacturers for explicit values is recommended. In general, the multiplier varies from about 0.6 to 0.9. For preliminary estimations, a rule-of-thumb factor of 0.7 may be used.

Additional information on laboratory procedures for determining detention time and overflow rate design criteria are presented in the previously cited paper by Oliver (1963).

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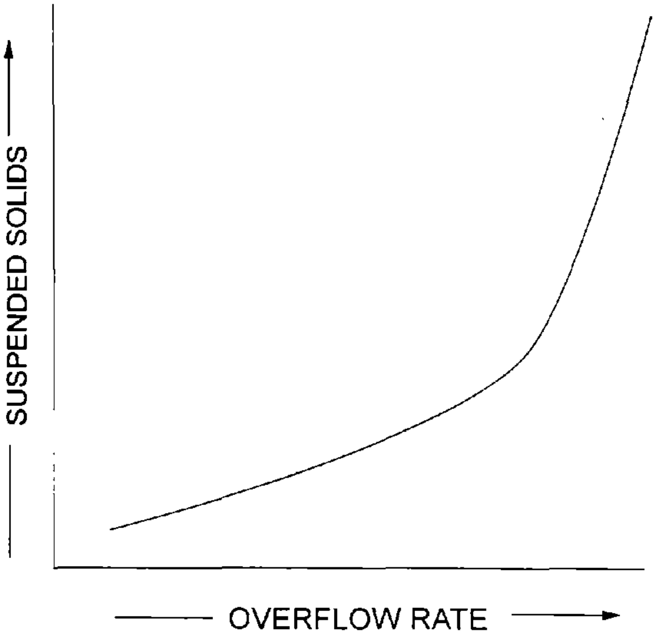
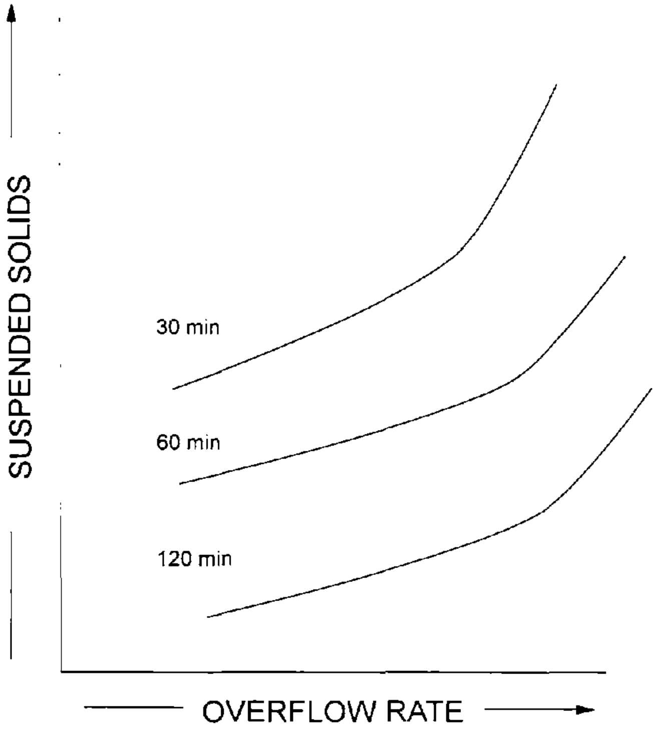
[4] EIMCO Solid-Liquid Separations Manual (undated).

Figure 4.11



Plot of long-tube data, if overflow rate is controlling.

Figure 4.12



Plot of long-tube data, if detention time is controlling.

4.2.4 High-Rate Thickeners

When high-rate thickeners were first introduced, literature references indicated that the mechanism of high-rate thickening was significantly different from that encountered in conventional thickening. There is a growing consensus, however, that the performance of high-rate thickeners relates primarily to near-ideal flocculation. The solids are flocculated with minimum shear in the flocculation zone of the thickener, where rapid contact of the flocculant with a large amount of pulp is achieved. One supporting proof of this concept is that no high-rate thickener has ever been installed to operate without the addition of flocculant. Also, there does not currently appear to be any sharp line of demarcation between what formerly had been classified as either "conventional" or "high-rate" thickening.

Manufacturers have developed special bench-scale equipment (e.g., the Enviro-Clear 3.5-in diameter laboratory unit) or other techniques for sizing their particular high-rate designs. Tests using the special equipment or procedures are best carried out with the assistance of the manufacturers because they have the specific experience that is often required to translate the laboratory data to practical design criteria.

4.3 FILTRATION TESTS

4.3.1 Introduction

In hydrometallurgical processing, the term "filtration" relates primarily to the separation of solids from liquids by use of a porous medium that retains nearly all of the solid particles contained in the feed slurry. Most of the liquid passes through the porous medium, and the moisture content of the retained cake depends predominantly on the many primary and secondary properties of the suspension being filtered. These properties also affect other functions of the filtration equipment being used. Since available theory lags behind practice, testing is required to select and size hydrometallurgical filtration equipment. Although theory cannot be used as the sole basis for sizing a filtration system, it is valuable for interpreting test data and predicting the effect of changes in operating conditions.

In general, filtration theory attempts to quantify the complex interactions of the following relationship:

Filtration rate = driving force divide by resistance,

where resistance includes that of both the filter cake and the filter medium. The following form of Poiseuille's equation can be used to represent the instantaneous filtration rate once a layer of solid particles has formed on the filtering medium:

$$\frac{dV}{A\,d\theta} = \frac{P}{\mu[\alpha(W/A) + r]},$$

where V = volume of filtrate collected,

A = area of filtering surface,

θ = time,

P = total pressure drop across cake and filter medium,

μ = viscosity of filtrate,

α = average specific cake resistance,

W = mass of accumulated dry-cake solids,

and r = resistance of filter medium and equipment restrictions.

The literature on filtration theory is extensive; the following references present information applicable to hydrometallurgical systems: Dahlstrom (1985a), Jacobs (1984), Poole and Doyle (1968), Purchas (1971, 1981), Tiller (1966), and Tiller and Lloyd (1973).

All solids-liquid separations should be treated as systems rather than isolated operations. This relationship holds particularly true for filtration separations, which can depend on a broad range of interdependent factors. Unless closely parallel experience is available, each filtration operation will nearly always require some form of bench-scale or possibly pilot-scale testing. As in nearly all hydrometallurgical operations, no rote procedure or formula exists for selecting the most suitable piece of equipment. Experience and a feel for the characteristics of the material being filtered can often be important. The following references present information and general guidelines on the selection of filtration equipment: Emmett (1988), Pierson (1981), and Tiller (1974).

4.3.2 Flocculation

Since filtration often follows a settling or thickening operation in hydrometallurgical flowsheets, the flocculation procedures discussed in section 4.2.2 also apply for filtration tests. In general, however, the flocculant dosage required to improve filtration rates usually exceeds that required for optimum settling rates. Filtration tests on a range of flocculated pulps are usually needed. To a significant degree, optimum flocculation depends upon the type of equipment that will be used for the filtration. For example, relatively small flocs may produce the best results when a rotary drum filter is used, whereas coarser flocs may produce the best results when a horizontal belt filter is used.

If additional flocculant is to be added to either a prethickened pulp or an untreated pulp, the following flocculation procedures have been recommended by flocculant manufacturers:

Procedure A

1. Place the pulp to be flocculated in a suitable container such as a large beaker or a plastic or enamelware pan.
2. Add the desired amount of diluted flocculant (concentration = 0.1% or less), and stir gently with a utensil such as a large perforated cooking spoon. Adding the flocculant in two or three increments is often the most effective procedure. Also, if possible, it is usually desirable to use clarified solution from the test pulp to prepare the diluted flocculant solution.
3. Start the filtration test immediately, or if the effect of pulp aging is being investigated, after the desired aging period.

Procedure B

1. Use two equal-sized containers (such as beakers A and B).
2. Add the desired amount of well-mixed slurry to container A.
3. Add one-third of the diluted flocculant (concentration = 0.1% or less) to container B.
4. Pour the contents of container A rapidly into container B to permit turbulent mixing of the flocculant and slurry.
5. Agitate gently and pour the contents of container B back into container A.
6. Repeat steps 3, 4, and 5 twice.
7. Start the filtration test immediately, or if the effect of pulp aging is being investigated, after the desired aging period.

Procedures A and B are usually interchangeable; but if flocculation difficulties are encountered, trying both procedures is suggested.

The references listed at the end of section 4.2.2.2 contain information and guidelines applicable to the flocculation of filtration feed slurries.

4.3.3 Filter Media

To a significant degree, the selection of a filter medium for a given separation remains an art. Unless the researcher has some experience, seeking help is prudent. This type of help can usually be obtained from filter media companies, filter fabric manufacturers, and filtration equipment manufacturers. Even with experience, testing will be required. Laboratory-scale tests can answer most questions, but not all. For example, a full-scale equipment test may be needed to identify problems related to blinding (clogging) of the filter media.

Many factors must be considered when selecting a filter fabric or medium for cake filtration. The selected medium almost always represents a compromise between the following two conflicting requirements:

1. The openings in the filter medium must be small enough to prevent passage of the solids; i.e., the medium must have the ability to bridge solids across its pores quickly.
2. The openings in the filter medium must be large enough to provide for a maximum solution flow; i.e., the fabric must exhibit the minimum resistance to flow.

Other factors that must be optimized during the process of selecting the filter media include the following:

- Minimum blinding proclivity.
- Resistance to chemical attack.
- Acceptable wear resistance.
- Dimensional stability and the strength needed to meet the mechanical requirements of the filtration equipment that will be used.
- Good cake release at the end of the filter cycle.
- Minimum cost.

Most hydrometallurgical filtrations use some type of woven fabric medium. Polypropylene is one of the most widely used fabrics. Other available fabrics include nylon, polyethylene, polyesters, and Dynel, Kynar, Orlon, Saran, and Teflon synthetics. Recently, GORE-TEX membrane filter cloths have become available. The characteristics and potential applications for these cloths, which consist of polytetrafluoroethylene membranes bonded to a variety of fabrics, have been discussed by Smith and others (1991). The filtering characteristics of woven fabrics depend primarily on the type of yarn and the weave. Fabrics are produced from monofilament, multifilament, and staple fiber yarns. Table 4.1 illustrates the relative effects of weave and yarn on filtration. Other types of filter media include metal fabrics or screens, nonwoven fabrics, and filter papers (Flood and others, 1966; Jacobs, 1984; and Talcott, 1980).

Industrial experience shows that cloth-covered continuous filters cannot produce an absolutely clear filtrate. Invariably, some of the solid particles in the feed slurry are smaller than the largest passages through the medium. Some of these particles will pass through the filter cloth. After bridging occurs, the solids themselves form a trap for these fine particles, and the filtrate becomes clearer. This bridging action makes it possible to achieve relatively clear filtrates even when using relatively open filter cloths.

Table 4.1.—Relative effects of weave and yarn on filtration

	Highest flow rate	Greatest retention	Best cake discharge	Least moisture in cake	Resistance to blinding
Weave:					
Chain	3	2	3	3	3
Plain	4	1	4	4	4
Twill	2	3	2	2	2
Satin	1	4	1	1	1
Yarn:					
Monofilament	1	3	1	1	1
Multifilament	2	2	2	2	2
Spun-staple	3	1	3	3	3

NOTE.—1 is best and 4 is poorest.
Source: Jacobs (1984).

Filter-cloth blinding by either the process solids themselves or by chemical precipitation can be a serious problem in an operating plant. In recent years the introduction of filters with media in the form of an endless belt has significantly reduced the potential for serious blinding problems. In these filters both sides of the filter media can be cleaned because the filter media belt separates from the vacuum source at some point in the filter cycle.

4.3.4 Vacuum Filtration

4.3.4.1 Introduction

Continuous vacuum filtration has become the most widely used filtration separation in hydrometallurgical flowsheets. Bench-scale filtration testing procedures are designed to determine the following three rate functions:

1. Cake formation rate.
2. Cake dewatering rate.
3. Cake washing rate.

All applications require the first two determinations, and if the cake must be washed to achieve either product purity or high solution recovery, the third rate function must also be assessed. The filtration test procedure determines each rate separately; the results are then combined to establish a filter cycle with the desired results. Usually one of the rates is controlling.

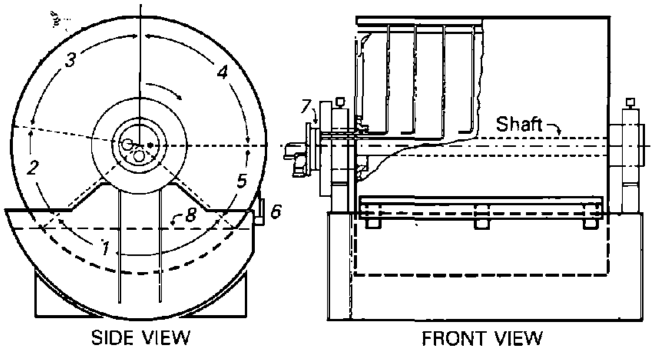
The three types of continuous vacuum filters most commonly used in hydrometallurgical and waste treatment flowsheets are (1) the drum filter, (2) the disk filter, and (3) top-feed filters such as belt and table filters. Specific mechanical descriptions and operating characteristics are presented in the following references: Dahlstrom (1985a), Emmett (1988), Flood and others (1966), Jacobs (1984), and Mead (1964). Briefly, these three filter types and their cycle characteristics can be described as follows:

Drum filters—The primary component of a rotary drum-type filter is a cylinder whose periphery forms the filtering surface (figure 4.13). The cylinder, which rests on bearings, is partially submerged (25% to 45%) in the filter tank. The drum surface is divided into sections parallel to the drum axis. Each section is separately connected to an automatic control valve that regulates the period under vacuum and other components of the filter cycle. The earliest versions of the drum filter used a scraper discharge. Variations of this filter include other discharge mechanisms such as continuous belt units, roller discharge arrangements, and string discharge filters.

Disk filters—The filtering surface of a rotary disk filter consists of a number of vertical disks mounted on a hollow, rotating horizontal shaft (figure 4.14). This trunnion conducts the filtrate to the automatic valve. Each disk is an assembly of from 8 to 30 pie-shaped sectors, depending on the disk diameter. The usual filter medium consists of a sewn bag that fits over each pie-shaped sector. The disks rotate in the slurry tank with a submergence of about 33%. A gentle blowback is normally applied to inflate the filter bags; this discharges the cake. Scrapers are also used. Disk filters are primarily dewatering devices and do not have washing capabilities.

Horizontal belt filters—A horizontal belt filter consists of an endless reinforced rubber belt with a filter medium riding on top. The belt and filter medium are driven and guided by head and tail pulleys (figure 4.15). Slurry is fed onto the moving belt, which passes over a series of stationary vacuum boxes, each of which has a long slit on the belt center line. The belt, which is grooved perpendicular to the direction of travel, connects to the vacuum boxes through drainage holes arranged in the center of the belt. The slit in the center of each vacuum box in effect becomes the valve between the vacuum source and the moving filter medium. As the filter cake passes over the series of vacuum boxes, it is dewatered, washed, and again dewatered prior to discharge, which occurs when the filter medium separates from the rubber belt and passes around the cake discharge pulley. Countercurrent cake washing is possible. After cake discharge, the filter medium can be effectively washed on both sides; this significantly reduces the potential for blinding.

Figure 4.13



Drum filter: (1) cake-forming zone, (2) drying zone between form and wash, (3) wash zone, (4) drying zone, (5) vacuum-break and blowback zone, (6) discharge scraper, (7) automatic control valve, and (8) slurry level.

Filter cycles—Table 4.2 lists typical cycle percentages for various types of vacuum filters. The cycle percentages do vary somewhat from manufacturer to manufacturer, but

Table 4.2.—Typical cycle percentages for various vacuum filters

Filter type	Submergence[1]		Maximum arc for washing[3]	Total available[2]	Required for cake
	Apparent	Effective (maximum)			
Disk	35	28	0	75	25
Drum:					
Belt	35	30	29	75	25
Coil	35	30	29	75	25
Precoat	35, 55, 85	35, 55, 85	5-30	95	5
Roll discharge	35	30	29	80	20
Standard scraper	35	30	29	80	20
String	35	30	29	75	25
Horizontal belt	AR	AR	AR	(4)	0
Horizontal table	AR	AR	AR	80	20
Tilting	AR	AR	AR	75	25

AR As required.

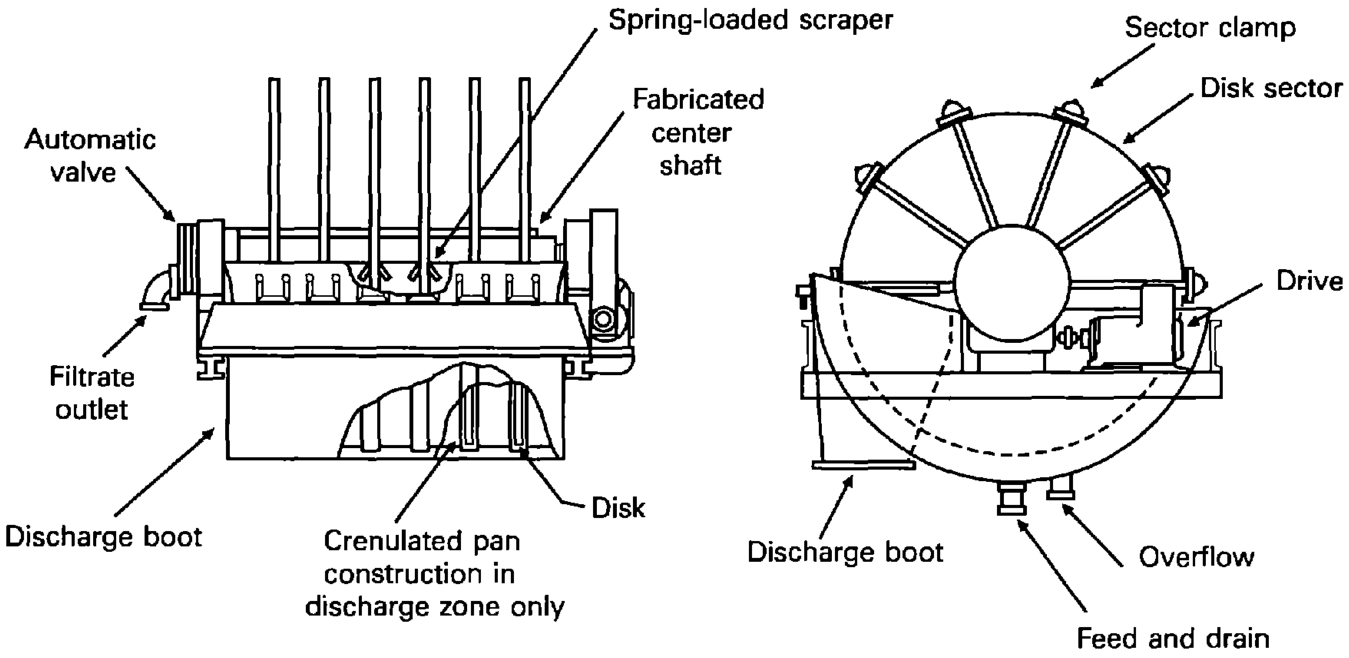
[1] Values for bottom-feed filters assume no trunnion stuffing boxes, except for precoat. Consult manufacturers for availability of higher submerges.

[2] Total available for effective submergence, cake washing, drying, etc., except for cake formation and discharge.

[3] Maximum washing on a drum filter starts at horizontal center line on rising side and extends to 15° past top dead center.

[4] Lengthen as required.

Figure 4.14



Disk filter.

the values listed are applicable for nearly all process development investigations. Requirements for each portion of the cycle are developed separately, and the results are then combined to define the overall filter cycle design.

4.3.4.2 Filter Selection and Sizing Considerations

A number of general factors must be considered when selecting and sizing vacuum filters. These include the feed slurry temperature, cake formation rates, cake thickness control, and cake discharge characteristics.

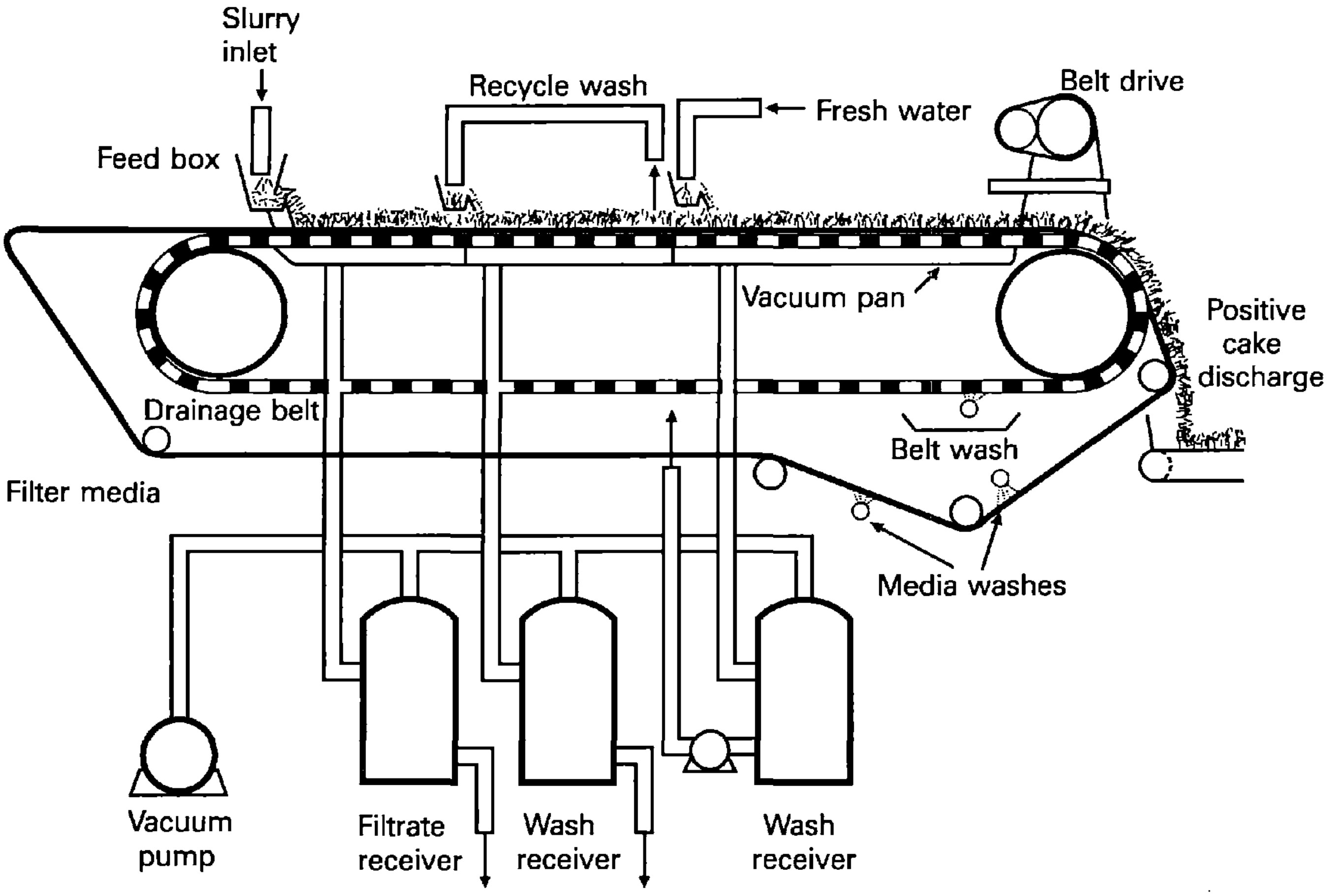
Temperature—The feed slurry temperature can have both positive and negative effects. Increased temperatures decrease the viscosity of the liquid phase; this effect increases the filtration rate and decreases the cake moisture content. Several negative effects occur when elevated temperatures increase the liquid-phase vapor pressure to the point where the liquid starts to flash (instantaneously evaporate) within the filter internals. This flashing disrupts the cake formation adjacent to the filter medium and also promotes scaling of the filter internals. If the liquid phase contains any significant amount of dissolved solids, the pressure drop across the filter drainage passages can increase sharply because of scaling. The temperature-vacuum relationship must be controlled so that the liquid phase does not boil. In most operations this means that the operating vacuum must be held at least several inches of mercury below the boiling point of the liquid phase.

Cake formation rates—The rate at which cake formation takes place influences both the type of vacuum filter chosen and the operational variables. For example, if the cake formation rate is quite rapid, control of the cake thickness may be necessary to meet subsequent operational requirements. When bottom-feed filters are used, this can be achieved by reducing either the form time or the vacuum level. If the filterability of the slurry is so great that these measures prove inadequate, some form of top-loading filter will probably be required.

Cake thickness control—Cake washing and final moisture requirements usually determine the optimum cake thickness. If the cake washing time is controlling, the maximum washing rate will usually occur when the minimum cake thickness is used consistent with good cake discharge. When a minimum cake moisture content is the primary requirement, the minimum thickness required for good cake discharge may still be controlling, but obtaining the desired moisture content with somewhat thicker cakes may also be possible.

Cake Discharge Characteristics - Effective cake discharge is a critical component of every successful filtration operation. Matching cake discharge characteristics with process requirements and mechanical discharge systems is a crucial part of the filtration selection process. Each type of discharge system has its own distinctive minimum discharge thickness; table 4.3 lists these minimum cake thicknesses. This table is applicable for many hydrometallurgical pulps. If the cake is made up primarily of high-specific-gravity solids, the minimum thickness may be somewhat lower. Low-specific-gravity solids may require a thicker cake.

Figure 4.15



Horizontal belt filter.

Table 4.3.—Minimum cake thickness for discharge

Filter type	*Cake thickness, in*
Disk	3/8 - 1/2
Drum:	
Belt	1/8 - 3/16
Coil	1/8 - 3/16
Precoat[1]	0 - 1/8
Roll discharge	1/32
Standard scraper	1/4
String discharge	1/4
Horizontal belt	1/8 - 3/16
Horizontal table	3/4
Tilting pan	3/4 - 1

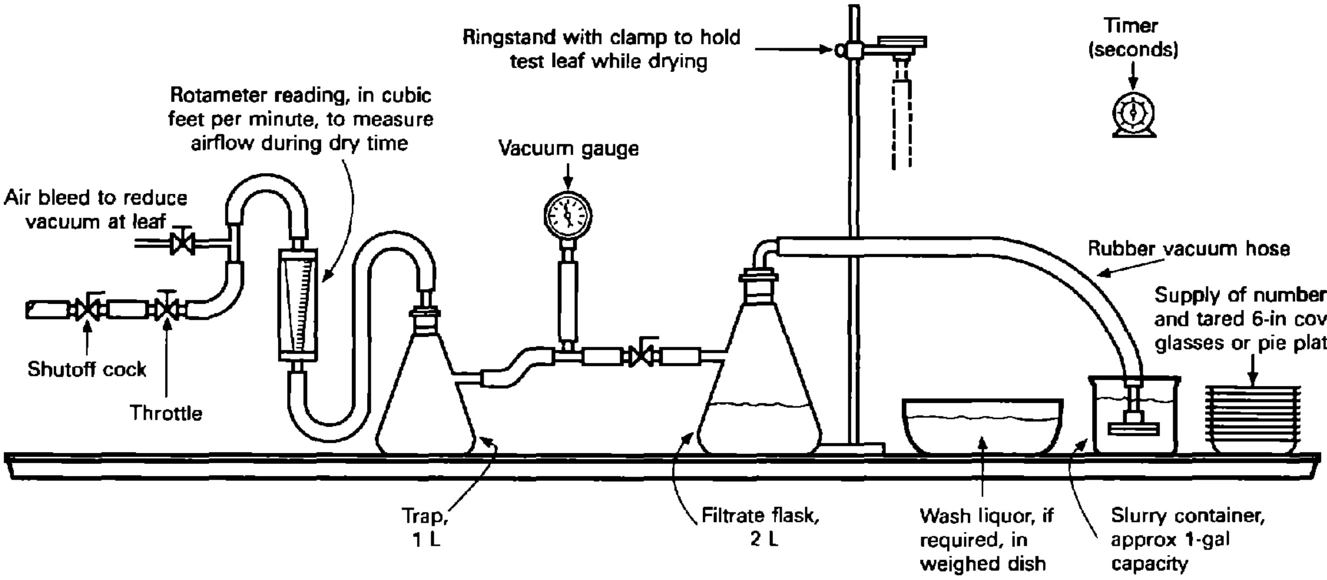
[1] Maximum thickness.

4.3.4.3 Leaf Test Equipment

Figure 4.16 illustrates the general layout and components of a bench-scale, filter leaf test setup for bottom-feed filtration tests. There is no valve between the test leaf in the slurry container and the filtrate flask. If a valve is installed, it should be a ball valve with an opening at least equivalent to the inside diameter of the vacuum hose connecting the filter leaf to the filter flask. If the line to the filtrate flask contains any restriction, this restriction, rather than the cake resistance, may control the rate at which the cake is forming. Also, if the filtrate line runs full bore into the filter flask during the cake formation period, a hydraulic restriction probably exists, and a larger diameter tubing system should be used.

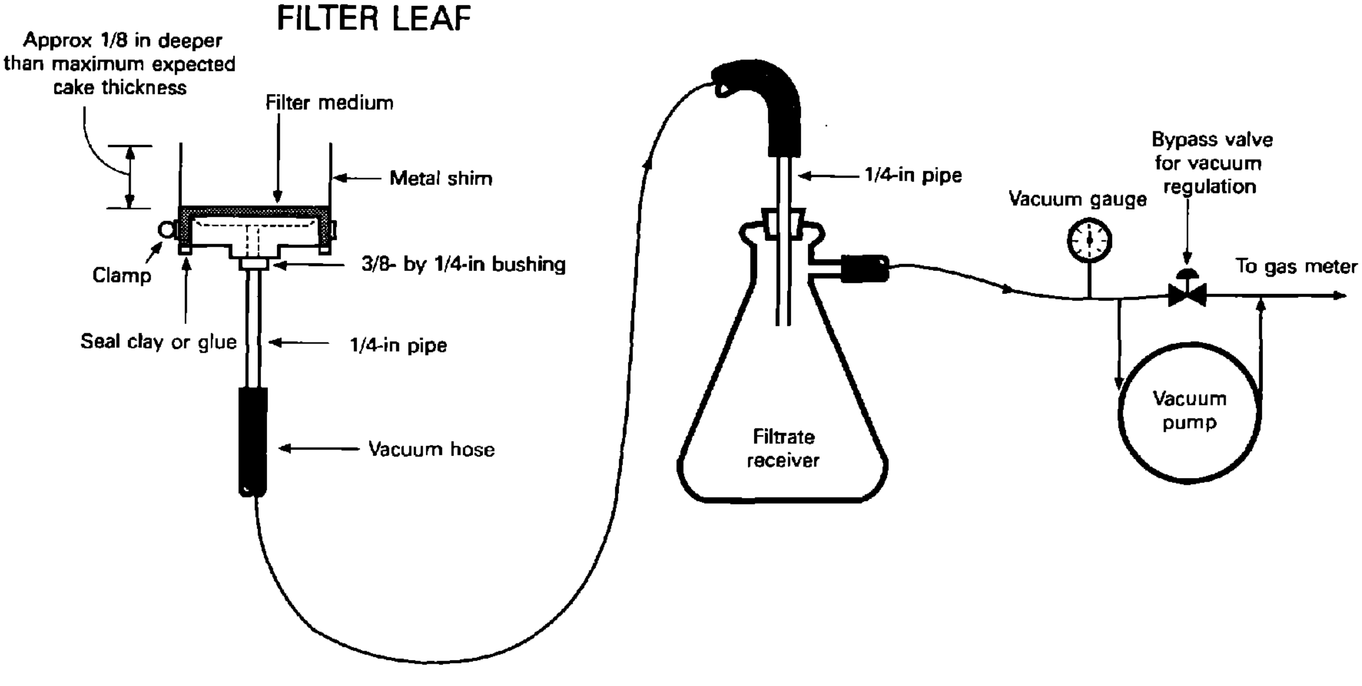
Most filter manufacturers recommend using a 0.1-ft^2 filter leaf, which is a circular disk approximately 4.3 in. in diameter. The face of the disk is grooved to provide ample drainage passages and also to support the filter medium. Figure 4.17 illustrates a test leaf fitted with a filter medium and a cake containment shim or dam. This assembly is clamped together, and the back of the leaf assembly is sealed with material such as modeling clay. The sealer ensures that the filtrate volume collected accurately represents the liquor associated with the deposited cake solids. For bottom-feed filter tests in which no washing is used, the shim height should be no greater than the maximum cake thickness. If washing is to be used, the shim height

Figure 4.16



Typical setup for bench-scale, bottom-feed vacuum filtration tests.

Figure 4.17



Filter leaf, 0.1 ft^2 equipped with containment shim.

should be approximately 1/8 in greater than the maximum expected cake thickness.

If a shim is not used, the cake usually mushrooms over the edge of the test leaf. This excess must be trimmed, weighed, and dried so that the filtrate associated with this portion of the cake can be calculated and subtracted from the collected filtrate volume. Some filter manufacturers use the shim technique and others the trimming procedures. With experience, apparently both can produce equivalent results. If enough slurry is available, the researcher may wish to try both procedures and compare results.

Test leaves with areas less than 0.1 ft^2 can be used when only limited quantities of pulp are available, but the results should be used with caution. For some slurries, the smaller test leaves may indicate appreciably higher filtration rates than can be obtained in practice. If a small leaf must be used to investigate a suite of variables, at least several tests with a standard 0.1-ft^2 leaf at the indicated optimum condition are highly desirable.

4.3.4.4 Leaf Test Procedures

In most hydrometallurgical and waste treatment studies, comprehensive filtration tests are usually not conducted until after process variables such as leaching time and temperature have been optimized. Flocculation or other prefiltration treatments are most often conducted on these optimized pulps. Several general considerations apply for all types of pulps. These include the following:

Representative samples—Filtration test results become truly meaningful only when the feed sample reasonably represents the type of pulp that will be produced in the full-scale plant operations. For example, variables such as pulp aging and temperature can significantly affect filtration test results. If filtration testing cannot be conducted immediately, some type of characterization test should be conducted on the fresh sample and then duplicated just before the test program. This characterization might take the form of a sedimentation test or Buchner filtration. If the variation is appreciable, test results on the aged sample could be misleading, and working with a fresh pulp will be necessary. This situation particularly applies when slurry samples are taken at a plant location and then shipped to a laboratory for testing.

Slurry and cake homogeneity—Optimum filter performance nearly always requires the formation of a homogeneous cake. Therefore, for accurate bottom-feed filtration test work, the slurry from which the cake forms must be a homogeneous suspension. In general, if the solids can be maintained in suspension by hand agitation, the slurry will be amenable to bottom-feed filtration. Thin rubber gloves should be worn when hand-agitating a slurry. Agitation with a stirrer-type agitator is seldom satisfactory. Either the pulp settles out in the corners, or the pulp velocity becomes high enough to partially scour cake from the leaf. Agitation with a wide spatula is sometimes acceptable. Some manufacturers, however, recommend that spatula agitation be used only after comparative tests show that the spatula agitation produces results equivalent to those obtained by hand agitation.

For top-feed filters, the feed slurry must either be homogeneous or have a settling rate that is very slow relative to the cake formation rate. For both top-feed and bottom-feed filtration, obtaining a homogeneous slurry may require flocculation or some other form of prefiltration treatment.

Slurry homogeneity can usually be checked by back-calculating the slurry concentration based on the wet filter cake weight, the dry filter cake weight, and the filtrate weight. If the difference between the actual and back-calculated slurry concentrations is more than 5%, the projected filtration requirements are probably questionable. The normal variation is about 2%.

Planning and developing a test program—Unless specific related experience exists for the type of slurry to be filtered, a relevant characterization of the feed slurry together with one or more exploratory filtration tests is almost always required before an applicable test program can be developed. Slurry characterization data include items such as percent solids, slurry specific gravity, pH, temperature, solids identification, particle size, particle specific gravity, liquor identification, and liquor specific gravity. The test conditions shown in table 4.4 are often applicable for the exploratory tests.

Table 4.4.—Test conditions for exploratory filtration tests

Test conditions	Disk filter	Drum filter	Horizontal belt filter
Filter medium, Frazier permeability[1]	10-50	10-50	100
Vacuum, in Hg	20	20	10-15
Form time,[2] s	30	30	20
Wash time, number of displacements	NAp	1.5	1.5
Dry time, s	30	20	20

NAp Not applicable.

[1] Frazier permeability rating identifies tightness of a filter cloth; it correlates with percentage of open area of the cloth (Talcott, 1980).

[2] Form time must produce a cake thickness that will reliably discharge.

The results from the exploratory test or tests are used to develop the subsequent test program. Even with the exploratory results, it is not unusual to find that the test program must be modified during the investigation.

Below are five techniques for conducting bottom-feed leaf filter tests. Procedures A and B outline techniques recommended by the EIMCO Co.[5] Procedures C, D, and E list the steps recommended by Dorr-Oliver Inc., Milford, CT.[6] The sequence of steps in each procedure represents one cycle, i.e., one revolution of the filter surface.

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[5] EIMCO Solid-Liquid Separations Manual (undated).

[6] Adapted from Dorr-Oliver bulletin (1988).

Procedure A, Bottom-Feed Leaf Tests (EIMCO Co.)

1. Fit the test leaf with a filter cloth expected to give reasonable results and seal the back of the leaf and side of the shim with modeling clay or other suitable material.
2. Hand-crimp the hose in back of the test leaf, and then turn on the vacuum pump and regulate the bypass on the pump to give the desired vacuum level in the receiver.
3. Agitate the slurry by hand or with a wide spatula to maintain a homogeneous suspension. Immerse the test leaf to approximately one-half the depth of the slurry.
4. Simultaneously start the timer and release the crimped hose to begin cake formation. Maintain agitation during cake formation and move the leaf as may be required to ensure that solids do not settle out in any part of the container. It is not necessary to try to simulate the velocity of the full-scale unit's filtration surface through the slurry in the filter tank.
5. Remove the leaf from the slurry at the end of the cake formation period and note the time. If the slurry is particularly thick and viscous, shake the leaf gently to remove excess slurry and prevent the shim from scooping up extra slurry. Maintain the leaf in an upright position (cake surface on top) and elevated so that liquor within the drainage passages may pass to the receiver. Continue this drying period until—

   - The preselected time has elapsed,
   - The cake cracks, or
   - It is time for the next operation.

6. If the cake is to be washed, pour on a measured quantity of wash fluid and note the time required for free water to disappear from the surface of the cake. Washing must begin before cake cracking occurs.
7. Continue with the various operations in the predetermined sequence.
8. During each of the operations, record all pertinent information such as vacuum level, temperature, time required for the cake to crack, filtrate foaming characteristics, and airflow rate during the drying periods, on a form such as that shown in figure 4.18.
9. At the end of the run, measure and record the filtrate volume (and weight, if appropriate), cake thickness, final cake temperature if appropriate, wet cake weight, and the cake discharge characteristics.
10. For runs involving cake dewatering or drying only, dry the total cake sample either in an oven or under infrared lamps. A portion of the cake may be used for moisture determination, but care must be taken to ensure that a representative sample is used.
11. When postfiltration cake washing is needed to determine washing efficiencies or other factors, repulp the wet-weighed cake with a known quantity of distilled water. Filter the resultant slurry using a clean, dry Buchner funnel and flask. Analyze a sample of the clear liquid for the constituent or constituents being traced. Should the mother liquor contain a significant quantity of dissolved solids, thoroughly wash the filter cake after the samples for solution analysis have been taken so that the final dry weight of the cake will represent suspended solids only. The quantity of trace constituent in the final washed cake can be readily calculated from the wet and dry cake weights and the amount of distilled water used for repulping. In cake washing tests, it is important that the feed-slurry liquor be analyzed for total dissolved solids and density as well as the trace constituent, unless the total dissolved solids content is negligible.

Procedure B, Top-Feed Leaf Tests (EIMCO Co.)

The procedure for conducting a top-feed filtration test, such as that used to size a horizontal belt filter, is essentially the same as the technique used for bottom-feed tests. If the test program requires a considerable number of tests, it is usually desirable to modify the test setup. The test leaf is mounted directly on top of the filtrate flask as shown in figure 4.19. Vacuum is applied to the filter leaf, and a measured amount of the feed slurry is transferred from the slurry pour on beaker onto the leaf. The range of the feed slurry additions is primarily a trial-and-error determination. Typically the volume of feed slurry added would be the amount needed to form cakes ranging from about 0.25 to 0.50 in. Although not shown in the figure, it is often convenient to install a ball valve between the leaf and the filtrate flask; this arrangement permits quick application and termination of the vacuum to the test leaf. The bore of the ball valve should be at least equivalent to that of the drainage pipe connected to the leaf.

When planning top-feed leaf tests, it is desirable to contact equipment manufacturers to discuss the advantages and limitations of horizontal belt filters and to obtain recommendations for the range of variables that should be investigated.

Procedure C, Bottom-Feed Filtration Without Wash (Dorr-Oliver)

1. Stir the slurry with a spoon or spatula to obtain a uniform suspension of the solids.
2. Turn on the vacuum source and adjust the test vacuum while pinching off the hose at the test leaf.
3. Submerge the leaf in the slurry, open the hose, and simultaneously start the timer. Stir the slurry as needed during form time.
4. At the end of the planned form time, rotate the leaf up and out of the slurry. This simulates the rotation of the leaf or sections of a production filter. During the dry time, slowly rotate the leaf, tilting it from its horizontal plane to help drain the leaf. Dry for the planned time.

Figure 4.18

Company ....
Address ....
....

VACUUM FILTRATION TEST DATA SHEET

TABLE NO. ....
Date Tested ....
By ....
Location..

MATERIAL TO BE FILTERED

.... % Suspended Solids, Consisting of ....

.... % Liquid, Consisting of ....

Slurry Temperature.......................°C/°F

Slurry pH ....

Specific Gravity of Liquid ....

% Dissolved Solids in Liquid ....

Filter Area..................Sq. Ft.

Filter Cloth ....

Slurry Feeding Technique: Bottom feed ☐
Top Feed ☐

Air Flow Meter: Gas Meter ☐
Rotameter ☐

Avg. Filtrate Suspended Solids,................Mg/L

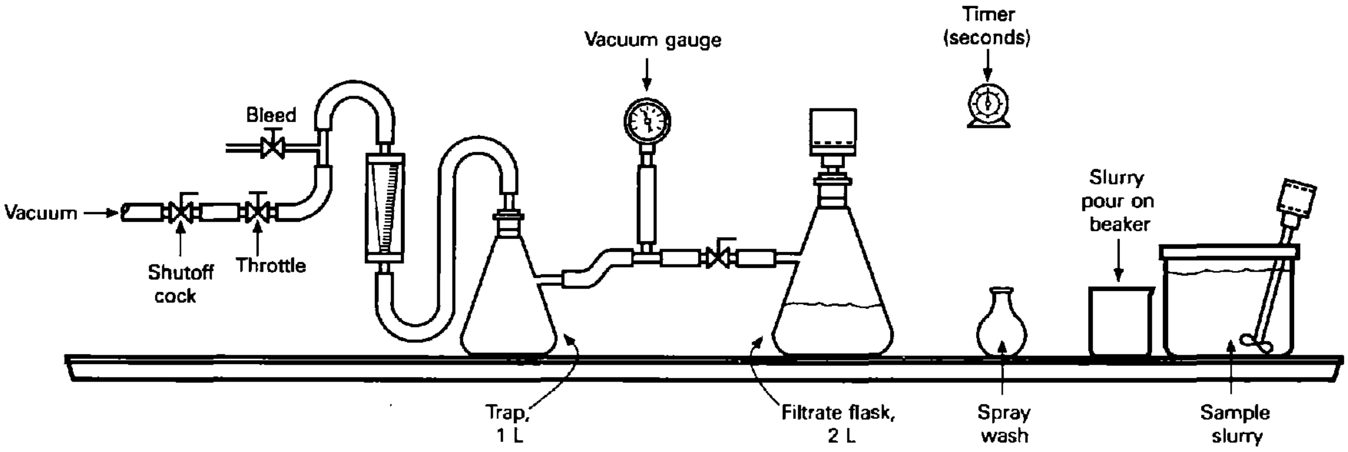
TEST NO.	FILTERING VAC. IN.HG.			FILTERING TIME-MINUTES				AIR METER READING	FILTRATE VOLUME, mL.	WASH VOLUME, mL.	CAKE THICKNESS, INCHES	CAKE WEIGHT GRAMS		CAKE MOISTURE, %	AIR FLOW CFM/SQ.FT.	DRY WT. X 100 / WET WT. + FILTRATE WT.	W. DRY LBS. PER SQ. FT.				
	FROM	WASH	DRY	PRE-WASH DRY	WASH	DRY	CAKE CRACKS					WET	DRY								
1																					
2																					
3																					
4																					
5																					
6																					
7																					
8																					
9																					
10																					

REMARKS: ____

____

EIMCO Co. vacuum filtration test data sheet.

Figure 4.19



Typical setup for bench-scale, top-feed vacuum filtration tests.

Record the vacuum during drying, the airflow rate, the time of any cake cracking, and other observations on a form such as that shown in figure 4.20.

5. Release the vacuum on the filtrate receiver, elevate the leaf, and gently shake the test leaf and hose to release any trapped filtrate. If necessary to facilitate the draining, lift a portion of the cake off the cloth.

6. If the cake has mushroomed over the edge of the leaf, trim off this material, weigh it, and record the weight. This weight together with the dry weight of the trim will be used to calculate a correction for the trim material and the filtrate volume proportional to the amount of cake trim.

7. Transfer the cake from the 0.1-ft^2 leaf to a tared dish. Again allow the leaf to drain any residual filtrate into the collection flask. Gently blow into the hose adapter to remove the cake. Remove any adhering portions with a spatula. Record all observations related to cake discharge, such as the cake nature, any abnormality, cake release from the cloth, and the condition of the cloth.

8. Measure and record cake thickness and any observations or variations such as cake cracking.

9. Weigh the dish and contents. Record the gross wet weight. Place the dish and its contents in an oven and dry overnight at 105 °C or at a lower temperature if necessary. Record the gross dry weight.

10. Measure and record the filtrate volume. If the cake had a mushroom shape that required trimming, the same proportion of filtrate must also be deducted. Comment on the quality of the filtrate, testing for solids content when pertinent. Measure and record the specific gravity and pH of the filtrate.

Procedure D, Bottom-Feed Filtration With Wash (Dorr-Oliver)

1. Cake washing applies primarily to tests for drum filtration because disk filters have only a very limited capability for cake washing. Dip the formed cake into a weighed dish of the wash liquid for a specified time. Subtract the weight of the wash liquid remaining in the dish to determine the wash volume used.

2. Conduct the test series for a series of different wash times on a number of different cake thicknesses.

3. Avoid cake cracking, which almost always produces misleading wash results, by shortening the air time immediately following submergence to less than 10% of the cycle. (In commercial practice this could be accomplished by positioning a spray wash close to the point where the cake emerges from submergence. The spray position and the wash volume are adjusted to keep the cake wet without allowing wash water runoff into the filter tub).

4. As an alternative washing technique, fit the filter leaf with a shim or collar that extends above the top of the cake and then spray the wash solution onto the cake surface. Add the wash solution at a rate that avoids flooding of the cake surface.

Procedure E, Top-Feed Tests With Wash (Dorr-Oliver)

1. Set up a bench-scale filtration system similar to that shown in figure 4.19.

2. In addition to the other preparations required for the bottom-feed filtration tests, measure out batches of slurry that will produce an appropriate range of different

Figure 4.20

VACUUM FILTRATION TEST DATA WORK SHEET

VACUUM FILTRATION TEST DATA	TEST LOCATION	TYPE FILTER	TEST LEAF SIZE	TEST DATE	WORK SHEET SECTION
COMPANY (NAME & ADDRESS)	MATERIAL		pH SPECIFIC GRAVITY SLURRY	LIQUID SOLIDS	
	SLURRY LIQUID	SOLIDS	VALUABLE PRODUCT		
	PARTICLE SIZE OR SCREEN ANALYSIS			TESTED BY	

		FEED			VACUUM (IN.Hg.)			TIME (sec.)						FIL-TRATE	WASH		CAKE				RESULTS			COMMENTS			CAKE WEIGHTS		
		% SOLIDS																											
TEST NO.	FILTER CLOTH	FEED BASIS	PRODUCT BASIS	TEMP °	FORM	WASH	DRY	FORM	AIR	WASH	DRY	CYCLE	CAKE CRACKS (sec.)	VOLUME (c.c.)	VOLUME (c.c.)		THICKNESS (IN.)	WET WEIGHT (GM.)	DRY WEIGHT (GM.)	% MOISTURE	DRY SOLIDS LB/SQ.FT./HR.	FILTRATE GAL./SQ.FT./HR.	AVG. CFM/SQ.FT. AT DRY VAC.	CAKE NATURE, DISCHARGE, FILTRATE, SOLIDS, ANALYSES, ETC.	ROTAMETER NO. READINGS	INSTANTANEOUS CFM	WET TOTAL (GM.)	TARE (GM.)	DRY TOTAL (GM.)

Dorr-Oliver worksheet for vacuum filtration test data.

cake thicknesses. Each test will require a separate representative batch of slurry.

3. Turn the vacuum on in the system up to the shutoff cock nearest the leaf.

4. Mix a batch of slurry and quickly transfer it into the boot that has been fitted on top of the filter leaf. Immediately open the vacuum to the leaf and start the timer. Note the time it takes for the liquid to disappear from the surface of the cake. This is the form time.

5. Start the wash application shortly after the form time and before any cracking starts. Apply a measured quantity of wash water from a rubber bulb or a soft plastic bottle fitted with a spray nozzle. Spray the wash onto the whole cake surface as quickly as it is absorbed. The wash time ends as soon as the liquid disappears from the surface of the cake. Determine the exact wash liquor volume by weighing the bulb or bottle before and after the wash. The wash test series should include a test with no washing to establish the baseline condition.

6. Dry for the planned time. On any horizontal filter, a 20-s dry time is reasonable for the first test. Note the time of any cake cracking and the time versus airflow at intervals. At the end of the dry time, turn off the vacuum, note the time, and quickly release the vacuum in the flask by removing the vacuum hose. Drain the test leaf by slowly tilting.

7. Measure the cake thickness, transfer the cake to a tared and numbered dish, and weigh and record the wet weight. Note and record any non-uniformity of the cake, e.g., segregated coarse solids or fines on the surface. Dry the cake in an oven, and weigh and record the dry weight.

8. Measure and record the filtrate volume. Describe the filtrate quality in terms such as "clear," "turbid," or "dirty." Determine the filtrate solids if necessary.

4.3.4.5 Data Reduction

The correlations used in the following data reduction examples are derived primarily from applied considerations that have been discussed by Dahlstrom (1978) and Silverblatt and others (1974). Correlations are presented for dry cake weight versus thickness, filtration rate, cake moisture, cake wash efficiency, cake wash time, air rate, and cycle time. The filter sizing examples show calculations for (1) disk filter—dewatering only, (2) belt-type drum filter—with cake washing, and (3) horizontal belt filter. The basic filtration data and the calculation steps have been adapted from information presented in an EIMCO Co. manual that is out of print.[7]

The data used for the filter sizing calculations are derived from the leaf test results. As mentioned previously, each filtration test represents one complete cycle or revolution of the disk, drum, or horizontal belt filter.

Data Correlations[8]

The initial step in the data reduction and filter sizing process is to correlate the test data as follows:

Dry cake weight versus thickness—For the particular type of filtration equipment being considered, the dry cake weight is converted to weight of dry cake per square foot per revolution and these values are plotted as a function of cake thickness (figure 4.21). These data usually plot as a straight line passing through the origin. If variations occur, they are usually due to inaccurate cake thickness measurements.

Filtration rate—The form filtration rate for each set of constant condition data is plotted versus form time on log-log paper (figure 4.22). The form filtration rate (i.e., based on cake formation time only) is used because the total cycle time is not known at this point. The rates are derived from leaf test results; they are calculated based on the dry weight of the cake collected during each form time tested and the cross-sectional area of the test leaf. Typically, the rate is expressed as pounds of dry solids collected per hour per square foot of leaf area. These plots should produce straight lines with a slope of minus 0.5 or steeper (normal range: minus 0.5 to minus 0.65). If the slope is flatter than minus 0.5, some significant resistance other than that of the cake solids exists. The most probable cause is a hydraulic resistance in the bench-scale test system or an exceptionally tight filter cloth.

Lines of constant cake thickness should also be included. These lines are formed by locating the times required to form the 1/4-in and 1/2-in cakes and then completing the lines graphically (these lines have a slope of minus 1).

If flocculation is used, a series of leaf tests should be conducted to determine if filterability decreases with time. This decrease is important because in practice there is a definite time lag before slurry fed to the drum filter tank reaches the filter medium surface. The aging data can be used to adjust the filtration rates to some constant lag time consistent with the anticipated full-scale operation. Experience indicates that allowing a lag time of 8 to 10 min before starting the first leaf test on a flocculated pulp is prudent practice when conducting drum or disk filter tests.

Cake moisture—The following factor has proved applicable for correlating cake moisture content data for a wide variety of materials:

$$\text{Correlating factor} = \left[\frac{\text{cfm}}{\text{ft}^2}\right]\left[\frac{\Delta P}{W}\right]\left[\frac{\theta_d}{\mu}\right],$$

---

[7] EIMCO Solid-Liquid Separations Manual (undated).

[8] Symbols used in the following equations are those used by EIMCO.

where cfm/ft^2 = air rate through filter cake,

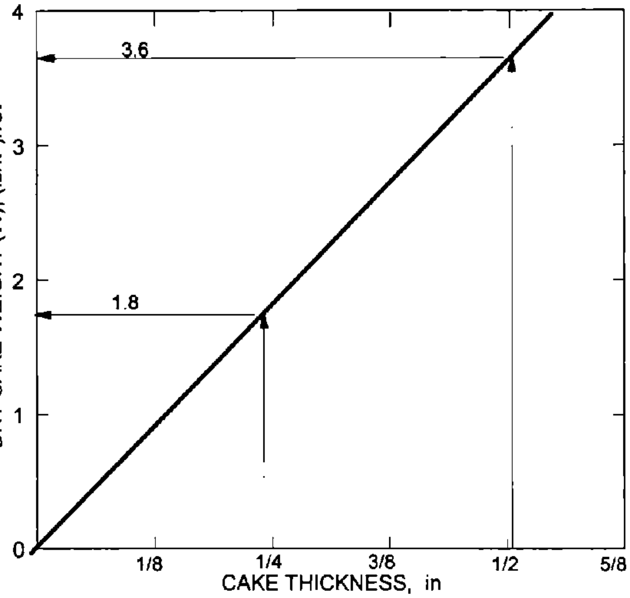
ΔP = pressure drop across cake,

W = dry cake weight per square foot per revolution,

θ_d = dry time,

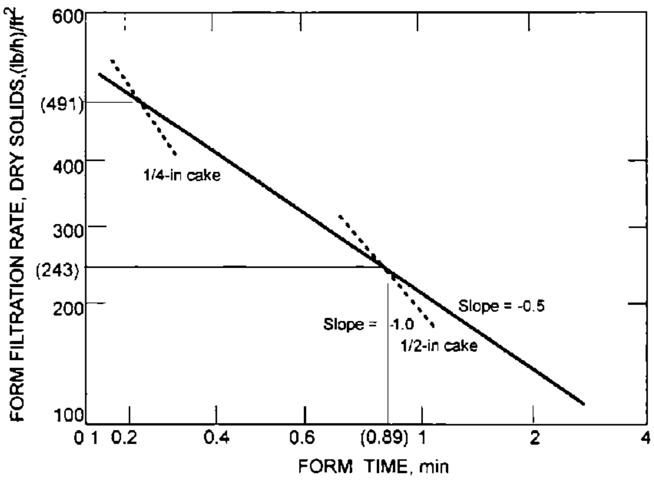
and μ = viscosity of liquid phase.

Figure 4.21



Dry cake weight versus thickness.

Figure 4.22



Form filtration rate versus form time.

Nelson and Dahlstrom (1957) have presented an in-depth discussion of this cake moisture correlation.

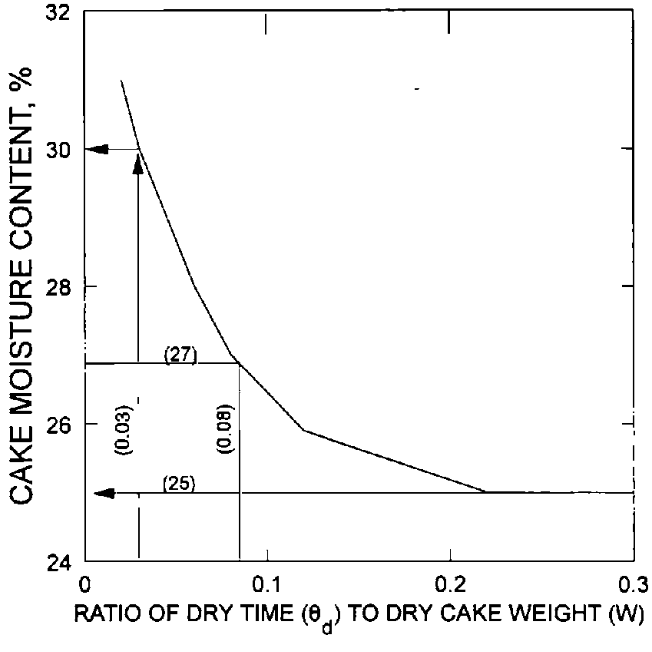
In many instances the correlating factor can be simplified. This simplification is possible when all of the tests are conducted at constant temperature and vacuum. Also, air-rate data are often not available, and reasonable correlations can be obtained without this information, particularly if the cakes are relatively nonporous. In these instances the correlation reduces to the following relationship:

$$\text{Correlating factor} = \theta_d/W.$$

Figure 4.23 illustrates the general shape of a correlating curve derived from leaf test data. To achieve consistent cake moisture contents, correlating values should be chosen that are somewhat to the right of the knee of the curve. If values to the left of the knee are chosen, small changes in operating conditions can produce relatively wide variations in the cake moisture content.

Cake wash efficiency—In hydrometallurgical operations, cake washing efficiency most often refers to the relationship between the amount of the valuable solute constituent removed from the dewatered cake during the washing operation and the amount of wash solution used. A convenient method for evaluating this relationship involves plotting the percent solute remaining versus the wash ratio

Figure 4.23



Cake moisture correlation: cake moisture versus θ_d/W.

on semi-log paper as shown in figure 4.24. The percent solute remaining refers to the following relationship:

$$\% \text{ remaining} = \left[\frac{\text{weight of solute in washed and dried cake}}{\text{weight of solute in dewatered but unwashed cake}}\right] \times 100.$$

If the cake is being washed with solute-free liquor, the percent remaining is calculated by dividing the solute concentration in the liquor remaining in the washed cake by the solute concentration in the original feed slurry liquor. When the wash liquor contains solute, the percent remaining may be calculated from leaf test results as follows:

$$\% \text{ remaining} = \left[\frac{C_c - C_w}{C_f - C_w}\right] \times 100,$$

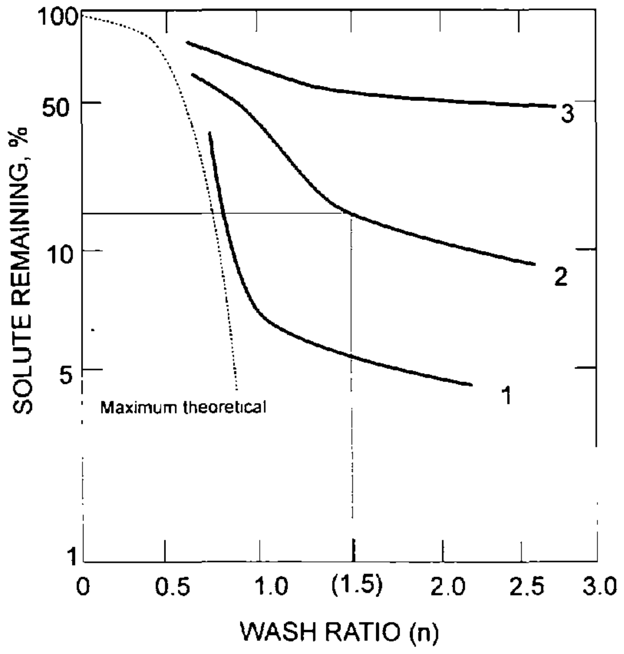
where C_c = solute concentration in final washed cake,

C_f = solute concentration in feed slurry liquid,

and C_w = solute concentration in wash liquid.

The wash ratio is the volume of washing fluid divided by the volume of original liquor in the cake at the time the wash is applied.

Figure 4.24



Cake washing relationships (percent remaining in cake versus wash ratio).

Perfect plug flow displacement would produce the maximum theoretical curve shown on the left side of figure 4.24. Curve 1 represents the relationship that can occur when (1) the cake porosity is very low, (2) the wash rate is also low, but (3) the washing efficiency is high. Washing a very porous cake often produces a correlation such as that shown by curve 3. The vast majority of filter cake washing efficiencies fall close to curve 2.

Cake wash time—Cake wash time can usually be correlated by plotting the following relationship:

Wash time versus WV_w,

where W = weight of dry cake per square foot per revolution,

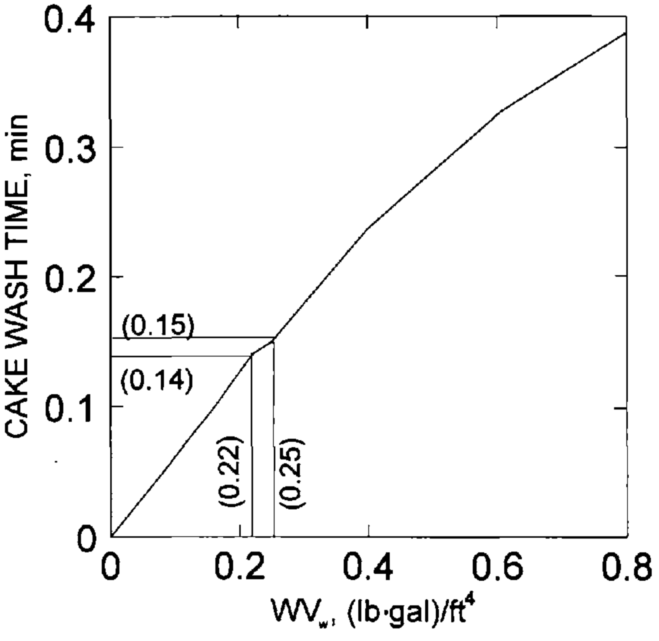
and V_w = volume of cake wash per square foot per revolution.

Figure 4.25 illustrates a plot of this relationship. Ideally, all of the washing data should fall on a single curve. If the scatter is significant, other correlations such as the following should be tried:

Wash time versus nW^2,

or wash time divided by form time versus wash volume divided by form volume,

Figure 4.25



Cake wash-time correlation.

where W = weight of dry cake per square foot per revolution,

and n = wash ratio.

Air Rate—Vacuum pump capacity (expressed as cubic feet per minute per square foot) is determined by totaling the gas volumes that pass through a square foot of filter area during each drying period and then dividing this value by the cycle time. The gas volumes are determined by measuring the total airflow for various lengths of time or from measurements of airflow rate as a function of time. Figure 4.26 illustrates a plot of instantaneous airflow rates versus drying time. The plot is developed from airflow measurements taken during the drying-cycle period of each filter test. The area under the curve represents the total volume of gas passing through the cake during the drying period.

Filter cycle time—The filter cycle in a continuous filtration operation is completed in one revolution of the filtration surface. The cycle time is determined by balancing the requirements of cake formation, washing, drying, and cake discharge. One of the stages will be controlling. For example, if the filter cake washes easily or the washing requirements are minimal, the cake formation time will usually be controlling. Conversely, if cake washing is difficult, the controlling factor will likely be the washing time. In all instances, the cycle time must be such that the required minimum cake discharge thickness is obtained (see table 4.3).

Example Calculations

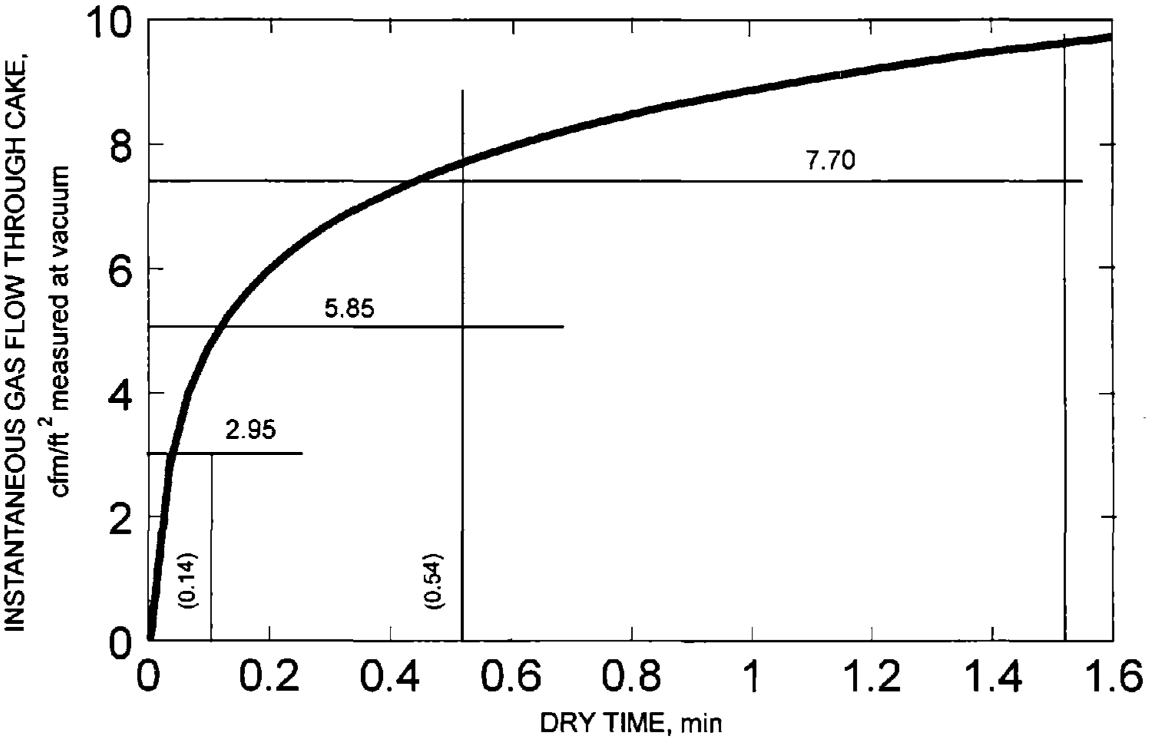
The following example calculations are based on the leaf test data and correlations presented in figures 4.21 through 4.26 and also on the equipment information listed in tables 4.2 and 4.3.

Each of the calculations applies a scaleup factor, which is primarily a safety or risk factor covering areas of uncertainty such as the following:

- Was the sample representative of average plant conditions?
- To what degree will normal plant variations affect the filtration operation?
- What will be the effect of plant upset conditions?
- To what degree will cloth conditioning or blinding be a factor?
- What percentage of the cake will discharge?

The following examples use a scaleup factor of 0.8; a higher factor could introduce excessive risk of undercapacity.

Figure 4.26



Drying-time correlation (instantaneous airflow versus drying time).

Some manufacturers recommend more conservative factors, in the 0.7 to 0.75 range. For many years, a factor of 0.65 was commonly recommended; this more conservative factor related primarily to risks associated with cloth blinding and the limited cloth selection then available.

Example 1—Disk Filter (Dewatering Only)

Assumptions:

- Final cake moisture (from leaf test data) = 25%.
- Scaleup factor = 0.8.
- Maximum effective submergence = 28% (table 4.2).
- Total cycle except for cake discharge and resubmergence = 75% (table 4.2).

Selected cake thickness = 1/2 in (table 4.3).
Dry cake weight (W) = 3.6 $(\text{lb}/\text{ft}^2)/\text{rev}$ (figure 4.21).

Form time = 0.89 min (figure 4.22).
Form filtration rate = 243 $(\text{lb}/\text{h})/\text{ft}^2$ (figure 4.22).

Simplified cake moisture correlating factor (θ_d/W) = 0.30 (figure 4.23).
Dry time $(\theta_d) = W \times \theta_d/W = 3.6 \times 0.30 = 1.08$ min.

Cycle time based on form time and the maximum effective submergence of 28%
= 0.89/0.28 = 3.18 min/rev.
Cycle time based on dry time and total cycle except for cake discharge and submergence (75%) minus maximum effective submergence
= 1.08/(0.75 - 0.28) = 2.30 min/rev.
Therefore, the cake formation rate is controlling and the cycle time is 3.18 min/rev.

Since the effective submergence is 28%, with an 0.8 scaleup factor, the design filtration rate
= $243 \times 0.28 \times 0.8 = 54.4\ (\text{lb}/\text{h})/\text{ft}^2$,
or the design filtration rate
= $3.6 \times 60 \times 0.8/3.18 = 54.3\ (\text{lb}/\text{h})/\text{ft}^2$.

Dry time = $3.18 \times (0.75 - 0.28) = 1.5$ min.
Integrated average air rate during drying = 7.70 cfm/ft^2 (from figure 4.26, area under curve for 1.5-min dry time).

Volume of air passed during drying
= $7.70 \times 1.5 = 11.55\ (\text{ft}^3/\text{rev})/\text{ft}^2$.

Air rate on total cycle basis
= 11.55/3.18 = 3.63 cfm/ft^2, measured at vacuum.

(When sizing the vacuum pump, allowance must be made for the pressure drop in the filter system. See following example.)

Example 2—Belt-Type Drum Filter (With Cake Washing)

Assumptions:

- Final cake moisture = 25%.
- Wash ratio = 1.5.
- Specific gravity of feed liquor = 1.0.
- Scaleup factor = 0.8.
- Figure 4.23 applies to both washed and unwashed cakes.
- Leaf test vacuum = 18 in Hg.
- Maximum apparent submergence = 35% (table 4.2).
- Maximum effective submergence = 30% (table 4.2).
- Maximum arc (percentage of cycle) for cake washing = 29% (table 4.2).
- Total cycle except for cake discharge and resubmergence = 75% (table 4.2).

Selected cake thickness = 1/4 in (table 4.3).
Dry cake weight (W) = 1.8 $(\text{lb}/\text{ft}^2)/\text{rev}$ (figure 4.21).

Form time = 0.22 min (figure 4.22).
Form filtration rate = 491 $(\text{lb}/\text{h})/\text{ft}^2$ (figure 4.22).

Minimum cycle time based on cake formation time and maximum effective submergence
= 0.22/0.30 = 0.73 min/rev.
Therefore, minimum dry time between form and wash
= time for cake travel from slurry level to horizontal centerline (25% of drum surface minus 50% of apparent submergence)
= 25 - 35/2 = 7.5% of total drum surface.[9]

Therefore, initial dry time (θ_d)
= $0.73\ \text{min/rev} \times 0.075 = 0.06$ min.

Moisture content of dewatered but unwashed (D/U) cake, using simplified cake moisture correlating factor (θ_d/W)
= 0.06/1.8 = 0.03.
Therefore, moisture content = 30% (figure 4.23).

Liquor in D/U cake
= [(% moisture)/(% solids)] × W
= $(30/70)1.8 = 0.77\ (\text{lb}/\text{ft}^2)/\text{rev}$.
Therefore, at a 1.5 wash ratio,
Wash quantity (V_w)
= $0.77 \times 1.5/8.35\ \text{lb/gal} \times 1.0$
= $0.14\ (\text{gal}/\text{ft}^2)/\text{rev}$.
$WV_w = 1.8\ (\text{lb}/\text{ft}^2)/\text{rev} \times 0.14\ (\text{gal}/\text{ft}^2)/\text{rev} = 0.25$.
Therefore, wash time = 0.15 min (figure 4.25).

Value of simplified correlating factor (θ_d/W) for final cake moisture of 25% = 0.30 (figure 4.23).

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[9] Minimum dry time factor is used in calculations of initial dry time.

Final dry time (θ_d) = W × θ_d/W = 1.8 × 0.3 = 0.54 min.

Required minimum times:

Form	0.22 min
Initial dry	0.06 min
Wash	0.15 min
Final dry	0.54 min
Total	0.97 min

Maximum arc (percentage of cycle) for wash plus final dry

= horizontal centerline to discharge

= 75% minus effective submergence minus slurry level to horizontal centerline

= 75 - 30 - 7.5 = 37.5% of cycle.

Cycle time based on wash plus final dry times required

= (0.15 + 0.54 min)/0.375 rev = 1.84 min/rev.

Required washing arc = (0.15/1.84 min/rev)100 = 8.2% = 29°, starting at the horizontal centerline. This is satisfactory but will require careful adjustment of the wash sprays to prevent runback and will require the use of at least two wash headers.

At a cycle time of 1.84 min/rev,

Initial dry time[10] = 1.84 × 0.075 = 0.14 min.

Correlating factor (θ_4/W) = 0.14/1.8 = 0.08.

D/U cake moisture content = 27% (figure 4.23).

Liquor in D/U cake = (27/73)1.8 = 0.67 $(\text{lb/ft})^2$/rev.

Now, at a wash ratio of 1.5,

Wash quantity (V_w)

= 0.67 × 1.5/8.35 lb/gal × 1.0

= 0.12 (gal/ft^2)/rev.

WV_w = 1.8 × 0.12 = 0.22 $(\text{lb·gal})/\text{ft}^4$.

Therefore, wash time = 0.14 min (figure 4.25).

Cycle time = (0.14 + 0.54 min)/0.375 rev = 1.81 min/rev.

Initial dry time[11] = 1.81 × 0.075 = 0.14 min.

(Minimum initial dry time was 0.06 min; therefore, 0.14 min is acceptable.)

Required effective submergence = (0.22/1.81)100 = 12.2%.

This is much less than the 30% submersion available. Therefore, when the filter is installed, one of the following modifications must be made: (1) the valve bridge setting must be adjusted to delay the start of form until bottom dead center, (2) the slurry level must be lowered, or (3) vacuum regulation must be adjusted to control cake thickness.

Required washing arc = (0.14/1.81) = 7.7% = 28°.

Design cycle:

Form	0.22 min (could be longer but at reduced vacuum)
Initial dry	0.14 min (would be longer, if submergence lowered)
Wash	0.14 min
Final dry	0.54 min
Discharge and resubmergence	0.77 min
Total	1.81 min

Design filtration rate

= 491 × 0.122 × 0.8 = 47.9 $(\text{lb/h})/\text{ft}^2$,

or design filtration rate

= 1.8 × 60 × 0.8/1.81 = 47.7 $(\text{lb/h})/\text{ft}^2$.

Use of a thinner cake would increase filtration by only a nominal amount in this case because the final dry time is controlling. If wash or form time were controlling, a decrease in cake thickness would have a significant effect.

Air rate:

Volume through cake during initial dry

= 0.14 × 2.95 = 0.41 ft^3/rev (figure 4.26).

Volume through cake during final dry

= 0.54 × 5.85 = 3.16 ft^3/rev (figure 4.26).

Therefore, total volume through cake

= 0.41 + 3.16 = 3.57 ft^3/rev.

Air rate on total cycle basis

= 3.57/1.81 min

= 2.0 cfm/ft^2 (measured at 18 in Hg vacuum).

If pressure drop through the system = 1.0 in Hg, and the barometric pressure = 30 in Hg, the design air rate

= 2.0 × (30 - 18)/(30 - 19)

= 2.2 cfm/ft^2 (measured at 19 in Hg vacuum).

Solute recovery:

Refer to curve 2 of figure 4.24. With a 1.5 wash ratio, the percentage of solute remaining in the cake = 14.5%. (Use 20% remaining for design.)

Therefore, if the feed slurry contains 40% suspended solids, and the feed liquor contains 2% solute:

---

[10] Factor 0.075 indicates minimum dry time between form and wash, calculated as percent of total drum surface.

[11] Factor 0.075 indicates minimum dry time between form and wash, calculated as percent of total drum surface.

Solute in feed (C_f)
= $(60/40) \times 0.02$
= 0.0300 lb solute per pound of suspended solids.
Solute in D/U cake
= $(27/73)0.02$
= 0.0074 lb solute per pound of suspended solids.
Solute in washed cake (C_c)
= 0.0074×0.20
= 0.0015 lb solute per pound of suspended solids.
Solute recovery
= $(0.0300 - 0.0015)100/0.0300 = 95\%$.

Example 3—Horizontal Belt Filter

Data and correlations obtained from leaf tests:

- Cake thickness = 1/2 in.
- Dry cake weight (W) = 3.6 (lb/ft^2)/rev.

- Cycle specifications:

Cycle component	Time
Form	0.15 min
Initial dry	0.20 min
Wash	0.60 min
Final dry	0.50 min
Total	1.45 min (per revolution)

Assumptions:

- Dry solids production rate = 30,000 lb/h.
- Width of filtration surface = 9 ft.
- Scaleup factor = 0.8.

Required belt speed
= $30{,}000/(60 \times 9 \times 3.6) = 15.4$ ft/min.
Minimum filter length (including scaleup factor)
= $15.4 \times 1.45/0.8 = 27.9 = 28$ ft under vacuum.
Filtration area
= $9 \times 28 = 252$ ft^2.
Equivalent filtration rate
= $30{,}000/252 = 119$ (lb/h)/ft^2.
Design filtration rate calculated from cake weight and cycle time
= $3.6 \times 60 \times 0.8/1.45 = 119$ (lb/h)/ft^2.

When sizing a horizontal belt filter, always determine the minimum belt speed to give the required production and the minimum length to give the required cycle time.

4.3.5 Batch Pressure Filtration

4.3.5.1 Introduction

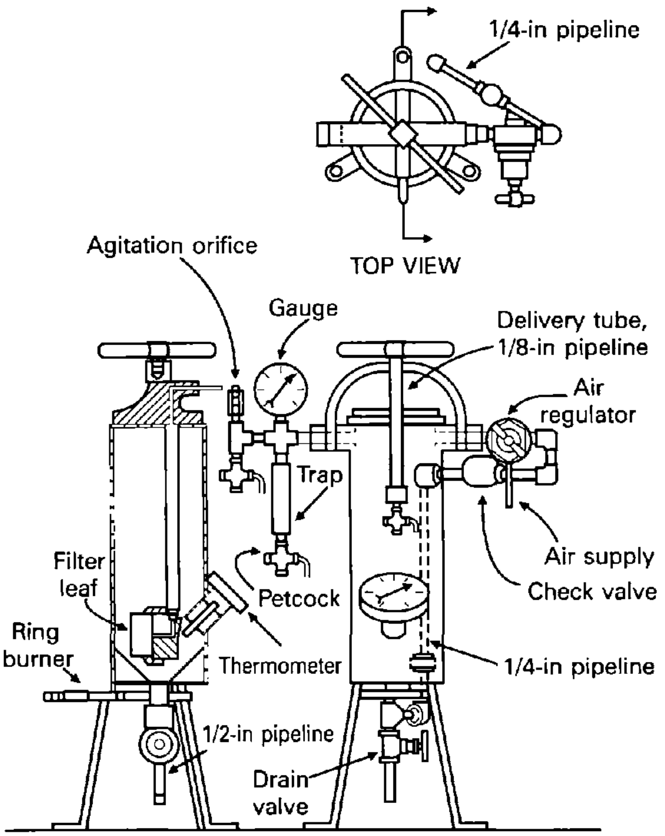
Manufacturers produce a wide variety of batch-type pressure filters. Some of the more common types that have been used in hydrometallurgical processing and waste treatment operations are filter presses, horizontal plate filters, leaf filters, and tube filters. Descriptions and appropriate applications for these filters are discussed in the following references: Dahlstrom (1985a) and Jacobs (1984).

4.3.5.2 Test Procedures for Pressure Filtration

Test procedures for pressure filtration often require specialized equipment. Therefore, early contact with equipment manufacturers is nearly always advisable unless the researcher has specific prior experience. Vendor experience can also be valuable because small-scale tests can sometimes produce misleading results for relatively free-filtering materials. For these materials, obtaining reliable data on pressure filtration may require pilot-scale tests. The following paragraphs present references together with brief comments on procedures for pressure leaf tests, plate-and-frame tests, and compression permeability tests.

Pressure leaf tests—A pressure filter unit such as that shown in figure 4.27 is applicable for predicting the performance of leaf filters; it can also be used for preliminary evaluation of plate-and-frame filtration. The equipment

Figure 4.27



Pressure filter test unit.

consists of a small leaf (2-by 2-in) suspended in a pressure vessel. The pressure vessel must be large enough to contain sufficient slurry to form the desired cake. The leaf can adapt to a variety of different types of filter media. An air-sparging system is sometimes used to provide gentle agitation of the slurry prior to applying the pressure.

Filter sizing data are usually developed by conducting a series of constant-pressure tests for different lengths of time. Tests at several different pressures must also be conducted to evaluate the compressibility of the solids. Jacobs (1984, p. 19-69) discusses procedures for correlating the data from each constant-pressure test series.

Plate and frame tests—If a potential industrial-scale filtration application envisions a filter press installation, at least a few confirmatory laboratory-scale plate-and-frame tests are recommended. These tests are usually conducted after the general design and sizing criteria have been established by leaf tests. A laboratory-scale filter press normally consists of two plates and a single frame. This type of test equipment can provide data on solids-settling, cake-packing, and washing behaviors, any or all of which may be significantly different from the data and observations obtained in leaf tests. The manufacturer of the laboratory-scale filter press being used should be contacted for specific operating instructions.

Compression-permeability tests—If the compressibility of the solids being filtered is appreciable, compression-permeability experiments may provide design data that are more applicable than those derived from leaf tests. Figure 4.28 illustrates the type of cell used to develop compression-permeability data. The basic unit shown consists of a cylindrical cell fitted with two close-tolerance, hollow pistons, which have fritted faces.

With the lower piston in place, the test slurry is poured into the cell, and a gentle vacuum is applied through the filtrate drainage tube to form a cake. The cell is then filled with filtrate; the upper piston is inserted and allowed to settle to the cake level. Successive load increments are then applied to the cake through the upper piston. The permeability of the cake is determined at each load increment by passing filtrate through the cake from the constant-head reservoir. Specific procedures for conducting compression-permeability tests have been described by Tiller (1953, 1966).

Additional information on the test procedure and methods for correlating the experimental results are discussed in the following references: Grace (1953) and Tiller (1975).

Belt presses—Belt filter presses, such as that shown in figure 4.29, have been used to dewater fine coal, sand and gravel fines, sewage sludges, and similar materials. These units enclose the feed slurry between two moving filter media belts. The liquid is expressed through these belts under pressure applied by rollers. The filter shown has three dewatering zones: (1) a gravity drainage zone, (2) a wedge zone in which gradually increasing pressure expresses surface and interstitial water, and (3) a press zone in which high pressure induces further expression.

When compared with drum, disk, or horizontal belt filters, this type of dewatering equipment has the advantage of relatively low power costs because vacuum systems are not required. Disadvantages include higher filter media costs, increased flocculant requirements, and no cake-washing capability. Typically, the filter cake moisture content is about equivalent to that obtained on a vacuum filter.

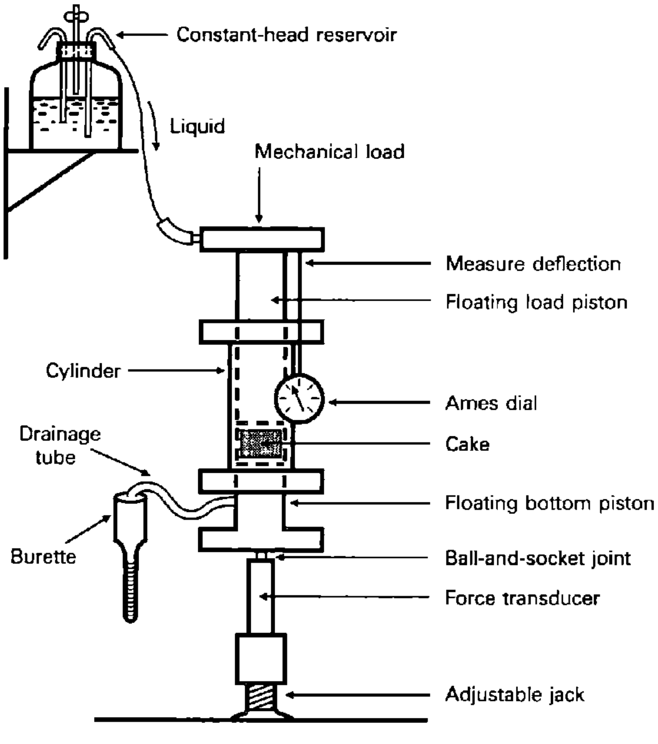
Since expression of liquid is a complicated operation involving many phenomena, equipment manufactures should be contacted to determine if this solids-liquid separation technique is applicable. Special equipment and testing procedures will probably be required.

4.4 SAFETY

4.4.1 Introduction

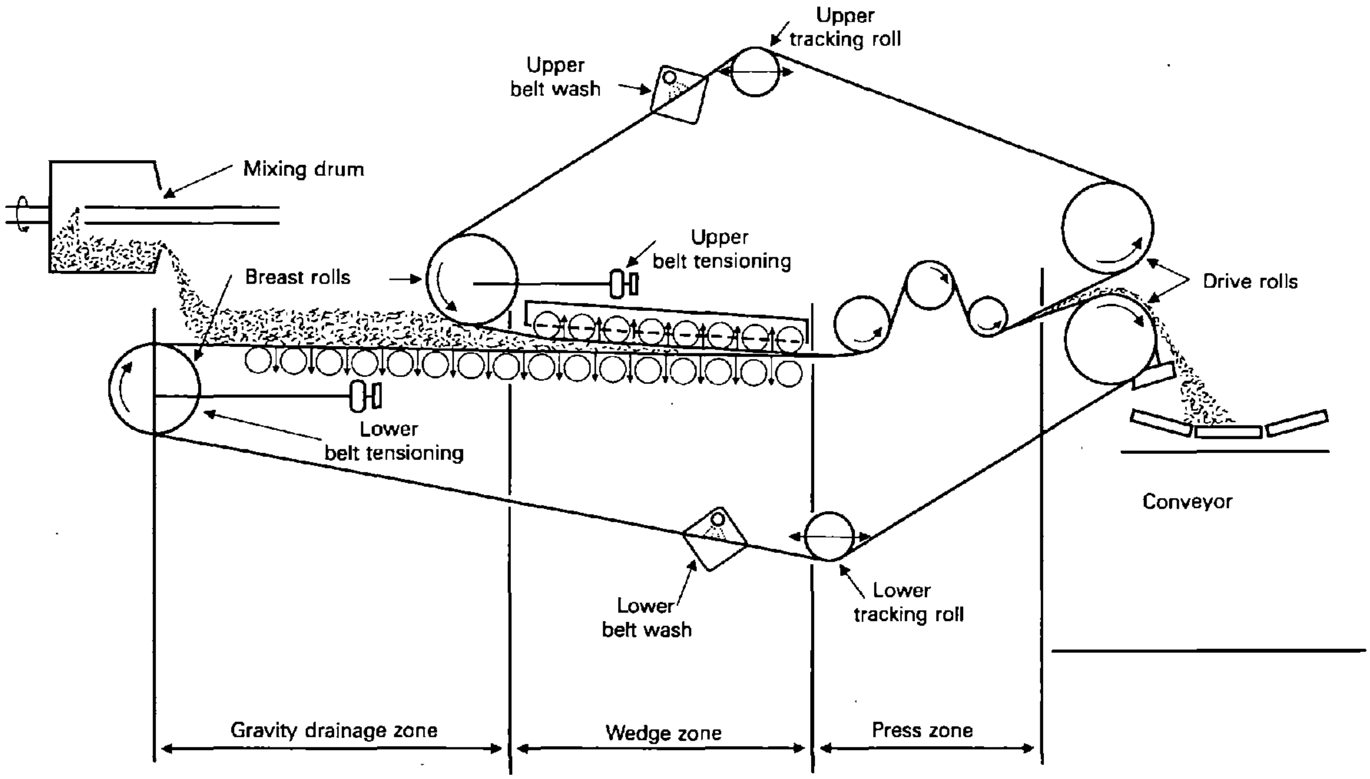
Even though the hazards associated with laboratory-scale solids-liquid separation tests are usually relatively small, the need for careful planning and safe practices always exists. The researcher must work defensively and appraise the intrinsic danger of each experimental procedure and setup. Reviewing all potential hazards of the solids

Figure 4.28



Compression-permeability cell.

Figure 4.29



Belt press schematic.

and liquids being handled becomes an important consideration. Disposal of test residues is under increasingly stringent regulation, and safe disposal requires special planning, especially during experiments related to waste management investigations.

4.4.2 General Practices

All of the general laboratory safety rules discussed in sections 1.2.4.1 and 1.2.5.1 of chapter 1 apply for solids-liquid separation experiments. Practices relating to general housekeeping, the use of personal protective equipment, ventilation, and personal hygiene are always important. For example, when any type of potentially hazardous residue is being produced or handled, the researcher should do most of his or her own housekeeping.

Equipment arrangements and setups should be neat. If the equipment arrangement is not balanced, securely fixed, and aesthetically pleasing, it is probably dangerous.

4.4.3 Specific Considerations

- *Vacuum systems*—Implosion is a potential hazard associated with all laboratory vacuum filtration systems; it can be particularly dangerous if corrosive or toxic filtrates are being handled. All glassware, such as filtrate receivers and traps, must be rated for vacuum service.
- *Pressure systems*—Laboratory-scale filter presses can develop spray leaks between the plate and frame components. A spray shield should be installed around the filter press. If the slurry being filtered contains a corrosive liquid, a full face shield and suitable protective clothing should be worn.
- *Waste disposal*—Waste-disposal requirements should be thoroughly considered before any solids-liquid test program is started. The information contained in Material Safety Data Sheets is useful in this planning. Consultations with laboratory safety officers or other appropriate personnel should be a part of the planning process. Handling and preparing wastes for proper disposal should be carried out by the research team or other properly trained personnel.
- *Hand protection*—When hand agitation is used to mix and suspend filtration test slurries (see 4.3.4.4), long (14- to 18-in) rubber gloves should always be worn. It is also strongly recommended that rubber gloves be worn whenever slurries are handled, especially when the toxicity of the slurry components is unknown.

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CHAPTER 5.—RECOVERY FROM SOLUTION

5.1 INTRODUCTION

As used in this chapter, "recovery from solution" refers to hydrometallurgical operations that involve the ion-exchange, carbon-adsorption, or solvent-extraction treatment of leach liquors and other process solutions. These operations also have application for the treatment of waste streams containing toxic metal ions or other contaminants.

Other procedures and techniques, such as chemical precipitation, electrolysis, evaporation, and crystallization, have also been used to recover metal values from processing solutions. Typically, the use of these recovery systems requires a relatively unique processing approach for each processing situation. Therefore, generalized laboratory procedures may not be applicable. For example, at least five different precipitation procedures have been used to recover uranium from processing solutions. Therefore, when planning experiments that use these recovery techniques, the researcher is advised to consult literature that is closely related to the particular system being investigated. Descriptions of industrial practice can be particularly valuable. The following references are suggested as starting points for developing background and planning information:

Precipitation—Dutrizac and Monhemius (1986); Gordon and others (1959); Merritt and others (1985); Robinson and Sum (1980); Rolia (1974); Shonel (1992); and Walton (1967).

Electrolysis—Chapman (1985); Heitz and Kreysa (1986); Mantel (1960); O'Keef (1981); Prentis (1991); and Rousarand others (1986).

Evaporation and Crystallization—Biedis and Kuttanberg (1987); Mullin (1972); and Wilson (1965, 1985).

Most of these references contain extensive bibliographies.

The following sections discuss experimental techniques and procedures for bench-scale ion exchange, carbon adsorption, and solvent extraction. The discussions focus on the equipment and techniques required for initiating an experimental program. In general, the approach assumes that the engineer or metallurgist conducting the studies has studied the literature related to the system being investigated, but has limited experience in the specific experimental procedures.

The initial step in planning and designing an experimental program must include defining the nature of the stream to be processed. This analysis should be as accurate and complete as possible. For example, a reliable anion-cation balance will help provide a realistic basis for selecting the processing procedure or procedures to be investigated. Characterization of the feed stream can be particularly critical when investigating pollution-control operations. For relevant results, the feed solution must be representative of the stream that will be processed. If projections indicate that the feed-stream composition may vary, the effect of this variability should be investigated.

Even when detailed solution-characterization data are available, experimental studies are nearly always required because the complex chemical nature of hydrometallurgical systems restricts theoretical evaluations. For example, in resin ion exchange, difficulties related to defining the activities in the resin phase severely limit using equilibrium constants.

5.2 RESIN ION EXCHANGE

5.2.1 Introduction

As practiced in hydrometallurgical or waste treatment operations, resin ion exchange may be defined as a reversible interchange of ions between the solid resin phase and the solution phase. During this exchange, there is no permanent change in the structure of the resin phase. The process is primarily applicable to treating large volumes of solutions containing low concentrations of the ions to be recovered. Ion exchange is usually most economically suited to situations where recovering one specific ion, such as a metal or metal ion complex, is desired.

Laboratory-scale ion-exchange studies have used both batch-mixing and column techniques. Both have application, but column techniques have received wider use because the experimental results translate more readily to full-scale operations. The bench-scale column procedures that are discussed relate primarily to fixed-bed operations. References are listed for procedures describing the type of experimental equipment required for investigating continuous ion-exchange systems.

When the researcher is planning ion-exchange studies, contacts with resin suppliers can be particularly helpful. Extensive information is available on resin characteristics, properties, and applications. The following is a partial list of suppliers that offer resins applicable to both hydrometallurgical and water-treatment systems:

Bayer AG, Leverkusen, Germany.
Dow Chemical Co., Midland, MI.
Illinois Water Treatment Co., Rockford, IL.
Mitsubishi Kasei Co., Tokyo, Japan.
Organo Corp., Tokyo, Japan.
Purolite Co., Bala Cunwyd, PA.
Rohm and Haas Co., Philadelphia, PA.
Sybron Chemical Inc., Birmingham, NJ.

In addition to supplying technical data on the ion-exchange resins they produce, a number of the companies listed also offer literature on ion-exchange principles, ion-exchange applications, and laboratory techniques. The general literature on ion exchange has become very extensive and covers many special applications. The following selected references contain information on ion-exchange theory, principles and waste treatment technology related to hydrometallurgical operations: Calmon and Gold (1979); Dorfner (1972, 1991); Korkisch (1989); Kunin (1972); Royal Society of Chemistry (1993); Society of Chemical Industry (1984); and Wheaton and Lefevre (1981).

As with all bench-scale studies, ion-exchange tests have certain limitations. Failure to replicate experiments is probably one of the greatest dangers. Since the ionic form of resins supplied by the manufacturer almost always differs from the ionic forms that will be in equilibrium with a process stream, the results obtained with new resins are not typical of those that will occur in a cyclic process. The results may be either better or worse. All final design data should be based on at least duplicate results from multicycle tests.

Definitions of the specialized terms used throughout section 5.2 are presented in the following section (5.2.2).

5.2.2 Ion-Exchange Terminology

The initial transfer of metallic ions from the feed solution to the ion-exchange resin has been referred to in the literature by a number of different terms including "adsorption," "absorption," "sorption," "loading," and "exhaustion." The term "adsorption" is used in the following descriptions and discussions. The subsequent operation of stripping the adsorbed metal ion from the ion-exchange resin is termed "elution." Any further treatment that may be required to prepare the resin for cycling to the adsorption step is designated as "regeneration." The following terminology list presents definitions of these and additional terms that apply in the ensuing descriptions and discussions.

Adsorption—The operation of transferring ions from an aqueous to an organic phase.

Attrition—The wear and breakage of ion-exchange resin particles.

Backwashing—The upward flow of water through a resin bed in a column at a velocity sufficient to fluidize the bed. Typical objectives of backwashing are to cleanse the bed of foreign material, to expand the bed, and to classify the resin.

Batch operation—A method of solution-resin contacting in which a known quantity of resin is gently agitated in a vessel along with a given quantity of the solution to be treated. After the desired equilibrium is attained, a solids-liquid separation is made, usually by some form of filtration or screening.

Bed depth—The depth of the bed of ion-exchange resin contained in a column.

Bed expansion—The increase in bed depth that takes place when a column of resin is backwashed.

Bed volume (BV)—The space occupied by a bed of resin. This volume is usually determined by first backwashing the resin or mixing a resin-solution mixture and then allowing the resin to settle. The resulting resin bed is often referred to as "wet-settled resin" (WSR). Occasionally, the term "wet-settled and tapped resin" is encountered. This refers to mixing the resin with water in a graduated cylinder, allowing the resin to settle by gravity, and then tapping the side of the cylinder with a wooden stick until no further settling occurs.

Breakthrough—The volume of effluent at the point where the concentration of the exchanging ion in the effluent reaches a predetermined limit. This point usually denotes the end of the adsorption cycle and the beginning of the washing and elution cycles.

Breakthrough curve—A plot of the concentration of ion-exchange column effluent versus the volume of solution passing through the column. Sometimes also referred to as a "loading curve."

Channeling—The flow of water or solution taking an undesirable "line of least resistance" through a resin bed. It is caused by the introduction of air pockets, dirt, or any other factor that could produce uneven pressure gradients in the bed. Channeling results in nonuniform contact between the resin bed and the solutions.

Chemical stability—The characteristic of a resin that enables it to resist degradation of its properties or structure when contacted by the relatively aggressive chemical solutions encountered during ion-exchange operations.

Crowding—The displacement of one metallic ion by another metallic ion that has a greater affinity for an ion-exchange site under the equilibrium conditions that exist.

Effluent—The solution that discharges from an ion-exchange column. In hydrometallurgical operations, the term "barren effluent" has been used to designate the discharge from an adsorption column. The term "eluate" refers to the product effluent from the elution step.

Elution—The stripping of sorbed ions from an ion-exchange resin by passing through the bed a solution containing a higher ionic concentration or ions of greater affinity. The feed solution is the eluant, and the product solution is the eluate.

Freeboard—The space above the resin bed in the column. This space is provided to accommodate the expansion of the resin bed during backwashing.

Head loss—The hydraulic pressure loss that occurs because of the resistance of the resin bed when solutions pass through it.

Influent - The solution entering an ion-exchange column, e.g., the feed solution to an adsorption column.

Ion-exchange isotherm—The concentration of a counter-ion, such as Zn^{2+}, adsorbed on the ion exchanger, expressed as a function of the counter-ion concentration in the solution in contact with the resin under specified conditions. (In some of the ion-exchange literature, the term "adsorption or loading isotherm" has been used interchangeably with the term "breakthrough or loading curve.")

Leakage—The early and typically undesirable appearance of valued ions in the column effluent. Leakage can result from factors such as channeling, unfavorable equilibria, and incomplete elution or regeneration.

Loading - The amount of a given ion being held by the ion-exchange resin. In hydrometallurgical operations this quantity is typically expressed, e.g., as grams of metal per liter of wet-settled resin (M g/L WSR) or pounds of metal per cubic foot of wet-settled resin (M lb/ft^3 WSR).

Loading curve—See "Breakthrough curve."

Physical stability—A resin characteristic that enables it to resist breakage due to either physical handling or the volume changes that can be produced by osmotic shock or cycling between different ionic forms.

Poisons—Competing ions that are so strongly adsorbed by the resin that they resist normal elution. Temporary poisons can be removed by special regeneration techniques. Permanent poisons are those that cannot ordinarily be removed without seriously damaging or destroying the exchange capacity of the resin.

Porosity—The degree of openness in the structure of a resin particle. Porosity relates directly to the water content of the resin and inversely to the cross-linkage of the resin structure.

Regeneration—The process of converting an ion-exchange resin to the ionic form desired or required for reuse. Sometimes both elution and regeneration can be achieved during a single step, but in other instances, two or more sequential operations may be necessary.

Superficial linear velocity—The rate of solution flow per unit area of column cross section. For example, a solution flowing at the rate of 2 gpm through a column with a 1-ft^2 cross section would have a superficial linear velocity of 2 gpm/ft^2.

Total capacity—The ultimate exchange capability of an ion-exchange resin.

5.2.3 Resin Handling, Conditioning, and Storage

Ion-exchange resins are nearly always shipped in the hydrated form and should be stored in tightly sealed containers to prevent drying. When resins dry, considerable shrinkage occurs. The resins can be rehydrated, but even with care, rehydration can often produce severe strains that cause resin breakage. If rehydration is necessary, the manufacturer's recommendations should be followed. For example, some cation resins that are in the sodium form can be rehydrated by contacting them with a saturated sodium chloride solution. The sodium chloride rehydration technique can also apply to anion resins that are in the chloride form. Rehydration can be carried out by soaking the resin in an open beaker. The recommended contact time is typically about 12 h, and periodic, very gentle mixing can be beneficial. After rehydration, the resins are washed free of the salt solution by successive decantations with deionized water. It is likely that other resins or resin forms will require different rehydration techniques.

Even if the resin has not dried, soaking the resin in deionized water overnight is prudent. Manufacturers caution that water should never be added to dry resins in a column because swelling may shatter the tube. This caution is particularly critical for anionic resins.

Ion-exchange resins are usually supplied in a regenerated form, but the form supplied may not be that desired for the experimental studies to be conducted. For example, an anionic resin may be shipped in the chloride form, but the system to be evaluated requires that the resin be in the sulfate form. Prior to starting adsorption experiments, the resin should be conditioned and converted to the desired form. This is usually best accomplished by contacting the as-received resin with the elution or elution-regeneration reagent combination that will be used in the initial tests. A procedure for conducting this conditioning step during column tests is discussed in section 5.2.5.2. If the ion-exchange resin is received in the desired ionic form, conditioning with deionized water will be adequate. The primary objective of this contact is to remove components that may have formed or leached from the resin during storage.

5.2.4 Batch Tests

Batch tests are usually most applicable for preliminary screening experiments when a large number of resins are being evaluated for a specific separation. This type of test is typically carried out by gently agitating a known volume of conditioned resin with a specific quantity of the solution to be treated. A variety of contacting techniques can be used for screening tests, but the technique of placing the resin-solution mixture in an Erlenmeyer flask and agitating the mixture overnight on an orbital shaker has been satisfactory for most investigations. An indication of a given resin's selectivity and capacity can be developed by varying the resin-to-solution ratios. After the contact period is completed, the residual solution is analyzed. Comparative loadings and selectivity are calculated based on the feed and residual solution analyses in conjunction with the resin-to-solution ratios.

Batch procedures have been used to produce a quantity of loaded resin for elution studies. A batch of resin is sequentially contacted with increments of fresh feed solution until the desired loading is achieved.

Batch contacting techniques have also been used to develop equilibrium relationships, such as those needed for modeling continuous ion-exchange systems. The procedure is generally equivalent to the crosscurrent pyramid-type technique used in solvent-extraction studies (Treybal, 1963). Figure 5.1 illustrates the progression of both the solution and the resin through the repeating series of batch contacts. In step 1, both fresh resin and feed solution are equilibrated, and then a solids-liquid separation is made. The partially depleted solution from step 1 is next contacted with fresh resin in step 2. The partially loaded resin from step 1 is contacted with fresh solution in step 3. This sequence of equilibration followed by solids-liquid separation is continued throughout steps 4, 5, etc. of the pyramid. At each level of the pyramid, both fresh resin and solution are added to the exterior batch contacts while those in the interior of the pyramid combine the previously contacted components. All final resin and solution products (from steps 16 to 21) are analyzed for the ions of interest. The resin-solution contact time in each step must be such that equilibrium is achieved. The solution-to-resin ratios throughout all of the steps of the pyramid must be the same as those that would be used to achieve a given resin loading in a continuous circuit.

Equilibrium relationships can also be developed by a series of separate batch contacts in which the solution-to-resin ratio is varied over a wide range (typically 1:1 to 300:1). This procedure is much simpler, but a significant advantage of the pyramid technique is that it simulates the "crowding" conditions of an actual countercurrent ion-exchange circuit (Traut and others, 1978).

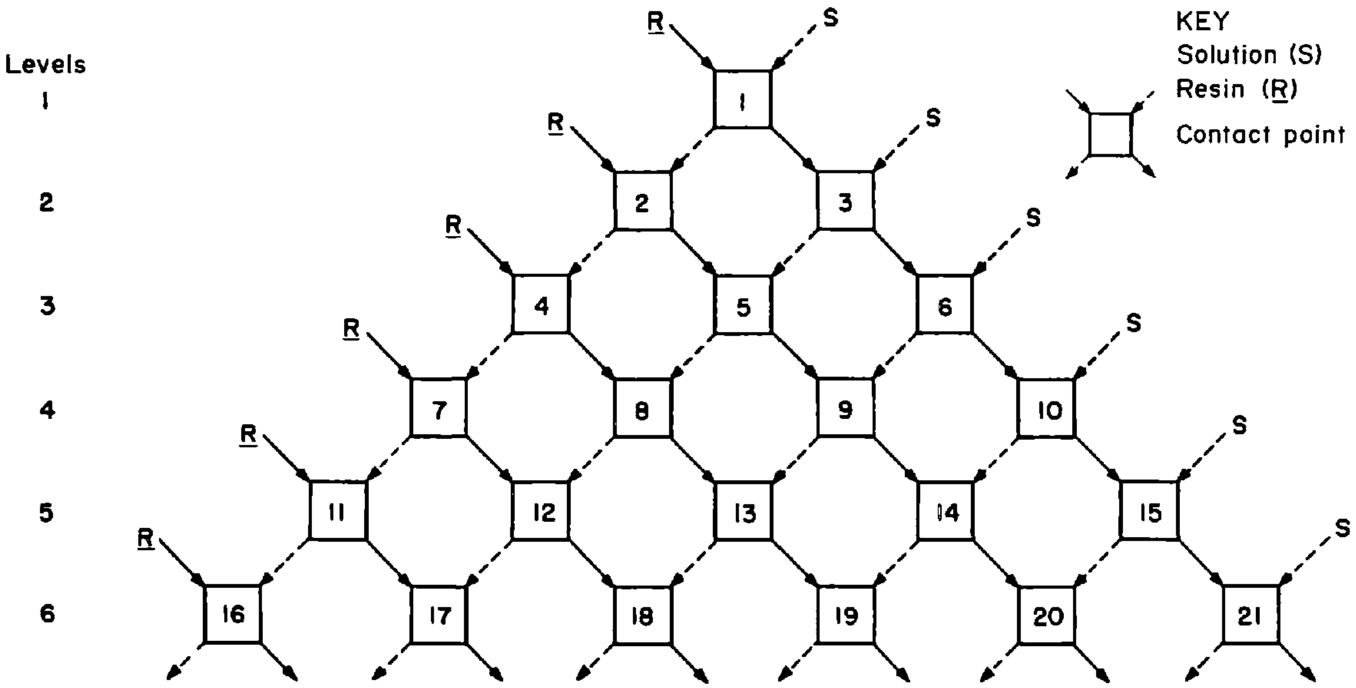
Batch kinetic tests using a gently stirred reaction vessel can be used to determine the residence time required to achieve equilibrium in a continuous system. Solution samples are withdrawn from the resin-solution mixture at predetermined times and analyzed.

5.2.5 Column Tests

5.2.5.1 Introduction

Typically, column ion-exchange studies are initiated after literature information and batch tests have been used to both select promising resins and to narrow the range of

Figure 5.1



Resin-solution contact pyramid applicable for development of equilibrium relationships.

variables that must be investigated for a fixed-bed ion-exchange application.

When a laboratory-scale experimental program and the equipment involved are planned and designed, the following general questions should be considered:

- What resin or resins will be tested, and is the equipment arrangement compatible with these resins?
- What volume of solutions will be treated per volume of resin, and what flow rates will be required?
- What kind of eluant or regenerants will be used, and how much solution and feed capacity will be required?
- What measurements and degree of control will be required?
- Will temperature control be required?
- What will the volume and concentration of the various waste streams be, and how can they be disposed of?
- What provisions are required for the cyclic operations necessary to investigate variables such as resin life or resin poisoning?

To answer these questions, the laboratory-scale experiments of column ion-exchange must define the interrelationships between variables such as the following, for each solution that will be treated:

- Type of resin.
- Feed solution pH.
- Solution retention time.
- Temperature.
- Type and concentration of eluant and/or regenerant solutions.

Typically, the test program must develop the data required to:

- Determine the loading capacity of each resin tested.
- Prepare breakthrough and elution curves.
- Determine retention times for adsorption and elution so that column size and resin inventories can be calculated.
- Determine resin life and/or poisoning effects after repeated cycling.
- Produce sufficient eluate for subsequent product-recovery studies or additional processing steps.

The following sections (5.2.5.2, 5.2.5.3, and 5.2.5.4) discuss both single-column and multiple-column tests that are applicable in developing the data outlined above.

5.2.5.2 Single-Column Tests

A wide variety of columns have been used for single-column ion-exchange tests. The following general descriptions discuss equipment arrangements and procedures that have been recommended by resin manufactures and used by a variety of researchers. There appears to be general agreement within the ion-exchange industry that experimental data generated from a 25-mm-ID column can provide reliable scaleup information if the resin-bed depth is at least 500 mm. Some manufacturers have recommended minimum bed depths of 600 mm for hydrometallurgical separations, and the ASTM (1974) procedure D-1782 specifies a resin-bed depth of 750±75 mm for operations such as water softening, where the ionic concentration in the feed solution is relatively low. Since, however, the 25-mm-ID column requires relatively large volumes of feed solution, smaller columns are usually necessary during the initial phases of an experimental program. With experience, applicable scaleup information can be developed from smaller columns. For example, the 200-ft^3 columns (approximately 5,700 L) used for uranium recovery in the South African operations were designed from data developed in 50-mL burettes containing 25 mL of resin. These columns had a diameter of about 10 mm. In some instances, when only very limited quantities of feed solution were available, even smaller columns with 5-mm diameters were used (Fisher and McGarvy, 1979). Drawing on the experience of resin manufacturers can often be valuable when using very small columns becomes necessary. Particular care is necessary because experimental results related to flow rates, pressure drop, and bed expansion can be misleading.

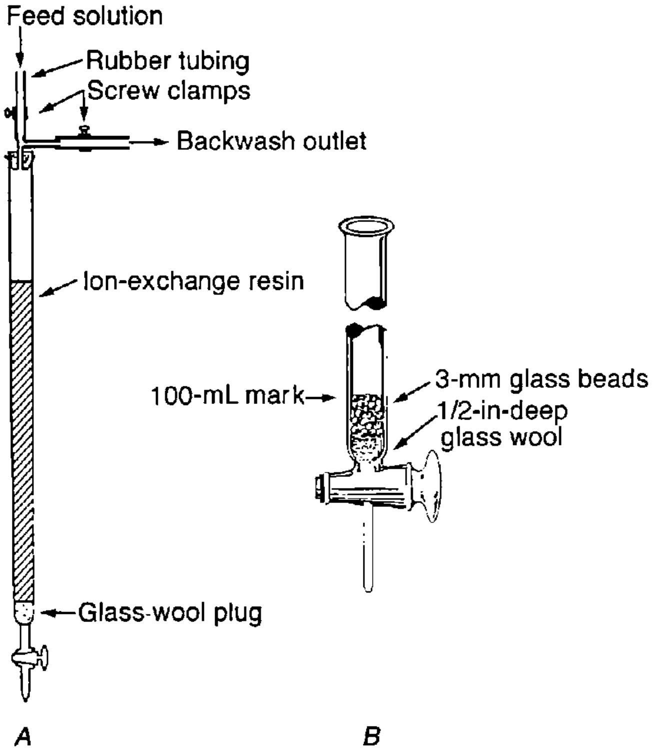
Columns With Internal Diameter of Less Than 25 mm

Standard 50- and 100-mL burettes, such as that shown in figure 5.2*A*, have been successfully used in a variety of bench-scale ion-exchange studies. The resin is retained in the column by a plug of glass wool inserted in the restriction above the stopcock. Extending the glass-wool plug up to the bottom of the burette calibration permits direct resin-volume measurements.

If this glass-wool plug significantly restricts the solution flow, a bed of glass beads or similar material can be substituted for part of the glass-wool plug, as shown in figure 5.2*B*.

In general, resin manufacturers recommend that for realistic breakthrough results, a 50-mL burette should contain at least 25 mL of resin. Since the inside diameter

Figure 5.2



Burette ion-exchange column. A, Standard burrette; B, glass-wool plug.

of a 50-mL burette is approximately 10 mm, the ratio of resin-bed depth to the column diameter would be approximately 30:1. The recommended ratio for a column with a 25-mm ID is usually about 20:1 (i.e., a 500-mm bed depth). The typical resin-bed depth in a 2-m-ID industrial-scale fixed-bed column, such as that used in the uranium industry, is about 1.5 m. Waste treatment operations may require somewhat deeper beds than those shown in typical hydrometallurgical flowsheets.

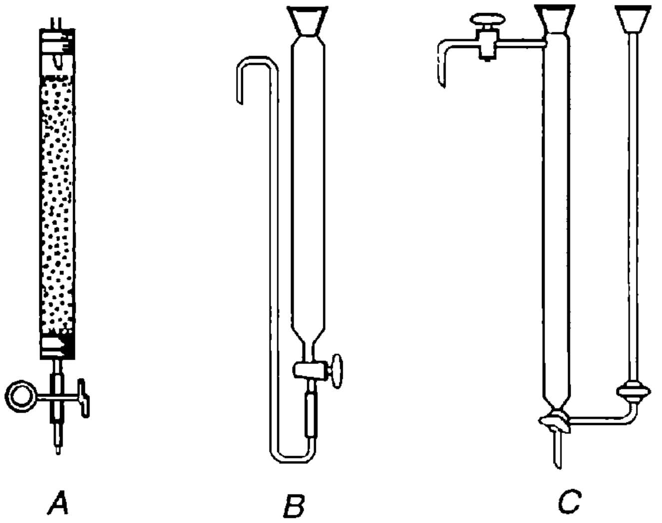
Experience has shown that if recommendations such as those discussed above are followed, the results obtained in the relatively shallow bench-scale tests do translate to the performance in the appreciably deeper industrial-scale columns.

The freeboard above the resin bed in a column should permit at least a 50% bed expansion during backwashing operations.

A variety of other small-column arrangements have also been used; several of these are shown in figure 5.3.

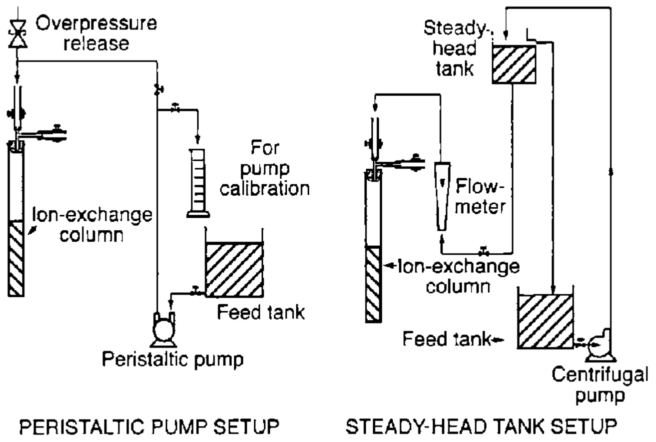
Since solution residence time is an important variable, obtaining relevant data from small columns requires precise control of column feed rates. Both manual and automated systems for feed solution control have been used successfully. Figure 5.4 illustrates two manually controlled column feed systems that can also be fitted for automatic control.

Figure 5.3



Other small-column arrangements. A, Laboratory-made ion-exchange column; B, ion-exchange column with overflow; C, countercurrent ion-exchange column.

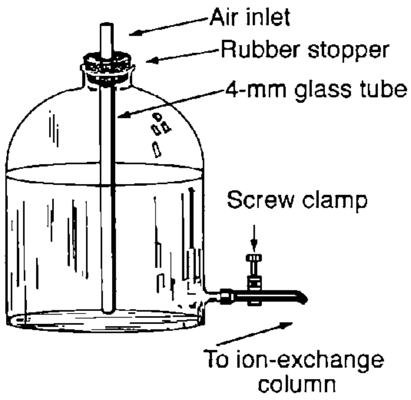
Figure 5.4



Ion-exchange column feed systems.

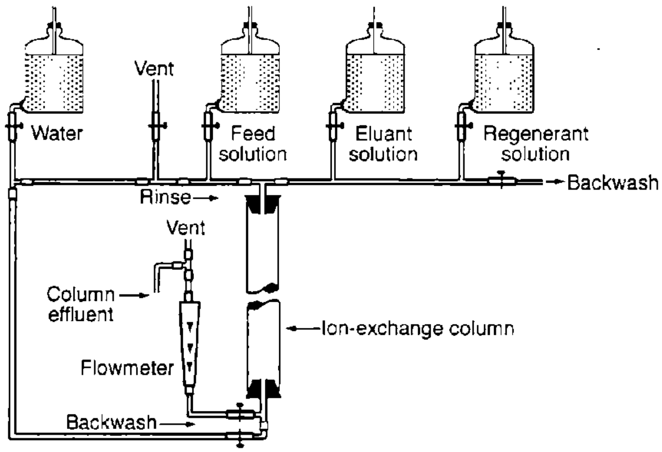
In exploratory or preliminary tests, a simple column setup has often been used (figure 5.2*A*), in which a constant fluid head has been provided by a Mariotte bottle, such as that shown in figure 5.5. For these tests, satisfactory feed-rate control can usually be achieved by manual adjustment of the stopcock on the bottom of the column. Separate bottles are provided for each feed, wash, eluant, or regenerant solution. Figure 5.6 illustrates one

Figure 5.5



Mariotte-bottle steady-head arrangement.

Figure 5.6



Versatile single-column ion-exchange arrangement.

type of a more versatile arrangement that uses a Mariotte-bottle steady-head system.

Increment sampling of the column effluent during breakthrough experiments can be done manually, but using some form of automatic fraction collector is desirable. Since the breakthrough point is often relatively sharp, sampling in equal increments is recommended. An increment volume equal to 1 BV is usually a good starting point. Collecting precise effluent volumes is particularly important when operating small columns.

Very short resin columns (25 to 50 mm deep) have been used to develop maximum loading capacity data, but measurements on the column effluent do not usually provide reliable breakthrough information.

Columns With Internal Diameter of 25 mm or Larger

As discussed previously, a general consensus exists among resin and equipment manufacturers that experimental results obtained from columns with inside diameters of 25 mm or larger can be scaled up with confidence. If a sufficient volume of feed solution is available, using columns of this size is recommended.

Figure 5.7 illustrates two types of 25-mm-ID ion-exchange columns. The column in figure 5.7*A* is an adaption of a column design described in ASTM (1974) procedure D-1782. The column is fabricated from glass or clear plastic and calibrated so that the required bed volume readings can be made. Suggested resin-bed supports include glass beads, quartz particles, or other suitably resistant material with nominal diameters of 1.5 to 3.5 mm. Other supports, including one or more layers of corrosion-resistant screen, can also be used. The recommended resin-bed depth is 750±75 mm. The column in figure 5.7*B* illustrates a somewhat different design, described in a Permutit Co. (1952) manual. The resin-bed support in this column consists of a bed of glass beads or similar material retained by a corrosion-resistant 60-mesh screen. As shown in the figure, the screen is held in place by two rubber rings.

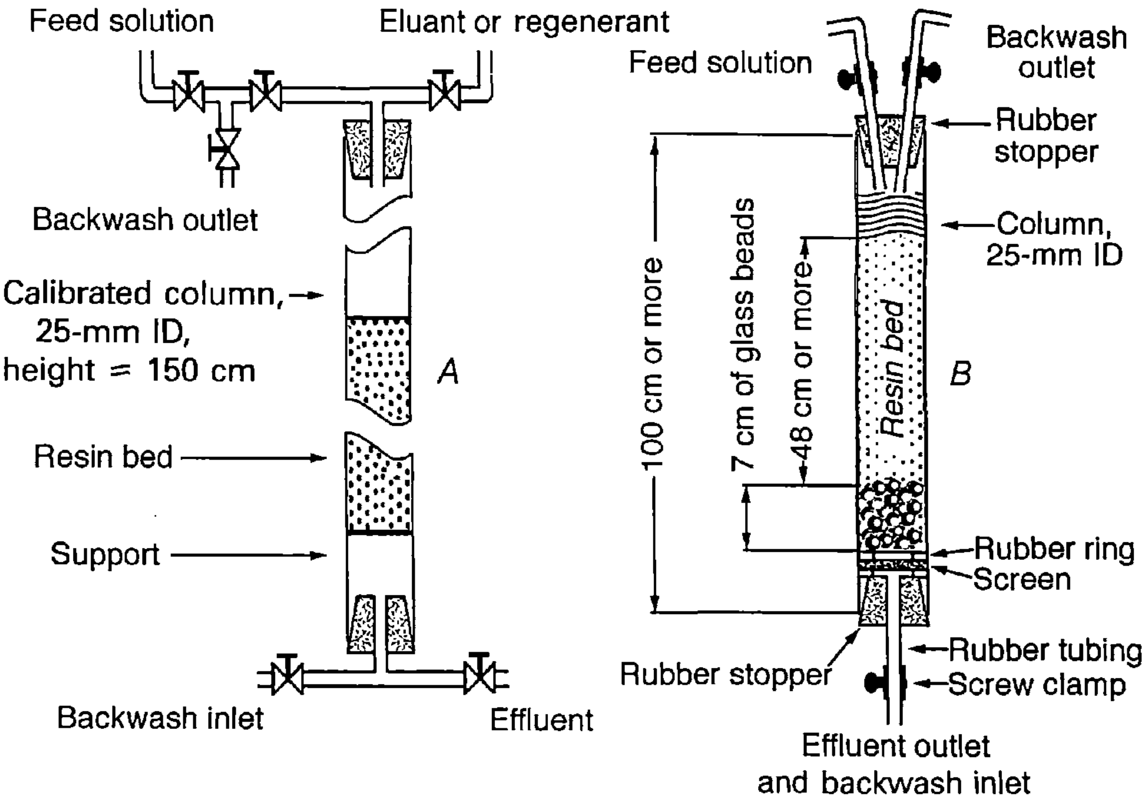
Low- or medium-pressure adsorption-chromatography columns, which are available from most laboratory supply houses, have been used for a variety of ion-exchange studies. These glass columns are available in several diameters and lengths. Typically, the resin-bed support consists of a woven nylon or polypropylene screen; in some columns, sintered-glass disks fused into the bottom of the column have been used. Manufacturers can supply jacketed columns if temperature control is desired.

Single-Column Test Procedure

The following procedure is generally applicable for experiments in which the test objective is to develop the data required for breakthrough and elution curves. Specifically, the procedure described outlines the steps of a hypothetical experiment to establish breakthrough and elution curves for the recovery of uranium from a sulfuric acid leach liquor. Typically, this test might be part of an experimental series to determine the effect of feed-rate variations on breakthrough capacities. The procedure includes the following operations:

- Column preparation.
- Resin conditioning.
- Adsorption.
- Elution-regeneration.

Figure 5.7



25-mm-ID ion-exchange columns. A, ASTM column; B, Permutit Co. column.

The specific test conditions are as follows:

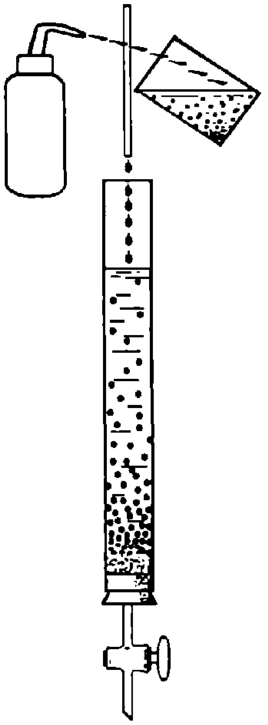
- Column size: Inside diameter = 25 mm, and length = 120 cm (see figure 5.7*B*).
- Feed-solution analysis: constituents in grams per liter = 8.10 SO_4, 1.0 U_3O_8, 0.60 Mn, 0.51 Ca, 0.28 Na, 0.26 Mg, 0.23 Fe, 0.21 Al, and 0.20 Cl; pH = 2.0.
- Feed solution temperature = 21 °C.
- Eluant = $0.9M$ NaCl plus $0.1M$ H_2SO_4 (approximately 1.0 pH).
- Eluant solution temperature = 21 °C.
- Ion-exchange resin: Strong-base anionic resin, such as Amberlite IRA-400 (Rohm and Haas) or Dowex 21K (Dow). The as-received resin is in the Cl^- form. Particle size ≈ 95% minus 20- plus 50-mesh (effective size ≈ 0.45 mm). Void volume of resin bed = 40%. Resin-bed depth = 50 cm (resin volume ≈ 245 mL).
- Flow Rates: *Backwash*—Flow required to get at least a 50% bed expansion ≈ 10 (ml/min)/cm^2. *Adsorption*—5 BV/h. (Retention time in resin bed = 5 min.) *Rinse*—5 BV/h. *Elution*—2.5 BV/h. (Retention time in resin bed = 10 min.)

The flow rates, volumes, etc. listed in the following discussions are applicable only for the specific column and resin beds described above, but the general bed-volume relationships listed above would also apply for both smaller and larger columns.

Column preparation—After the column and the auxiliary equipment, such as that described in the preceding sections, have been assembled, preparation of the resin bed can proceed. Soak the damp, as-received resin in deionized water; a 12-h soak is recommended. Then wash the resin by three or more successive decantations with deionized water. The objective of the soak and decantations is to remove components that may have formed or leached from the resin during storage.

Measure out approximately 245 mL (wet settled) of the washed resin. Next, add about 100 mL of deionized water to the column and transfer the resin to the column using a washing technique such as that illustrated in figure 5.8.

Figure 5.8



Transferring resin to an ion-exchange column.

Next, backwash the resin with deionized water at a flow rate sufficient to give at least a 50% bed expansion. For the resin being tested, this bed expansion will require a flow rate of about 50 mL/min in the 25-mm-ID column being used. Continue washing until the supernatant liquid remains clear. Stop the backwash and allow the resin to settle. Drain the water in the column until the water level is 20 to 30 mm above the top of the bed. If the column has been precalibrated, record the wet-settled volume of the resin. If the column has not been precalibrated, mark the resin level on the column so that the resin-bed volume can be determined after the test is completed.

Resin conditioning—Even though the resin in this instance was supplied in the chloride form, it is prudent to condition a new resin by contacting it with the eluant or regenerant solutions that will be used in practice. If the ionic form of the resin is unknown or if the resin has been used previously for other ion-exchange tests, the conditioning step becomes critical.

In this test, condition the resin by passing approximately 5 BV (245 mL × 5 = 1,225 mL) of the eluant (0.9*M* NaCl plus 0.1*N* HCl) through the resin bed at a rate of 2.5 BV/h (≈ 10 mL/min). After this volume of solution has passed through the bed, drain the residual solution from the column until the liquid level is 20 to 30 mm above the resin-bed surface.

Wash the residual eluant from the bed by passing deionized water through the bed at a rate of about 5 BV/h (20 mL/min) until the effluent pH is about 3.5. This pH is usually achieved after about 5 BV of wash has passed through the bed. After the washing is complete, drain the residual solution in the column until the liquid level is 20 to 30 mm above the resin bed.

If the column has been precalibrated for volume measurements, record the resin volume. If the column has not been precalibrated, mark the resin level on the column so that the exact resin volume can be determined after completion of the test.

The resin is now fully eluted-regenerated to the desired ionic form and has been rinsed free of the eluant-regenerant. The column is now ready to start the adsorption step.

Adsorption—Start the feed solution flow to the column to give the desired effluent rate of 5 BV/h (20 mL/min). In hydrometallurgical operations, this point is considered to be the start of the adsorption cycle, even though the resin bed at this time is still in contact with wash solution. Effluent samples are collected so that a plot of effluent grade versus effluent volume (breakthrough curve) can be generated. The effluent volume is usually expressed in terms of bed volumes. Samples can be collected on either a volume or time basis. If the volume basis is used, the samples can be collected manually using graduated cylinders or other volumetric containers. If an increment sampling device is used, the samples are collected periodically using time increments that will reflect the number of bed volumes desired for each sample. Measuring the actual volume of each increment sample collected will provide the most accurate basis for plotting the breakthrough curve. The appropriate increment sample volume will depend on the particular ion-exchange system being used. For uranium-leach solutions, increments equivalent to 1 or 2 BV will nearly always produce a sharp definition of the breakthrough point. This means that if each sample contains 2 BV of effluent, the initial samples can be composited to reduce the analytical requirements. Alternatively, only every 10th or 20th sample is analyzed to identify the general breakthrough area, and then additional samples from this area are analyzed to define the specific breakthrough and maximum loading points.

During initial breakthrough tests, the total volume of increment samples collected should contain at least twice the quantity of metal ion that will be adsorbed by the ion-exchange resin. For example, if literature references or exploratory adsorption tests indicate a potential saturation loading of 80 g/L U_3O_8, at least 160 BV of 1-g/L U_3O_8

feed solution should be passed through the column. If a rapid analytical technique is available, these analyses can be valuable guides for estimating the breakthrough and saturation points, even if the analytical results are only approximations. For some metals, analytical references should be consulted to determine if spot tests are applicable.

After the adsorption period is completed, the residual feed solution should be washed from the resin bed by passing deionized water through the bed at the rate of about 5 BV/h (20 mL/min) until the effluent pH is about 3.5. This usually requires no more than 5 BV of wash water. Following the wash, the column should be backwashed for about 5 to 10 min with deionized water at a flow rate sufficient to give at least a 50% bed expansion (approximately 50 mL/min for the 25-mm-ID column). The purpose of this backwash is to eliminate any fines or dirt that may have collected on the surface of the resin bed. Drain the supernatant water in the column until the liquid surface is 20 to 30 mm above the resin bed. Mark the resin-bed height on the column, or if the column has been precalibrated, record the resin volume. The column is now ready for the elution-regeneration step.

Elution-regeneration—The uranium is eluted from the resin bed by passing 8 BV of the eluant (0.9*M* NaCl plus 0.1*M* HCl) through the resin bed at a rate of 2.5 BV/h (≈ 10 mL/min). The 8-BV quantity was chosen based on literature references and recommendations from resin manufacturers. Column effluent samples are collected so that a plot of eluate grade versus volume (elution curve) can be generated. The general technique for collecting these samples is equivalent to that described in the preceding section "Adsorption." During the initial experiments, eluant samples are typically collected in increments representing no more than 0.5 BV. If suitable rapid analytical techniques or spot tests are available, this approach should be used to help determine the elution end point.

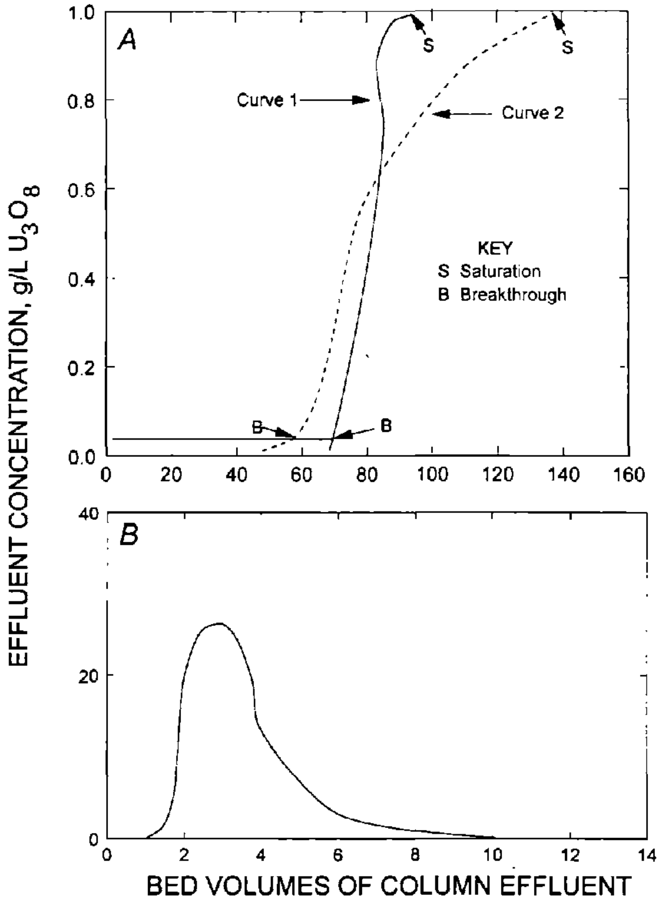
The residual eluant is washed from the resin bed by passing deionized water through the bed at a rate of about 5 BV/h (20 mL/min) until the effluent pH is about 3.5. After the washing is complete, the residual supernatant solution is drained from the column until the liquid level is 20 to 30 mm above the resin bed.

If the column has been precalibrated for volume measurements, the resin volume is recorded. If the column has not been precalibrated, the resin level is marked on the column so that the exact volume can be determined after completion of the test. In most instances, the resin volume determined at this point in the ion-exchange cycle is used as the basis for calculating the resin loadings and other determinations related to resin- bed volume.

5.2.5.3 Data Presentation (Single-Column Tests)

The analytical data and the volume measurements derived from the adsorption and elution tests are used to plot breakthrough and elution curves. These curves become the basis for evaluating the resin loading and elution efficiency under the test conditions used. Figure 5.9 illustrates typical adsorption (breakthrough) and elution curves. The three most significant factors of the breakthrough curve are (1) the breakthrough volume (points B, figure 5.9*A*, (2) the saturation volume (points S, figure 5.9 *A*), and (3) the steepness of the curve after breakthrough occurs. The steepness of the curve determines the ratio of the breakthrough volume to the saturation volume. If this ratio is greater then 50%, then it may be possible to use a two-column series operation (see section 5.2.5.4). Under these conditions, the first column in the series would reach saturation before breakthrough occurs from the second

Figure 5.9

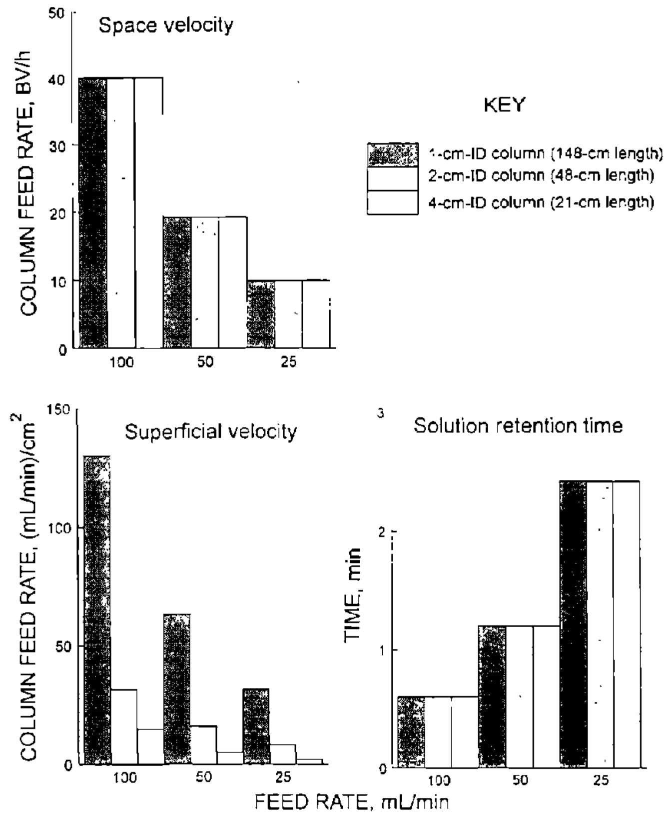


Typical breakthrough (A) and elution (B) curves.

column. Maximum uranium loading would be achieved together with minimal uranium-loss because of early breakthrough from the second column. Curve 1 of figure 5.9*A* illustrates this type of breakthrough curve. Curve 2 of figure 5.9*A* illustrates a loading relationship that does not meet this criteria. Preventing appreciable breakthrough losses of uranium would require either operating at less than saturation capacity or using a three-column loading system. Both of these options increase costs because they require a larger resin inventory. Decreasing the feed rate may also be effective, but this also increases costs. Therefore, column loading experiments usually investigate the effect of solution feed-rate variations on the adsorption efficiency of one or more ion-exchange resins.

A number of different terms have been used in the ion-exchange literature to express and correlate the effect of feed-rate variations on column performance. These terms include expressions such as "bed volumes of feed solution per hour" and "gallons per minute" of feed solution per square feet of column cross-sectional area. For example, if a laboratory column contains 150 mL of resin and the feed solution input rate is 50 mL/min, the feed rate is equivalent to 20 BV/h. The bed volume per hour term can be classed as a space-velocity relationship, which is defined as the volumes of feed solution per unit time per total volume of resin in the column. This relationship expresses the volumetric feed capacity of an ion-exchange column and is independent of all units except time. The "gallons per minute per square foot" (milliliters per minute per square centimeter), expression has also been used, but this superficial velocity term is dependent not only on time but also upon other variables such as column diameter. Figure 5.10 illustrates the relationships between column feed rate, in bed volumes per hour and milliliters per minute per square centimeter, and retention time for 1-, 2-, and 4-cm-ID laboratory columns, each containing 150 mL of resin. For most ion-exchange investigations, expressing the feed rate as bed volumes per hour is desirable because this term is also inversely related to the solution retention time in the column.

Figure 5.10



Comparison of column feed-rate expressions (resin bed volume = 150 mL at 40% void volume).

When the eluate concentration is plotted versus bed volume data from the elution operation, a curve such as that shown in figure 5.9*B* is obtained. This curve shows a shape typical of what would be obtained with the 0.9*M* NaCl plus 0.1*M* H_2SO_4 eluant solution used in this example. Other eluant concentrations or eluant reagents can produce significantly different curves. In general, the primary objective is to obtain a fast, efficient elution that recovers the uranium in a small volume of eluate while removing essentially all of the uranium that was loaded on the resin. If complete uranium removal is not achieved, early uranium breakthrough may occur during the next adsorption cycle. Typically, the elution end point is designated as the point where the eluate concentration decreases to approximately 0.1 g/L U_3O_8. A minimum "tail-off" of the elution curve is desirable.

Most fixed-bed column operations have used a "split-elution" technique. Evaluation of the elution data often indicates that the first half of the eluate contains 90% or more of the uranium. If the remaining half of the eluate is recycled (after readjusting the reagent concentration), essentially all of the uranium is recovered in approximately half of the total elution volume. This technique can produce appreciable reagent savings in both the elution and subsequent uranium precipitation operations.

A second split-elution technique involves dividing the elution column effluent into three irregular portions. The central portion, which constitutes approximately 50% of the total effluent, is transferred to the subsequent processing operation. The two remaining portions are recycled.

5.2.5.4 Multiple-Column Tests

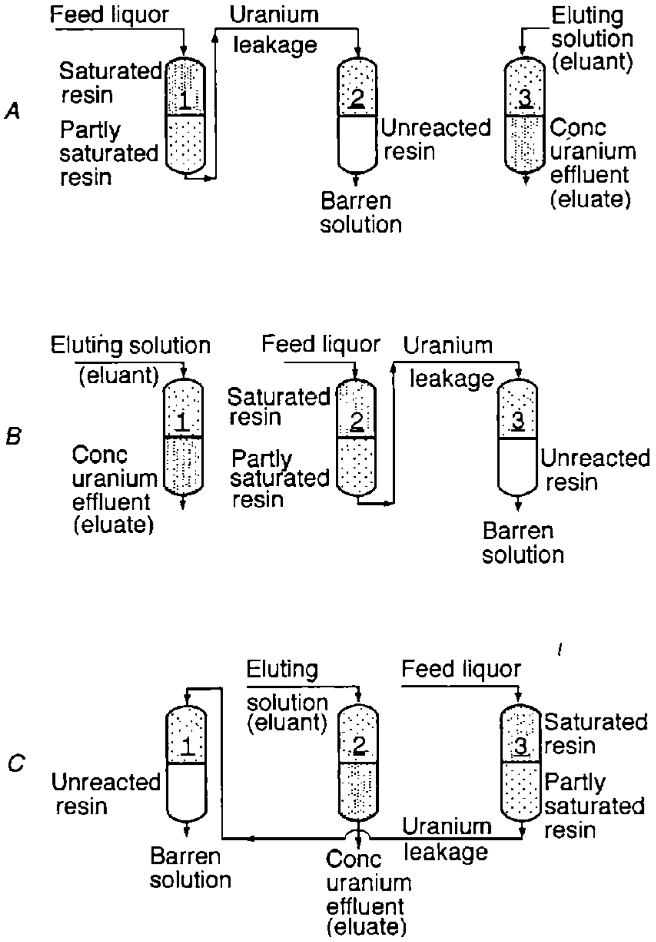
Most hydrometallurgical fixed-bed ion-exchange operations have used what has been termed the "merry-go-round" technique. This procedure involves the sequential operations of a three- or four-column loading and elution system. Figure 5.11 illustrates the steps of a three-column merry-go-round operation (International Atomic Energy Agency, 1990). The operational sequence for a typical uranium-recovery system using a split-elution technique is as follows:

1. Clarified feed liquor from the uranium-ore-leaching operation is fed to columns 1 and 2, which are connected in series (figure 5.11*A*). The first bed volume of water displaced from column 2 is mixed with the backwash water used in step 5.
2. The feed-liquor flow to column 1 is shut off when breakthrough occurs on column 2. Normally, breakthrough is defined as the point when the uranium concentration in the effluent reaches 1% to 2% of that in the feed liquor.
3. The residual feed liquor in column 1 is displaced to column 2 by passing 1BV of water through column 1.
4. Next, column 1 is disconnected from the series flow, and column 2 is connected to column 3, which contains freshly eluted resin. The valving system then directs the feed-liquor flow to column 2 (figure 5.11*B*).
5. Column 1 is backwashed with 2.5 to 3.0 BV of 1.5 pH wash water. The effluent from this backwash is collected separately. After the resin has settled, the column is drained until the liquid level is just above the top of the resin bed. The wash water remaining in the resin bed is displaced by feeding 1 BV of recycle eluant to the column. The effluent from this displacement is combined with the backwash effluent, and the total volume is sampled and analyzed for material-balance determinations.
6. The flow of recycle eluant to column 1 is continued until approximately 11 BV of high-grade eluate has been collected. (The optimum volume depends on variables such as resin characteristics and the elution conditions as determined by single-column tests.)
7. The high-grade eluate remaining in the column is displaced by feeding 1 BV of fresh eluant (e.g., $0.9M$ NaCl plus $0.1M$ H_2SO_4) to column 1. The effluent from this displacement is added to the previous 11 BV to give a total of 12 BV of high-grade eluate, which is transferred to the yellow cake precipitation operation.
8. The flow of fresh eluant to column 1 continues until 11 BV of recycle eluate has been collected.
9. The recycle eluant remaining in the bed of column 1 is displaced by feeding 1 BV of wash water to the column and combining this effluent with the other 11 BV recycle eluant to give a total of 12 BV for the next split-elution cycle.
10. One additional bed volume of wash water is passed through column 1 to prepare the column for the next loading cycle. The effluent from this washing is collected and analyzed for material-balance calculations.

After breakthrough occurs from column 2 (figure 5.11 *B*), column 2 is disconnected from the series flow and column 3 is connected to column 1, which contains freshly eluted resin. The valving system then directs the feed liquor to column 3 (figure 5.11*C*).

Figure 5.12 illustrates a typical piping and valve arrangement for a three-column ion-exchange system. This

Figure 5.11



Sequential operations of a three-column ion-exchange system using "merry-go-round" procedure. A, Columns 1 and 2 adsorption loading and column 3 on elution; B, columns 2 and 3 on adsorption and column 1 on elution C, columns 3 and 1 on adsorption and column 2 on elution. (Indicated resin loadings are for a partially completed cycle.)

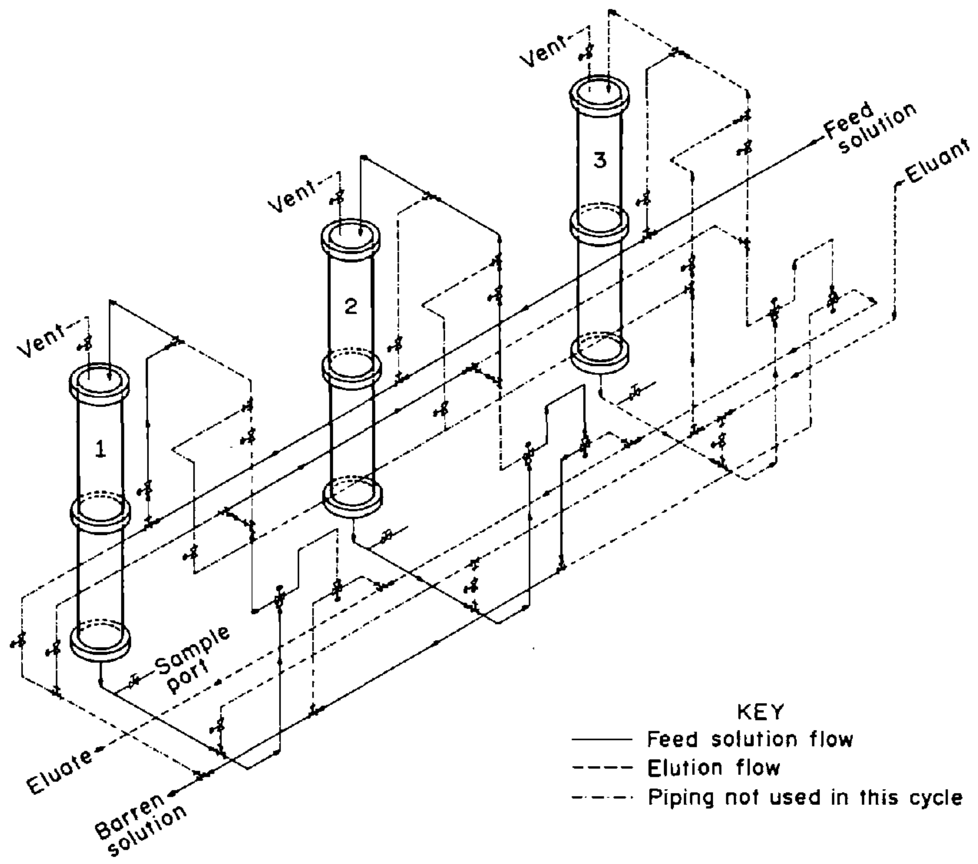
manual system contains 6 three-way valves and 20 one-way valves. Either glass or plastic stopcocks have proven satisfactory for most bench-scale systems that use 25-mm-ID columns. Plastic ball valves have been used successfully for larger systems (Altringer and others, 1985). The heavy lines in figure 5.13A) depict the feed solution flow pattern when columns 1 and 2 are on adsorption. The simultaneous elution flow pattern for column 3 is illustrated by the heavy lines in figure 5.13B).

5.2.6 Safety

The material safety data sheets (MSDS) (see chapter 1, section 1.2.4.10) for nearly all ion-exchange resins list the resins as "NOT OSHA HAZARDOUS," and the Department of Transportation hazard class is "NONREGULATED." Nevertheless, the MSDS for each resin should be studied before using the resin. In general, the MSDS indicate that eye contact can produce various degrees of irritation, and some resins may be moderately irritating to the skin. Other cautions include the following:

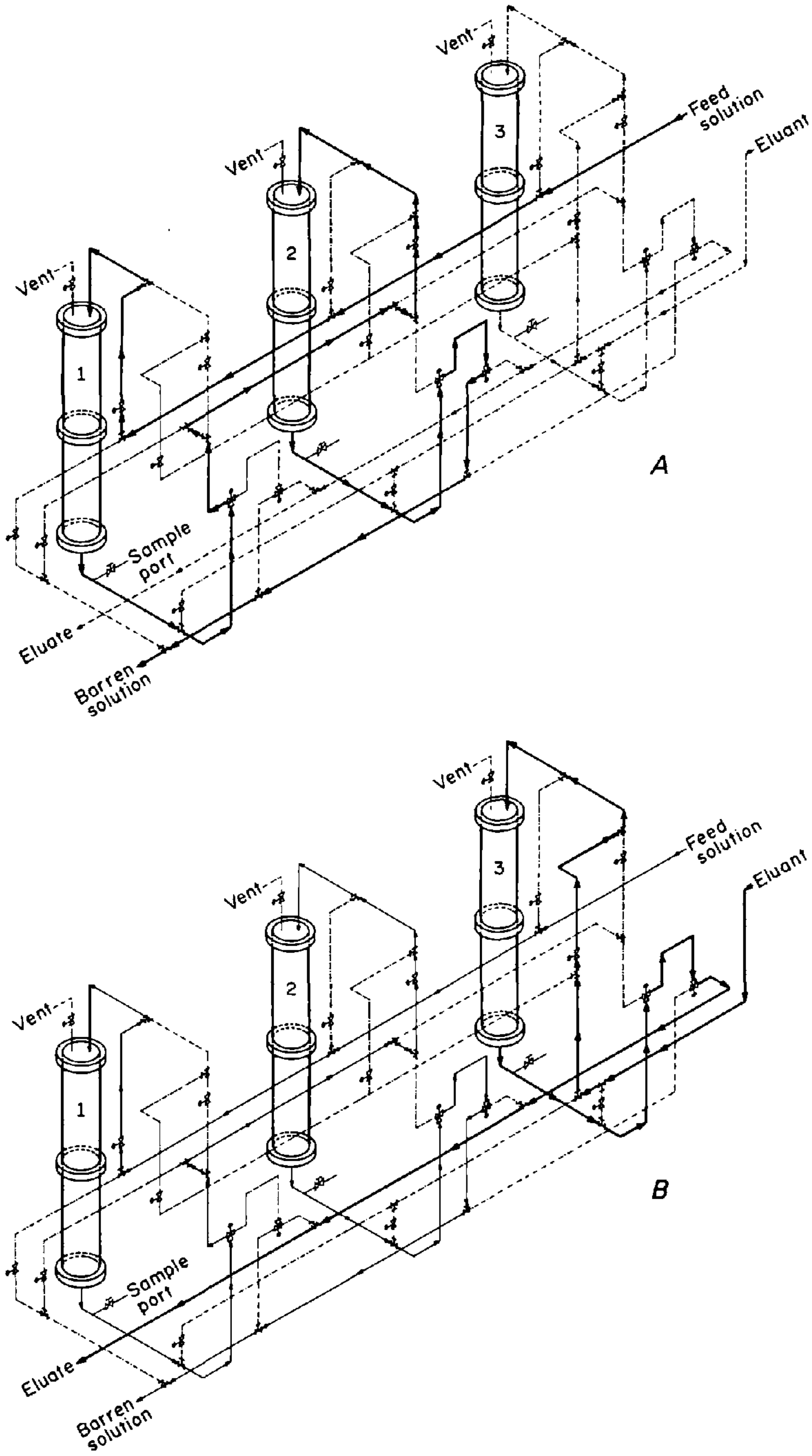
- Keep floors and other surfaces free of ion-exchange resin beads. The beads behave as plastic ball bearings and may cause accidents, e.g., falls.
- Do not pack resin columns with dry beads. When wetted, the resin beads swell and can cause a glass column to shatter. Always fully hydrate the resin before charging it to the column, and never allow the column to become dry.
- When ion-exchange resins are contacted with nitric acid or other strong oxidizing agents, explosive-type reactions can occur. Before contacting ion-exchange beads with strong oxidizing agents, consult the resin manufacturer or other sources knowledgeable in handing these materials. Also, if use of an oxidizing agent such as nitric acid is contemplated, the ion-exchange equipment must be designed to prevent any rapid buildup of pressure in the system.

Figure 5.12



Typical piping and valve arrangement for a three-column ion-exchange system. (Columns 1 and 2 are on adsorption [loading] and column 3 is on elution.)

Figure 5.13



Flow patterns for adsorption (A) and elution (B). (Columns 1 and 2 are on adsorption [loading] and column 3 is on elution.)

Before ion-exchange experiments are conducted, preparation of a job safety analysis (JSA) is always prudent (see chapter 1, section 1.2.5.3). For example, toxic ions, such as heavy metals, arsenates, chromates, or cyanide, may be present in the feed solutions, and the ion-exchange process may significantly concentrate these ions. Also, the acidic or basic elution-regeneration solutions are usually corrosive and should be handled in a manner that will prevent any skin or eye contact.

Some MSDS indicate that the waste resin can be disposed of as ordinary trash, but others specify incineration according to current local, State, and Federal regulations. Therefore, the MSDS for each resin must be consulted for proper disposal.

5.3 CARBON ADSORPTION

Activated carbon has been used for both gas-phase and liquid-phase adsorption (Baker and others, 1992). Gas-phase adsorption has found its principal application in operations such as the recovery of organic solvents and petrochemical processing. Liquid-phase applications include potable-water treatment, industrial and municipal waste-water treatment, decolorization, industrial chemical production, and food processing. Many of these applications involve the removal of organic contaminants. The principal application of carbon adsorption in hydrometallurgical operations has been the recovery of gold and silver from cyanide leach solutions (Heinen and others, 1978; Hussey and others, 1978, 1979; Potter, 1981; Schlitt and others, 1981; and USBM, 1986). The general process consists of leaching with a cyanide solution, adsorption of the precious-metal-cyanide complex on activated carbon, stripping of the precious metal from the carbon with a caustic solution, and precipitation of the gold from the strip solution. The stripped carbon is thermally reactivated and recycled to the adsorption step.

Other applications and potential applications include waste-water treatment and solution purification within hydrometallurgical processing operations. Under controlled conditions, molybdenum, tin, and antimony are appreciably absorbed. Other metals such as lead, iron, nickel, zinc, and cadmium usually show lower absorptions (Fischer and others, 1975; Lee and others, 1966; Sigworth 1962; and Singer, 1979).

Commercial activated carbons are available in a wide variety of forms and particle sizes. Precursor raw materials include substances such as coal, peat, lignite, wood, nut shells, petroleum coke, pitches, and sugar. Both thermal and chemical activation processes are used. The properties of the resulting activated charcoal depend primarily on activation conditions and the characteristics of the precursor. Companies that produce activated carbon products in the United States include the following:

American Norit Co., Atlanta, GA.
Anticarb Division of Royal Oak Enterprises, Romeo, FL.
Barneby and Sutcliffe, Columbus, OH.
Calgon Carbon Corp., Pittsburgh, PA.
Ceca Division of Atochem NA, Pryor, OK.
Trans-Pacific Carbon, Blue Lake, CA.
Westvaco Corp., Covington, VA.

Essentially all of these companies can provide information and advice on both selecting and evaluating their products for potential applications.

The following references present information on carbon adsorption theory, activation technology, applications and test data interpretation: Baker and others (1992); Bansal and others (1988); Cheremisinoff (1993), Cheremisinoff and Ellerbusch (1978); Culp and others (1980); Gerhartz and others (1986); Gregg and Sing (1982); Hassler (1963, 1974); Hutchins (1980); Slejko (1985); and Treybal (1968, pp. 490-568).

5.3.1 Test Procedures

The laboratory test procedures used to evaluate activated carbon adsorption are analogous to those described in the previous sections on ion exchange. The following sections summarize the general procedures for both batch and small-column carbon adsorption tests. Batch tests are used primarily to screen and select the most promising carbons for hydrometallurgical applications. Pulverized carbon is used, and Freundlich isotherms are used to correlate the data. The most promising carbons are then tested in small columns, using granular carbon. The objective of these tests is to provide a more accurate comparison of the carbons and developed data for scaleup and cost evaluations.

The procedures summarized below have been adapted from the following more detailed references: American Norit (1981); ASTM (1980, 1989); Fornwalt and Hutchins (1966, 1966b); and ICI Americas (1972).

5.3.1.1 Batch Testing

Batch carbon adsorption tests are usually carried out using pulverized granular carbons. The test conditions (temperature, pH, etc.) should duplicate the projected operating conditions as closely as possible. If the feed liquor contains suspended solids, clarification by filtration or flocculation is recommended. The following steps outline a procedure for an exploratory series of batch adsorption tests using 100-g clarified feed solution samples.

- Pulverize a representative 20-g sample of the granular carbon to be tested. Most manufacturers recommend that the carbon be stage ground until all it passes a

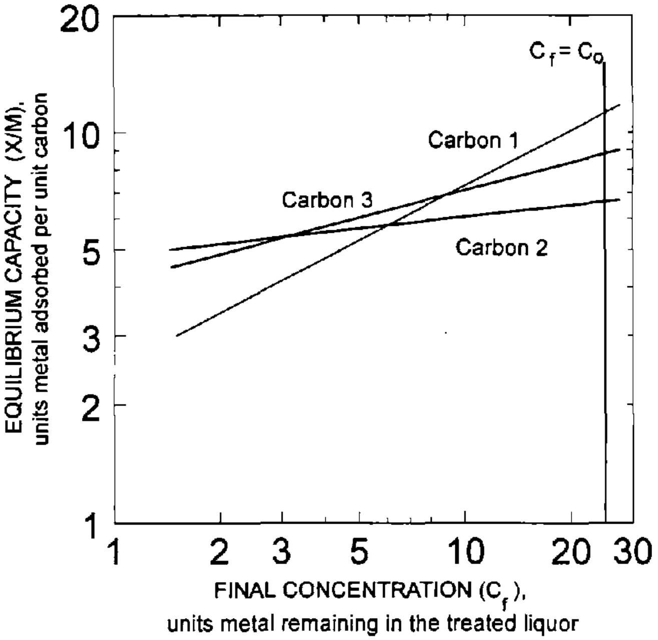
325-mesh screen. If more than one carbon is to be tested, the pulverizing procedure should be identical for all materials.

- Measure 100 g of the clarified feed solution into each of five 250-mL Erlenmeyer flasks. Add varying amounts of the pulverized carbon being tested to each of these flasks. Typical dosages for an initial series of tests are 0 (blank), 1, 2, 3, and 4 g. If this set of dosages does not produce the desired degree of adsorption, repeat the entire procedure using an appropriate range of carbon additions. To facilitate the subsequent filtration operation, approximately 5 cm^3 (one level teaspoon) of a suitable filter aid may be added to each flask. The filter aid must also be added to the blank.
- Vigorously agitate the flasks for 60 min at the desired temperature to achieve uniform mixing. Adjustable-speed orbital shakers have been found to be suitable agitation devices. The 60-min contact time is adequate for most batch tests, but if an entirely unknown system is being investigated, conducting batch kinetic tests such as those described in section 5.2.4 is prudent.
- After the appropriate agitation period has been completed, filter off the carbon without any washing, and submit the resulting filtrates for analysis. The amount of metal or other substance adsorbed by each carbon addition is determined by difference based on the feed and product analyses from each test.
- Plot the equilibrium carbon capacity (units of metal or other substance absorbed per unit of carbon = X/M) versus the final solution concentrations (units of metal or other substance remaining in the treated liquor = C_f) on log-log paper. Analyses from the 0 (blank) standard are used to make any necessary corrections of the raw data. With low concentrations, the absorption tests require utmost care. All glassware and filter papers should be thoroughly washed with distilled water before the tests are started. Any cross contamination may seriously bias test results.

Figure 5.14 illustrates typical plots of Freundlich adsorption isotherms for three different carbons. The relative effectiveness of the carbons tests is determined by extrapolating each adsorption isotherm until it intersects a vertical line that defines the concentration of the metal or other substance in the feed liquor (C_o), i.e., $C_f = C_o$. The carbon with the highest adsorption capacity (carbon 1) is the most favorable absorber under the conditions tested (ASTM, 1989; Fornwalt and Hutchins, 1966a; and Hutchins, 1973).

Batch tests can also be used to evaluate granular carbon materials, but appreciably longer contact times may be necessary. The longer contact times can be particularly important when treating very dilute feed solutions. Batch kinetic tests in which solution samples are withdrawn from the carbon-solution mixture at predetermined times are usually required before equilibrium studies can be conducted. This type of batch testing has been used to establish baseline equilibrium-contact time relationships for continuous countercurrent systems such as those used for the carbon-in-pulp recovery of gold and silver from cyanide leaching operations (Hussey and others, 1978, 1979; and Laxen, 1984).

Figure 5.14



Typical Freundlich adsorption isotherms for three activated carbons.

5.3.1.2 Column Testing

The general equipment arrangements and procedures for activated carbon performance tests in columns are analogous to those described for ion-exchange resin testing in section 5.2.5.2. Potential differences and cautions are outlined below.

Column size—The laboratory column diameters and bed depths recommended by the various producers of activated carbon products vary considerably. Minimum inside diameters range from 2.5 to 10 cm, and suggested minimum bed depths range from 60 to over 100 cm. Wall effects can become particularly critical when the coarser grades of carbon are used. The smaller diameter columns also require more precise control of the solution feed rates.

Column preparation—Most carbon producers indicate that meaningful breakthrough tests can be conducted using virgin activated carbon. Avoiding air entrapment in the column bed is critical because air bubbles in the bed will produce short circuiting, which can significantly reduce adsorption capacity. Air entrapment can be minimized by slurrying the carbon in hot water, boiling for 10 min, and cooling the slurry to room temperature. The cooled carbon slurry should immediately be wet bedded into the column using a procedure equivalent to that illustrated in figure 5.8. Any residual bubbles are removed by backwashing. This usually requires a backwashing rate that produces a 25% to 50% bed expansion for 2 to 5 min. Data on the relationship between bed expansion and backwashing rates are ordinarily listed in the carbon specifications supplied by manufactures. The backwashing operation also removes any residual fines that might restrict solution flow through the bed.

Activated carbon capacities are customarily expressed in terms of amount adsorbed per unit weight, whereas column size calculations are based on bed volume. Therefore, measurements on both the weight and volume of carbon charged to the column are required. Since activated carbon does not swell or shrink appreciably during loading, continuing volume measurements, such as those required for ion-exchange resins, are usually not necessary.

Adsorption—Column adsorption tests, which are sometimes referred to as "exhaustion tests," are most often conducted to compare the adsorptive capacity of several different activated carbons and develop design data for scaleup. Experience demonstrates that solution residence time is the major design parameter. For a given solution, other variables include pH, temperature, and superficial velocity (linear flow rate) through the column. Table 5.1 lists a suggested range of space velocities, residence times, and superficial velocities that are often applicable for the initial series of column loading tests. The 3- and 30-(mL/min)/cm^2 superficial velocities are respectively equivalent to 0.75- and 7.5 gpm/ft^2 superficial velocity expressions. (The terms "superficial velocity" and "linear flow rate" are often used interchangeably in the activated carbon adsorption literature.)

Table 5.1—Suggested ranges of retention time and corresponding solution feed rates for initial column adsorption tests

Space velocity, BV/h	Residence time,[1] min	Superficial velocity,[2]	
		(mL/min)/cm^2	gpm/ft^2
3	10	3	0.75
30	1	30	7.5

[1] For a 0.5 fractional void volume in bed of granular activated carbon.

[2] For 300 mL of granular activated carbon in 2.5-cm-ID column.

Some of the primary reasons that unreliable results are obtained in small-scale column tests include the following:

- Testing at unreasonable residence times.
- Testing at unreasonable solution feed rates.
- Unrepresentative feed solutions.
- Using columns with less than 2.5-cm diameters.
- Short runs.

Checking the general literature and consulting producers of activated carbon before defining a test program is always prudent.

Stripping—In hydrometallurgical operations, such as the adsorption of gold from cyanide leach solutions by activated carbon, the term "stripping" has been commonly used to designate the operation of desorbing the gold-cyanide complex from the carbon. The literature has also used the term "chemical regeneration," in particular for operations such as the desorption of chromium from activated carbon. Both of these operations use caustic solutions.

Both gold and silver may be stripped from activated carbon by contacting a column of loaded carbon with a stripping solution containing about 1% NaOH and 0.1% to 0.2% NaCN. The time required is strongly temperature dependent. At a temperature of about 90 °C, the required contact time normally ranges from 48 to 72 h. If the stripping is conducted at 120 to 140 °C in a pressurized column, the required contact time decreases to less than 6 h, when the feed rate is controlled at about 0.8 BV/h. The column pressure vessel will require a 100-psi (70,000-kg/m^2) rating, and the preferred material of construction is 316 stainless steel. A description of laboratory procedures for both atmospheric and pressure stripping of gold from activated carbon has been presented by Ross and others (1973). Greaves and others (1991) have reported on both the loading and elution of metallic gold from activated carbon.

After the recovered metal or other component has been chemically stripped from the carbon, thermal activation may be required to restore the adsorption capacity of the carbon. For example, after the gold has been stripped as described above, the carbon can be reactivated by a two-step procedure that consists of acid washing followed by heat treatment. The carbon is rinsed with water to remove any residual caustic and then contacted with a dilute nitric acid (5% or more). A contact time of about 1/2 h is usually sufficient, and the operation should be conducted in a hood to collect any dangerous fumes. After the acid contact, the carbon is given a water rinse. The damp carbon is then transferred to a nearly sealed container and heated to at least 625 °C for approximately 30 min. The hot carbon is then quenched in water or air. After screening to remove fines, the reactivated carbon is ready for recycle to the adsorption step.

5.3.1.3 Data Presentation (Column Tests)

Procedures for correlation and interpretation of the experimental data derived from column tests are generally equivalent to those discussed in section 5.2.5.3. The shape of the breakthrough (exhaustion) curves indicates whether single- or multiple-column arrangements may most efficiently achieve the desired separations. Specific procedures for evaluation of the data from column tests are described in the following references (Fornwalt and Hutchins, 1966a, 1966b; and Hutchins, 1973). The 1973 article by Hutchins describes in detail the bed-depth/service-time (BDST) procedure, which can be applicable for hydrometallurgical and waste-water treatment applications. The technique involves determining the breakthrough points for three or four different bed depths at a given feed rate. Results derived from the BDST analysis can be used as a means for predicting the effect of different feed rates, feed concentrations, or effluent compositions.

An alternative concept for mass-transfer zone design has been discussed by Lukchis (1973). This technique was originally suggested by Michaels (1962) for considering rate phenomena in fixed-bed ion-exchange systems. This concept also utilizes breakthrough curves to evaluate the conditions within the adsorption zone as it moves down the fixed-bed column under steady-state operating conditions.

Discussions with the activated carbon manufacturers can be particularly helpful when evaluating the performance of a given activated carbon. The manufacturers often have at least generalized data on a wide variety of applications for the specific carbon being tested.

5.3.2 Safety

Activated charcoal is listed under the MSDS heading of "Charcoal (Activated)." Although activated charcoal itself is not considered to be toxic, during hydrometallurgical or waste treatment operations it may adsorb toxic substances and under these circumstances should be considered as a potentially toxic material. Also, charcoal dust can be irritating to the eyes and the respiratory tract.

Charcoal dust can be an explosion hazard when exposed to heat or flame; therefore, dust-tight electrical systems should be used in areas where activated carbon is present, particularly powdered products. The MSDS also cautions that activated carbon may react vigorously or violently (with an explosion) when mixed with strong oxidizing agents, especially when heated. All aspects of the MSDS should be carefully reviewed.

Before experiments on activated carbon adsorption are conducted, experiments preparation of JSA is always prudent (see chapter 1, section 1.2.5.3). For example, toxic ions such as cyanide, heavy metals, arsenates, or chromates may be present in the feed solutions. The adsorption process may significantly concentrate these ions. The relative MSDS information on all solution components and waste disposal requirements should be consulted as part of the experimental planning process.

5.4 SOLVENT EXTRACTION

5.4.1 Introduction

The following sections present information on techniques and procedures for bench-scale solvent extraction experiments. The presentations focus on equipment and techniques appropriate for initiating an experimental program. The approach assumes that the researcher conducting the investigation has studied the related literature but has limited experience in the specific experimental procedures. The techniques described provide a starting point for solvent-extraction investigations, and the procedures are based on the assumption that the objective of the experimental studies is to develop a solvent-extraction process for recovering a particular metal or metals from a specific aqueous feed solution.

Over the years, the term "solvent extraction" has acquired a number of different meanings. For example, the third edition of Perry's Chemical Engineers' Handbook (1950) defines solvent extraction as those operations in which the separation of different mixtures of substances is accomplished by treatment with a selective liquid solvent. This definition applies to liquid-liquid and also to solids-liquid separations such as ore leaching and the solvent recovery of oils from seeds and other vegetable materials. As practiced in hydrometallurgical or related waste treatment operations, however, the term is used primarily to designate the separation of one or more metallic solutes from a mixture by mass transfer between two liquid phases that are immiscible and at least one of which is an organic liquid. Other uses of solvent extraction, such as acid recovery systems, may have potential for some hydrometallurgical operations, but general applications have not yet materialized.

The mass transfer in hydrometallurgical solvent extraction is defined by reversible reactions such as the following:

$$(Cu^{2+} + SO_4^{2-})_{(aq)} + (2R\text{-}H)_{(org)} \rightarrow (R_2Cu)$$
$$+ (2H^+ + SO_4^{2-})_{(aq)},$$

where the subscripts "(aq)" and "(org)" refer to the aqueous and organic phases, respectively, and (2R-H) represents a hydroxyoxime extractant. The left-to-right direction depicts the cation-extraction mass transfer during the extraction step, and the right-to-left direction represents the stripping-step mass transfer.

Solvent-extraction separations can also be based on anion transfers such as that shown in the following equation:

$$(FeCl_4^-)_{(aq)} + (R_2NH_2Cl)_{(org)} \rightarrow (R_2NH_2Fe\ Cl_4)_{(org)}$$
$$+ (Cl^-)_{(aq)}$$

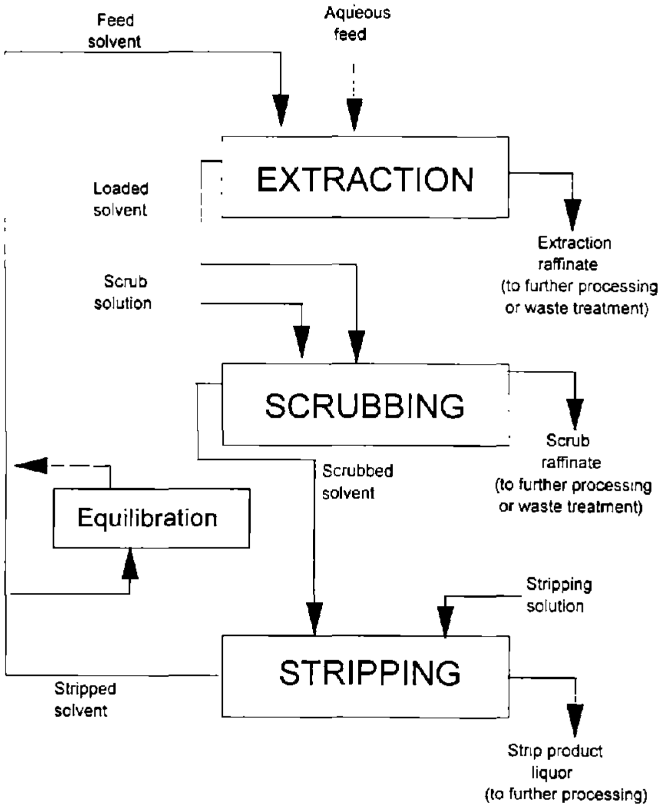
where "$(R_2NH_2Cl)_{(org)}$" represents a secondary amine extractant. Again, the left-to-right direction represents extraction and the right-to-left illustrates a potential stripping reaction. Both of these solvent-extraction examples are considered further in section 5.4.4.

Other stripping techniques are also possible. For example, one possible alternative uses a two-step stripping sequence. First, the metal values are stripped by a reaction that differs from the right-to-left reversal illustrated above, and this step is followed by a second reaction that regenerates (equilibrates) the solvent for recycle.

Figure 5.15 presents a schematic version of a typical hydrometallurgical solvent-extraction flowsheet. The metal-bearing feed solution is fed to the extraction step, where it is mixed with the feed solvent. The metal species transfers to the organic phase during the extraction step, which is usually a multistage operation using countercurrent flow of the aqueous and organic phases. After each mixing stage, the phases are allowed to separate. The raffinate, which is the barren aqueous phase from the extraction operation, may be at least partially recycled, treated for the recovery of other values, or transferred to waste treatment. Typically the loaded solvent, which contains the metal values, is scrubbed to remove impurities and then fed to the stripping operation. Examples include removing the nickel coextracted with cobalt during an organophosphate cobalt-recovery process (Ritcey and Ashbrook, 1979, pp. 13-15) and scrubbing manganese from a cobalt-rich solvent obtained by an amine-extraction technique (Redden and others, 1988, p. 18).

During stripping, the metal values in the loaded solvent are recovered into an aqueous phase by contact with an appropriate stripping solution. The strip product solution goes on to further processing for metal production. The stripped solvent recycles to the extraction circuit. In some instances the stripped solvent may require regeneration or equilibration with a suitable treatment solution to convert the solvent to the form required for the extraction operation.

Figure 5.15



Schematic flowsheet of typical hydrometallurgical solvent-extraction process.

Discussions with solvent-extraction reagent suppliers can be particularly helpful when planning solvent-extraction studies. Suppliers can provide a broad scope of information, including data on physical properties, chemical properties, handling procedures, and application information. The following is a partial list of suppliers that offer solvent-extraction reagents applicable to both hydrometallurgical and waste treatment systems.

Albright & Wilson Americas, Richmond, VA.
American Cyanamid Co., Wayne, NJ.
Daihachi Chemical Industry Co. Ltd., New York, NY.
Henkel Corp., Tucson, AZ.
Hoechst Aktiengesellschaft, Frankfurt am Main, Germany.

Mobile (Chemical Products Div.), Richmond, VA.
Rhone Poulenc (Basic Chemicals Co.), Shelton, CT.
Sherex Chemical Co., Inc., Dublin, OH.
Zeneca Specialties (Acorga Mining Chemicals), Phoenix, AZ, and Wilmington, DE.

In addition to giving technical data on the solvent-extraction reagents they supply, most of the companies listed also offer literature on solvent-extraction principles, applications, and laboratory techniques.

Variables and parameters that require investigation during a study of solvent-extraction process development may include the following: extractant type and concentration, diluents, modifiers, pH, temperature, and extraction and stripping contact times. In some instances, other components of the overall process may essentially fix some variables such as feed solution temperature or pH. When this occurs, the process developed must accommodate these restrictions.

The general literature on hydrometallurgical solvent extraction has become extensive and covers many special applications. The following selected references contain information on solvent-extraction theory, principles, and waste treatment technology related to hydrometallurgical operations: Alegret (1988), Blumberg (1988), Bridges and Rosenbaum (1962), Hazen (1985), Lo and Baird (1980), Ritcey and Ashbrook (1979, 1984), Robbins (1984), and Thornton (1992).

Definitions of the specialized terms used throughout section 5.4 are presented in the following section (5.4.2) on solvent-extraction terminology.

5.4.2 Solvent-Extraction Terminology

Literature references have used a number of terms, such as "solvent extraction," "liquid ion exchange," and "liquid-liquid extraction," to denote the mass transfer of metallic solutes between two immiscible liquid phases in hydrometallurgical operations. The term "solvent extraction" is used in the subsequent descriptions of experimental techniques. The following list presents definitions of additional terms that relate to hydrometallurgical applications of the solvent-extraction process (Bridges and Rosenbaum, 1962, pp 35-38; Rice, 1981; Ritcey and Ashbrook, 1984, pp. 342-345). Figure 5.16 also illustrates the nomenclature of the hydrometallurgical solvent-extraction process.

Antagonism—Suppression of extraction caused by using a combination of extractants or diluents; antonym of synergism. (Some early literature used the term "anti-synergism," but the term "antagonism" is preferred.)

A/O ratio—The ratio of the aqueous phase volume to the organic phase volume; may also be expressed as O/A ratio.

Aqueous feed—The aqueous feed solution to the extraction stage that contains the metal or metals to be extracted. The term "pregnant leach solution" has also been used.

Back extraction—See stripping.

Back mixing—Deviation from an ideal or plug flow pattern in a contactor such as a pulse column.

Coalescence—Growth or combination of small dispersed droplets into larger drops.

Contactor—A single stage or multistage device for dispersing and disengaging immiscible solution mixtures; the term includes mixer-settlers, columns, and certain centrifuges.

Continuous phase—The coherent phase in a contactor; i.e., the bulk component that contains droplets of the dispersed component in a mixture of two immiscible solutions.

Countercurrent extraction—Multistage extraction in which the aqueous and organic phases flow in opposite directions.

Crosscurrent extraction - Treatment of a batch aqueous solution by repeated contacts with fresh organic extractant.

Crowding—The displacement of an impurity from the organic extractant phase by contact with a solution containing the main extractable metal or other solute. To achieve crowding, the main solute must have a more favorable distribution into the organic phase than the solute being crowded.

Crud—The stable mixture of an organic phase, an aqueous phase, and fine solid particles. The mixture forms during agitation and usually collects at the interface between the aqueous and organic phases.

Diluent—The organic liquid in which an extractant and modifier are dissolved to form a solvent; some literature has used the term "carrier."

Dispersed phase—The phase, in a contactor, that is discontinuous; i.e., the component that is dispersed, generally as droplets, throughout the continuous phase in a mixture of two immiscible solutions.

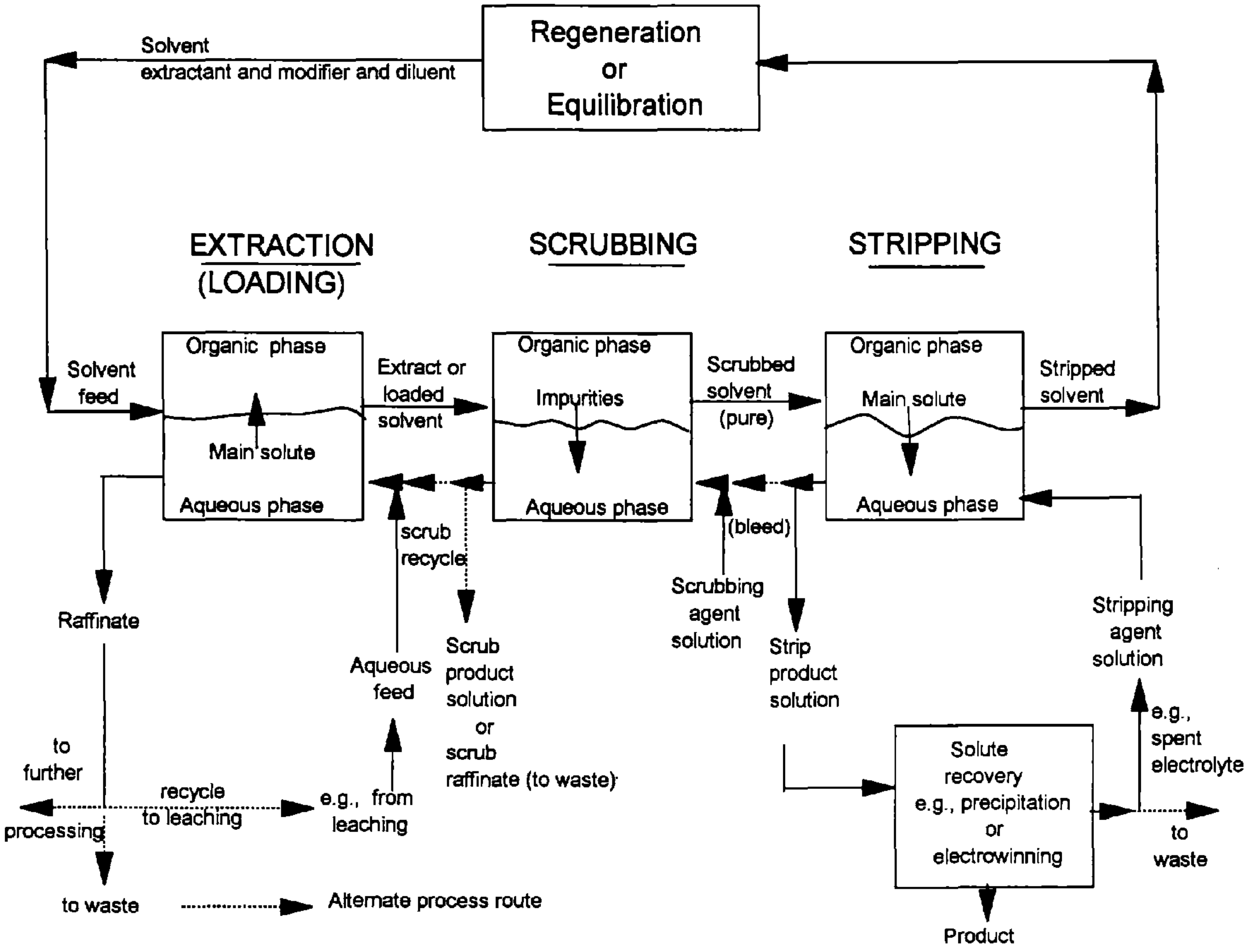
Distribution—The apportionment of a solute metal between two phases; some literature has used the term "partition," but the term "distribution" is preferred.

Distribution coefficient—See extraction coefficient and stripping coefficient.

Distribution isotherm—See extraction isotherm and stripping isotherm.

Emulsion—A mixture consisting of small droplets of one liquid dispersed in a continuum of another immiscible liquid.

Figure 5.16



Nomenclature of generic hydrometallurgical solvent-extraction flowsheet (adapted from Rice, 1981, p. 192).

Equilibrate—To bring a system of two phases in a single stage to a condition where further changes do not occur with time.

Equilibration—Treatment of the solvent prior to its entering the extraction stage; the terms "pre-equilibration" and "solvent regeneration" have also been used to designate this operation.

Equilibrium—The condition that exists when the chemical potentials of both the aqueous and organic phases are equal.

Extract—When used as a verb, the term describes the transfer of metal from one phase to another; the term has also been used as a noun to designate the loaded solvent after the extraction step or the aqueous product liquor from the stripping operation.

Extractant—The active organic component of the solvent primarily responsible for the extraction of a metal; sometimes the term has been used to designate the total organic phase.

Extraction coefficient, (E)—The ratio of total metal concentrations (in any form) in the organic and aqueous phases after contacting the aqueous and organic phases under specified conditions. (E = ratio of metal concentration in organic phase to metal concentration in aqueous phase.)

Extraction isotherm—A graphical (or algebraic) representation of the isothermal equilibrium concentrations of a metal solute in the aqueous and organic phases over an ordered range of extraction conditions.

Extraction raffinate—The aqueous phase from which a metal or metals have been removed by contacting with an organic phase.

Flooding—The discharge of mixed phases from one or both exit ports of a contactor.

Internal recycle—Circulation of aqueous or organic solutions from a settler to the mixer in the same stage for control of the phase ratio during mixing independently of the feed ratios.

Inversion—Change in the continuous phase from organic to aqueous or vice versa.

Jack leg—An adjustable overflow-weir arrangement used to adjust the interface position in the setter of a mixer-settler unit.

Load—To transfer a metal from an aqueous phase to an organic phase.

Loaded solvent—An organic solvent phase containing the maximum concentration of a metal for the conditions under which extraction occurred. The term "loaded extractant" has also been used.

Loading capacity—The saturation limit of a solvent for a metal or metals.

Maximum loading—See loading capacity.

McCabe-Thiele diagram—A composite plot of the distribution isotherm (extraction or stripping) and the operating line for an explicit liquid-liquid system.

Mixed solvent—A solution of more than one extractant in an organic diluent.

Mixer-settler—A solvent-extraction contactor consisting of separate mixing and settling compartments.

Modifier—A substance added to a solvent to increase the solubility of the extractant, salts of the extractant, or the extracted metal species during extraction or stripping; also added to suppress emulsion formation or enhance phase separation. Modifiers can also affect the kinetics and selectivity.

Operating line—The line or curve depicting the relationship between the metal solute content of the organic and aqueous phases in a countercurrent system. In a McCabe-Thiele diagram (Cartesian coordinates), the operating line is linear with a slope equal to the ratio of feed volume to solvent volume. The line contains points representing the solute concentration in the influent and effluent streams throughout the system. The operating line can be defined either by two points or by one point and a slope. For example, if the two-point method is used and the first point is delineated by the solute concentration in the aqueous feed and the desired solute concentration in the loaded solvent, then the second point is determined by the solute concentration in the raffinate and the solute concentration in the recycled organic. The line can also be defined by either of the above points and a slope equal to the A/O ratio.

Partition coefficient—The ratio of the concentration of a solute in a single definite form in the organic phase to that of the same form in the aqueous phase at equilibrium.

$pH_{1/2}$—The pH value at which the extraction coefficient is unity.

Phase inversion—Reversal of the continuous and dispersed phases: i.e., the change in a solvent-extraction system when the dispersed phase becomes the continuous phase, or vice versa.

Phase ratio—See A/O ratio.

Primary break—Separation of a dispersion into two layers with a distinct common boundary.

Pulse column—A multistage vertical-column contactor containing parallel horizontal perforated plates (disks) through which the aqueous and organic feed streams are advanced countercurrently by a pulsing motion.

Raffinate—The aqueous phase from which the metal solute has been removed by extraction; a raffinate may go on to further processing, may be at least partially recycled to other parts of a hydrometallurgical flowsheet, or may go to waste treatment and disposal.

Scrub raffinate—The aqueous phase after contacting the loaded solvent during the scrubbing step.

Scrubbed solvent—The organic phase after removal of contaminants by scrubbing.

Scrubbing—Selective removal of a contaminating metal or other impurity such as entrained aqueous phase from the loaded solvent prior to stripping; also may refer to the removal of solvent degradation products and nonstrippable complexes from the solvent usually after the stripping step.

Scrubbing solution—The aqueous solution used to contact the loaded solvent for the removal of contaminants.

Secondary break—Coalescence and separation of a fine dispersion present in either or both phases after the primary break.

Sedimentation—The separation of immiscible liquids into separate layers as the result of natural differences in specific gravity.

Separation factor—The ratio of the extraction coefficients of two metals being compared.

Settling—The separation of dispersed immiscible phases by coalescence or sedimentation.

Solvent—In hydrometallurgical solvent-extraction systems, the term "solvent" is typically used to designate the organic phase; in general liquid-liquid extractions it is the liquid phase that preferentially extracts a desired solute from the feed stream. The term "organic" has also been used to designate this phase.

Solvent extraction (SX)—The separation of one or more metallic solutes from a mixture by mass transfer between immiscible phases in which at least one phase is an organic liquid. Other terms used to designate this type of separation include liquid ion exchange (LIX) and liquid-liquid extraction.

Solvent inventory—The total quantity of solvent in a given solvent-extraction processing system.

Specific flow—A term used to designate settler capacity in terms of the total flow of organic plus aqueous phases per unit time per unit of cross-sectional area of the settler (e.g., gallons per minute per square foot or liters per minute per square meter).

Stage—A single contact (dispersion and disengagement); also sometimes refers to a single contact stage in which the mass transfer between phases attains theoretical equilibrium conditions.

Stage efficiency—The ratio of actual mass transfer in a specific stage to the theoretical transfer in that stage under equilibrium conditions.

Steady state—The state of a system operating in such a way that the concentration of solutes in exit streams remains constant with respect to time for constant feed concentrations, even though the two phases are not necessarily in thermodynamic equilibrium in any part of the system.

Strip liquor—The aqueous solution containing the metal recovered from a loaded solvent by stripping; also sometimes referred to as the "strip product liquor." In copper operations, the strip liquor is typically designated by terms such as pregnant electrolyte or "advanced electrolyte."

Stripped solvent—The solvent after removal of extracted metal by stripping; also referred to as "barren organic."

Stripping—The removal of extracted metal from the loaded solvent; also sometimes referred to as "reextraction" or "back extraction." Selective stripping refers to separate removal of specific metals from a solvent containing more than one metal.

Stripping coefficient—The reciprocal of the extraction coefficient.

Stripping isotherm—A graphical (or algebraic) representation of the isothermal equilibrium concentrations of a metal solute in the aqueous and organic phases over an ordered range of stripping conditions.

Stripping solution—The aqueous solution used to contact the loaded (or scrubbed) solvent to recover the extracted metal. In copper operations, the stripping solution is often referred to as "spent electrolyte."

Synergism—The cooperative and beneficial effect of two or more extractants or modifiers that exceeds the sum of the individual effects.

Thief sampling—Taking a small but representative sample from a large amount of solution or other material.

5.4.3 Solvent Pretreatment and Conditioning

In many instances, the solvent solutions will require some pretreatment (equilibration) prior to their initial use. The purpose of pretreatment is to convert the solvent to the form most applicable to the extraction operation. For example, since tertiary aliphatic amines are typically supplied in the amine form [R_3N], it is normally desirable to convert the amine to a salt form, such as $(R_3NH)_2SO_4$, before using it to extract uranium from a sulfuric acid leach solution. The salt form extracts the uranium by an ion-exchange mechanism. The pretreatment can be accomplished as follows:

- The solvent mixture is prepared by combining the desired amounts of amine extractant, modifier, and diluent.
- The solvent mixture is contacted with a sulfuric acid solution to convert the amine to the salt form. Typically, two or three contacts with 0.5*M* to 1.0*M* H_2SO_4 are used. A 1- to 2-min agitation time is usually adequate. The phases are separated after each contact, and the aqueous phase is discarded.
- After the final phase separation, the pretreated solvent mixture is ready for the uranium-extraction step.

Optimum pretreatment techniques can vary considerably for different extractant systems; therefore, discussions with extractant manufacturers can produce valuable guidance.

Solvent conditioning refers to the removal of byproducts or contaminants that may have been formed or introduced during manufacturing processes used to produce an extractant, modifier, or diluent. These impurities, which can either enhance or diminish extractant performance, are usually lost to the aqueous raffinate after some recycling of the solvent. Therefore, the contaminants should be removed by conditioning the solvent mixture prior to bench-scale studies. Conditioning is particularly important when working with new or experimental extractants.

Although there is no standard technique for conditioning a solvent, the method typically used involves multiple contacts of the solvent mixture with a feed solution similar to that used in the experimental program. For example, both actual and simulated leach liquors have been used. The contacting procedure should involve both extraction and stripping operations. Again, when possible, manufacturers' recommendations should be sought when conditioning treatments are planned. Preferably, the initial experimental studies should include a comparison of both conditioned and unconditioned solvent mixtures.

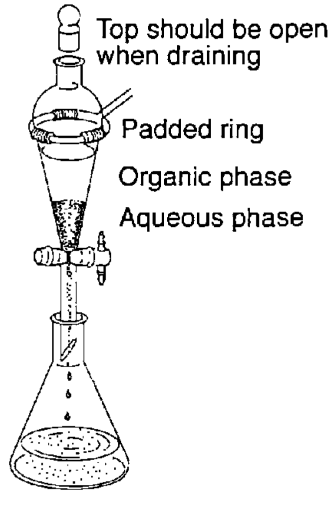
5.4.4 Batch Testing

5.4.4.1 Introduction

When process-development studies are conducted for a hydrometallurgical leach and solvent-extraction operation, a systems approach that integrates exploratory leaching and solvent extraction investigations is often desirable. Definitive criteria for the solvent-extraction process can be finalized once the coordinated leaching requirements have been identified and the leach liquor has been characterized. This concept becomes particularly applicable when the process requires rigorous leaching conditions or when relatively high grade leach liquors are produced.

The initial solvent-extraction experiments are almost always batch tests. In many instances the exploratory test program is designed to screen potential extractant systems and then investigate the effect of processing variables such as extractant concentration, diluents, modifiers, temperature, pH effects, etc., on the equilibrium and kinetics of the extraction and stripping operations. Most of these variables can be evaluated using what have been termed "shakeout tests." This is basically a procedure for contacting and then separating the organic and aqueous phases using a separatory funnel, such as that shown in figure 5.17. In general, the shakeout test procedure can be carried out as follows:

Figure 5.17



Separatory funnel apparatus for shakeout tests.

1. Select a clean separatory funnel of a size such that the total volume of the organic plus aqueous phases will occupy approximately 50% to 70% of the total separatory funnel capacity. For example, a 250-mL funnel can effectively handle a total volume of about 125 to 175 mL. Separatory funnels with stopcocks that do not require lubrication are normally preferred.
2. Add the aqueous phase solution to the funnel, and then add the organic phase. Insert the stopper.
3. Shake the funnel gently. Then invert the funnel and open the stopcock slowly to relieve any pressure buildup. It may be necessary to repeat this operation several times.
4. Continue shaking the funnel for the desired contact time. (If a mechanical shaker is used, the stopper must be fully secured; this can usually be accomplished by using elastic bands. Conducting mechanical shaking in a hood with a suitable spill tray under the shaking device is recommended.)
5. After the shaking period is complete, place the funnel in a ringstand or other suitable support and allow the organic and aqueous layers to separate. Remove the stopper. (Small droplets of the organic phase often adhere to the inside of the separatory funnel at its narrowest point; unless dislodged, these droplets can drain off with the aqueous phase, causing contamination. Such contamination can be minimized by allowing the phases to separate and then swirling the contents of the funnel using a sharp snapping motion of the wrist. Swirling should not be vigorous enough to cause remixing of the separated phases. Since the droplets often adhere to irregularities on the glass surface, the problem can be minimized by exercising care when washing the funnels. Avoid scratching the inside surface of the funnel with the wire found in the center of most laboratory brushes.)
6. Slowly open the stopcock and carefully drain off the aqueous and organic phases into separate containers.
7. Sample the organic and aqueous phases as required.
8. Use appropriate procedures (see applicable MSDS) to dispose of any excess solutions.

5.4.4.2 Extraction

A primary objective of batch extraction tests is to develop an extraction (distribution) isotherm for a given set of variables and conditions. The procedure involves a series of shakeout tests. Since the mixing contact time must be enough to achieve equilibrium between the aqueous and organic phases, the initial step in the procedure is to establish the contact time required. This can be accomplished by a series of shakeout tests in which only the contact time is varied. For example, if available literature indicates that the equilibrium contact time for an extraction system is normally 4 min or less, the following test procedure is generally applicable.

1. Place 40 mL of the aqueous feed liquor in a 125-mL separatory funnel and add 40 mL of the solvent mixture.
2. Shake the mixture for 0.5 min, allow the two phases to separate, and sample the aqueous phase.
3 Repeat steps 1 and 2 for contact times of 1, 1.5, 2.0, 3.0, and 4.0 min.

4. Analyze the aqueous phase samples for the metal of interest, and plot the metal concentrations versus the contact times (see figure 5.18).

As indicated in the figure, the minimum contact time for developing the equilibrium data should be no less than 1.5 min and preferably more. (If the phase ratio varies significantly from the 1:1 ratio used in this example, appreciably longer contact times may be required.)

Data for the extraction isotherm can be developed by several different techniques. Some of the most commonly used are as follows:

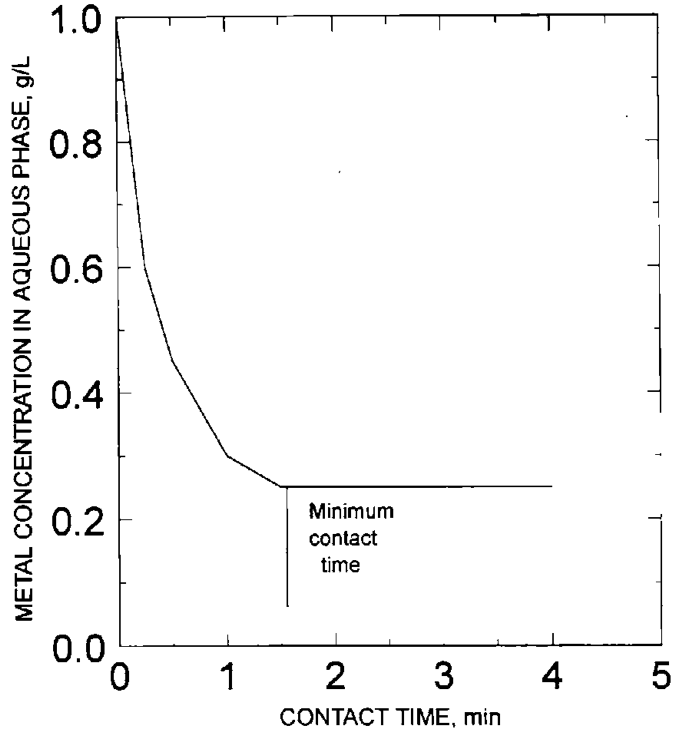
1. *Variation of the phase ratio*—A series of single contacts using a given volume of the aqueous feed with different volumes of the organic solvent.
2. *Constant phase patio*—A series of contacts in which a single charge of the organic phase is contacted with fresh charges of aqueous feed while maintaining the same phase ratio throughout the successive contacts.
3. *Pyramid procedure*—A crosscurrent technique used to simulate countercurrent extraction.

Sometimes a combination of procedures 1 and 2 is used. The following paragraphs outline the above procedures.

1. *Variation of the phase ratio*—This procedure consists of a series of shakeout tests in which the A/O ratio is varied. Normally the A/O variation ranges from about 1:10 to 10:1. The equilibrium pH after contacting should be held constant throughout the shakeout test series.

- Aliquots of the aqueous and organic phases in the desired ratio are placed in a suitably sized separatory funnel. The minimum acceptable quantity of either phase is often dependent upon the volume of sample required for the subsequent analytical determinations. For example, if a 10-mL aqueous sample is required for the analytical determinations, and the desired A/O ratio for the test is 1:10, a 250-mL separatory funnel can be used (15 mL of aqueous phase plus 150 mL of the organic solvent). This shakeout test volume allows for handling losses that may occur because of incomplete drainage from the separatory funnel.
- The mixture is shaken for the time required to reach equilibrium.
- The phases are separated and then analyzed. Complete phase separation to remove any entrained solvent from the aqueous phase and any aqueous phase from the organic phase is necessary. This separation may require centrifuging. Sometimes adequate removal of any residual organic phase from an aqueous phase can be achieved by filtering the solutions through a bed of packed cotton or through dry filter paper. A silicone-treated filter paper can be used to remove any residual aqueous phase from an organic liquid.
- A separate shakeout test is carried out for each phase ratio desired. Table 5.2 and figure 5.19 illustrate equilibria data and the resulting extraction isotherm for a cobalt chloride and triisooctylamine system. As shown in the table, the following A/O ratios were used: 1:5, 2:5, 1:2, 2:3, 1:1, and 2:1. The aqueous feed contained 0.37*M* $CoCl_2$ in 8*N* HcL. The organic phase was 0.57*M* triisooctylamine hydrochloride in a xylene diluent (Bridges and Rosenbaum, 1962, pp. 6, 12). The temperature was 25 °C.

Figure 5.18



Determination of contact time for equilibrium studies.

2. *Constant phase ratio*—This procedure consists of a series of shakeout tests in which the A/O ratio is held constant. The optimum ratio depends upon the particular system being investigated, but an A/O ratio of 1:1 is often an appropriate choice for the initial tests. Again, the equilibrium pH after contacting should be maintained at a constant level throughout the series of tests.

Table 5.2.—Equilibria data for cobalt distribution between 8*N* HCl and 0.57*M* triisooctylamine hydrochloride at 25 °C

Approximate aqueous-to-organic (A/O) feed ratio	Cobalt, g/L		Extraction coefficient (E)
	Organic phase	Aqueous phase	
1:5	4.5	0.1	45.0
2:5	8.0	0.4	20.0
1:2	9.2	1.8	5.1
2:3	10.2	3.9	2.6
1:1	11.0	12.0	0.9
2:1	11.0	15.9	0.7

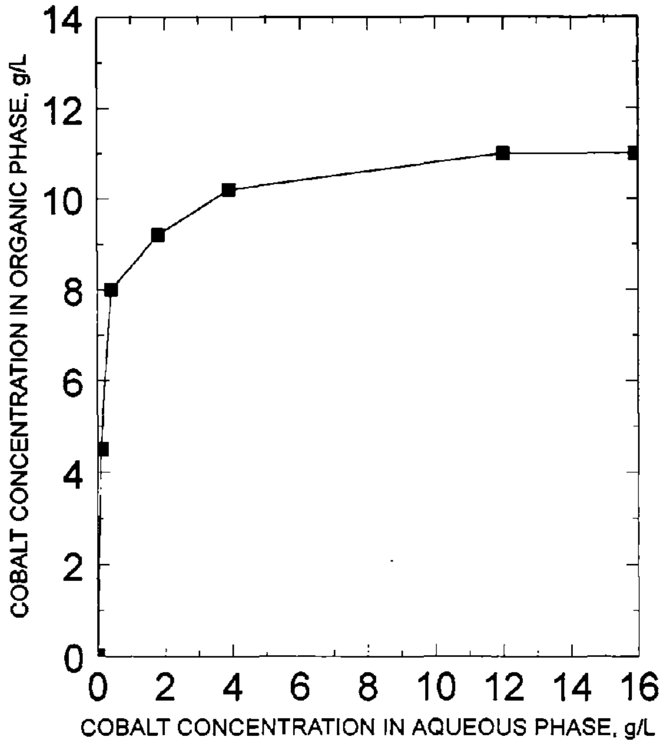
E Ratio of concentration of cobalt in organic phase to concentration of cobalt in aqueous phase.

- The aqueous feed solution and the organic solvent mixture are placed in a suitable separatory funnel and shaken until equilibrium is attained.
- The phases are allowed to separate. The aqueous phase is drained from the funnel and sampled for analysis. A measured aliquot of the organic phase is also taken for analysis. Again, complete phase separation is necessary to remove any entrained solvent from the aqueous phase and any aqueous phase from the organic phase.
- A measured volume of the aqueous feed solution is then added to the organic phase remaining in the separatory funnel. The amount of aqueous added should be such that the A/O ratio is the same as that originally used. For example, if the initial contact used 100 mL of aqueous and 100 mL of organic and a 5-mL aliquot of the organic phase was taken for analysis, the second contact would use 95 mL of aqueous and 95 mL of organic. After the second shakeout contact is complete, the phases are again sampled for analysis.
- The above sequence of operations is repeated until saturation of the solvent with the metal being recovered is achieved. Material balances should be made on each of the sample pairs. If the balances vary by more than about plus or minus 5%, the reason for the discrepancy should be determined.

If a large number of contacts are required to achieve saturation of the solvent, the original volume of organic must be large enough to provide for the sampling needed.

When a combination of the two procedures is used, procedure 1 is often used to develop the upper portion of the extraction isotherm, and the first two or three contacts of procedure 2 are used for the equilibrium points near the origin. The combination approach was used to develop the data points for the extraction isotherm shown in figure 5.20*A*. This isotherm represents a solution-purification operation. The objective is to remove essentially all of the iron from the feed solution so that is does not contaminate subsequent cobalt-recovery operations (Redden and others, 1988). No concentration is realized during the extraction; in fact, the iron concentration in the loaded solvent is considerably lower than that in the aqueous feed solution. Figure 5.20*B* illustrates a solvent-extraction separation in which both purification and copper concentration take place (Tumilty and others, 1979). Nearly all uranium solvent-extraction separations also achieve both purification and concentration.

Figure 5.19



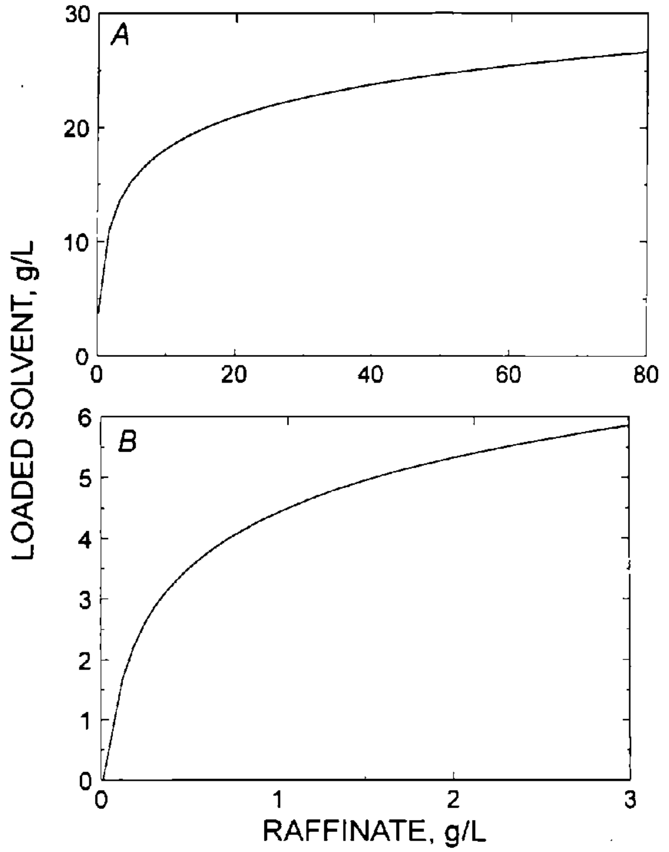
Extraction isotherm for cobalt distribution between 8N HCl and 0.57M triisooctylamine hydrochloride at 25 °C.

3. *Pyramid procedure*—This crosscurrent technique, which has been described in detail by Treybal (1963) is equivalent to the procedure described in section 5.2.4 and outlined in figure 5.1. The pyramid procedure is more complex than either variable or constant A/O techniques, but it simulates the crowding conditions of a countercurrent solvent-extraction system. This effect can be critical, for e.g., when the feed solution contains two metals, both of which can be extracted by the solvent, but one of the metals has a more favorable distribution into the organic phase.

5.4.4.3 Scrubbing

The shakeout test procedures used to investigate scrubbing variables are essentially the same as those discussed in section 5.4.4.2. The chemistry involved in scrubbing

Figure 5.20



Extraction isotherm examples. A, Iron extraction isotherm test conditions: Solvent 0.5M LA-2 extractant in Cycle Sol 633 naphtha diluent; aqueous feed = grinding waste leach liquor; contact time = 3 min; temperature = 25 °C (Redden and others, 1988). B, Copper extraction isotherm test conditions: Solvent = 10 vol % Acorga P-5100 extractant in Escade 100 diluent; aqueous feed = copper leach liquor; contact time = 3 min; pH = 1.9; temperature = 21 °C (Tumilty and others, 1979).

operations is often unique and applies specifically to the system being studied. A wide variety of scrubbing solutions, including water, various acids, and ammonia solutions, have been used. Scrubbing can often be achieved in a single stage, and therefore, test procedures based on variation of the A/O ratios are typically applicable. As mentioned in section 5.4.1, scrubbing examples include removing nickel coextracted during an organophosphate cobalt-recovery process (Ritcey and Ashbrook, 1979, pp. 13-14) and scrubbing manganese from a cobalt-rich solvent obtained by an amine extraction technique (Redden and others, 1988, p. 18).

5.4.4.4 Stripping

The shakeout test procedures used to develop the data needed for construction of the stripping isotherms are in essence equivalent to those described in section 5.4.4.2. In most instances, however, pH control is not required. All three procedures are applicable, but an adaption of the constant-phase-ratio technique, such as the following, is typically used.

- An adequate volume of loaded solvent is prepared by conducting multiple contacts of the chosen solvent mixture with fresh charges of the aqueous feed solution until the desired loading is achieved. Typically, the same phase ratio is used in all of the multiple contacts.
- The shakeout test procedure is then used to contact a sample of the loaded solvent with the chosen stripping solution using an appropriate phase ratio. A 1:1 ratio is often applicable for the initial experiments. (The stripping kinetics may be appreciably different from the extraction kinetics. It is always prudent to consult the manufacturers recommendations when conducting stripping tests.)
- After equilibrium is achieved, the phases are separated and aliquots are taken for analysis.
- The remaining organic phase is again contacted with fresh stripping solution using the same phase ratio as that used in the initial contact. After equilibrium is reached, the phases are again separated and sampled for analysis.
- This sequence of operations is continued until as much as possible of the metal has been stripped from the solvent. The resulting data are used to plot the stripping isotherm. The concentration of the extracted metal or species in the aqueous phase is plotted along the y-axis (ordinate), and the corresponding concentration in the organic phase is plotted along the x-axis (abscissa). Figure 5.21*A* illustrates a stripping isotherm obtained when the iron-loaded solvent depicted in the extraction isotherm of figure 5.20*A* is stripped with water. (If no volume change occurs during stripping, sampling and analysis of only the aqueous strip liquor is usually adequate. The metal content of the organic phase after each strip is calculated by difference.) Figure 5.21*B* illustrates the stripping isotherm obtained when a copper-loaded solvent such as that depicted in figure 5.20*B* is stripped with spent electrolyte containing 30 g/L Cu and 150 g/L H_2SO_4.

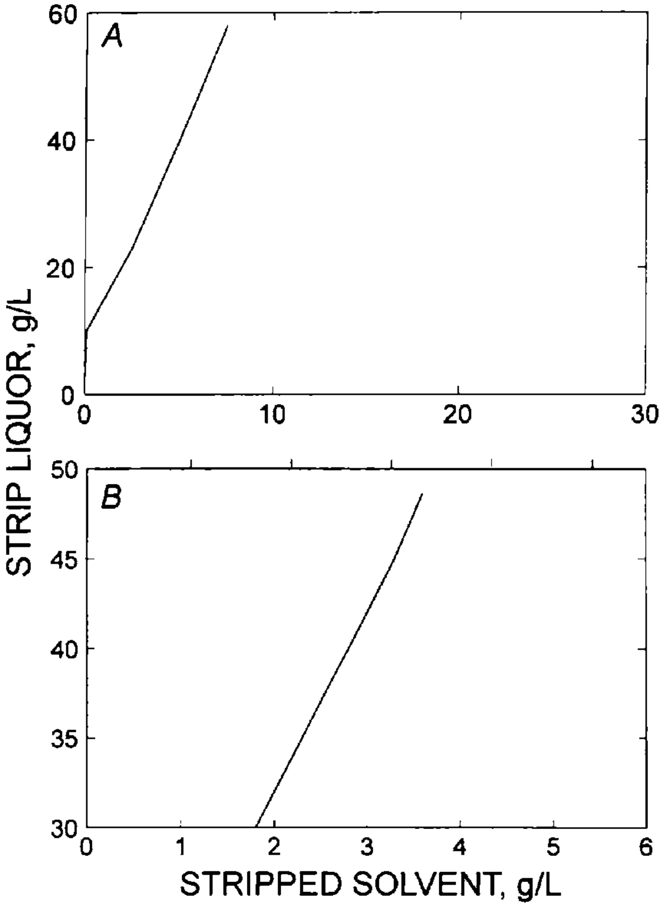
5.4.4.5 Data Presentation (Extraction and Stripping)

Graphical forms are particularly useful for presentation of solvent-extraction data. Examples include representations of pH effects, equilibrium data, and McCabe-Thiele evaluations such as those discussed in the following paragraphs.

pH effects—A significant number of the hydrometallurgical solvent extraction systems are pH sensitive. The data from studies that investigate pH effects are usually presented in graphical forms such as that shown in figure 5.22 (Dannenberg and others, 1987). This graph depicts the effect of pH change on the loading of cobalt and nickel from an acidic sulfate leach liquor. The extractant was 0.5*M* Cyanex 272 (an alkyl phosphinic acid-type extractant) dissolved in kerosene. The curves indicate that the maximum cobalt extraction and selectivity can be achieved if the extraction pH is held between 5.0 and 5.9.

Other forms of plotting the pH effects can also be useful. These variations include plotting the extraction coefficient versus the equilibrium pH and also plotting the log of the extraction coefficient versus the equilibrium pH.

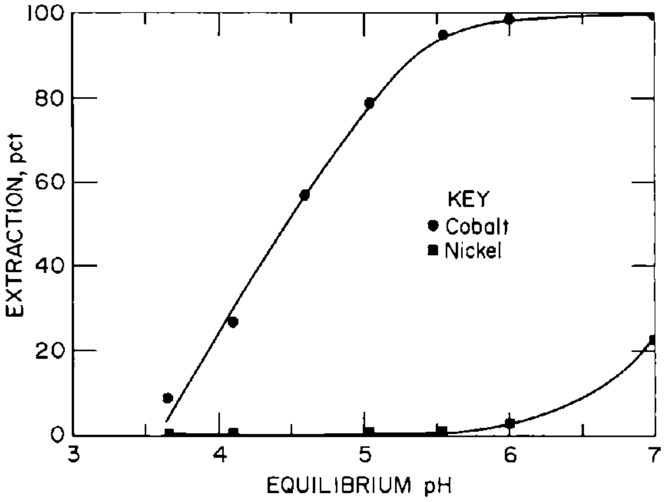
Figure 5.21



Stripping isotherm examples. A, Iron stripping isotherm test conditions: Solvent feed = iron-loaded solvent depicted in figure 5.20A; stripping solution = water; temperature = 25 °C (Redden and others, 1988). B, Copper stripping isotherm test conditions: Solvent feed = copper-loaded solvent depicted in figure 5.20B; stripping solution = 30 g/L Cu in 150 g/L H_2SO_4 (spent electrolyte); temperature = 21 °C (Tumilty and others, 1979).

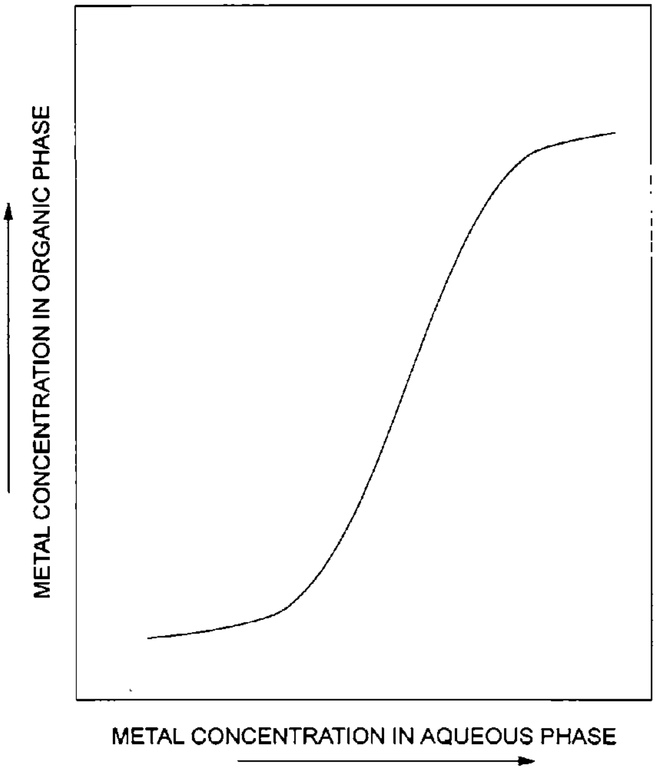
Equilibrium data—lots of the equilibrium relationships for several extraction and stripping systems have been shown in figures 5.19, 5.20, and 5.21. Figures 5.19 and 5.20 illustrate the type of equilibrium curves obtained for many hydrometallurgical systems. Figure 5.23 represents

Figure 5.22



Effect of pH on cobalt and nickel extraction with Cyanex 272 extractant.

Figure 5.23

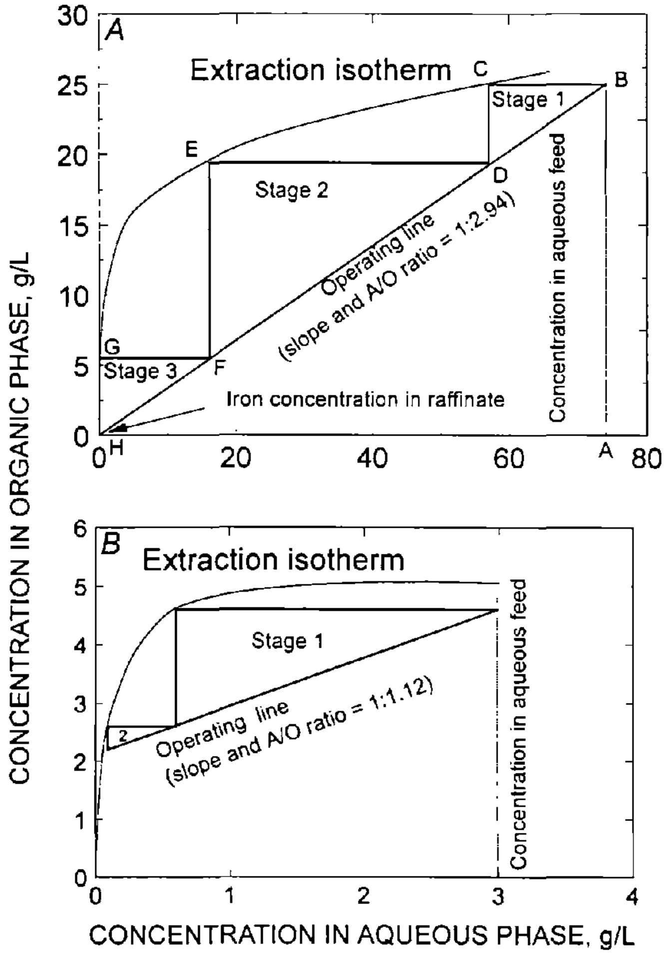


S-shaped type of extraction isotherm.

the so-called S-shaped isotherm. This shape can be produced if significant concentrations of nonextractable metal complexes are present in the aqueous phase or by polymerization in the solvent phase when the solvent mixture is in contact with low metal concentrations in the aqueous phase (Ritcey and Ashbrook, 1984, p. 75). In general, low metal concentrations in the extraction raffinates cannot be obtained with systems that display S-shaped isotherms because an impractical number of extraction stages may be required. The extraction of vanadium (Ritcey, 1979, p. 528) and molybdenum (Ritcey and Ashbrook, 1984, p. 75) with amines can generate this type of extraction isotherm.

McCabe-Thiele diagram—A McCabe-Thiele diagram, such as that illustrated in figure 5.24*A*, is used to predict the number of theoretical stages required for a continuous countercurrent solvent-extraction system. The diagram for the loading operation is constructed using a composite plot of the extraction isotherm and the operating line that represents the A/O ratio used in the continuous system. McCabe-Thiele diagrams can be prepared for both extraction and stripping operations. The procedure involves the following general steps.

Figure 5.24



McCabe-Thiele diagram examples for extraction. A, Iron extraction (see figure 5.20A for extraction conditions). B, Copper extraction (see figure 5.20B for extraction conditions).

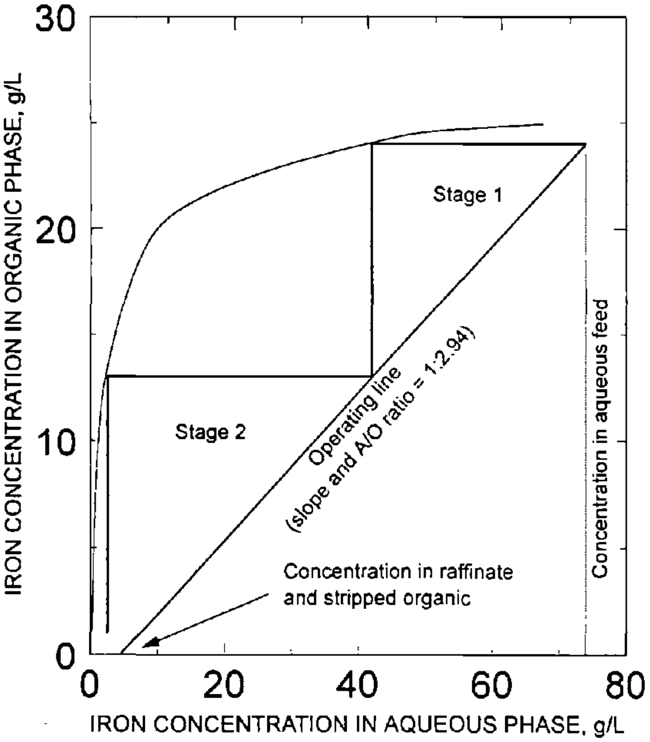
- An extraction isotherm is prepared, such as that shown in figure 5.20*A*.
- A vertical line (AB) is drawn from the x-axis at the concentration of the metal in the feed solution (73.4 g/L Fe).
- For the initial estimation, the operating line (HB) is drawn from the origin, with a slope equal to the A/O ratio in the feed stream to the proposed extraction circuit. The A/O ratio shown in figure 5.24*A* is 1:2.94. Since the operating line represents a mass balance, the concentration of iron in the solvent entering any stage and the concentration of iron in the raffinate leaving that stage are coordinates of points on the operating line (e.g., point D in stage 1 and point F in stage 2). Similarly, the concentration of iron in the aqueous feed entering any stage and the iron concentration in the organic leaving that stage are coordinates of points on the operating line (e.g., point B in stage 1 and point D in stage 2). The operating line is a straight line and is fixed by any two points or by one point and the slope, which is determined by the A/O ratio in the system.
- The theoretical or ideal stages are "stepped off" as follows. A horizontal line (BC) is drawn from point B, the intersection of the operating line with the vertical line AB (which represents the iron concentration in the aqueous feed), until it intersects the extraction isotherm at point C.
- A vertical line CD is then dropped to intersect the operating line. Lines AB, BC, and CD define the conditions in the first extraction stage, i.e., the iron concentration in aqueous phases entering and leaving the stage and the iron concentration in the organic phases entering and leaving the stage.
- The procedure is repeated to define stage 2 by lines DE and EF, and then to define stage 3 by lines FG and GH.

Refinements and modifications to the initial McCabe-Thiele diagram may be necessary as additional information is developed during the course of solvent-extraction studies. For example, if essentially complete removal of the metal during the stripping operation is not possible, or if the allowable metal concentration remaining in the raffinate is appreciable, the origin point for construction of the operating line will change. Figure 5.25 illustrates this type of modification. This change reduces the required number of stages to less than two full stages, but the organic loading decreases. Also, the effect of system changes such as variation of the organic phase flow rate relative to that of the aqueous phase can be evaluated by changing the slope of the operating line.

Constructing a McCabe-Thiele diagram with an exact match between the number of stages and the slope of the operating line for a given set of feed and raffinate conditions is an iterative process. The horizontal and vertical lines shown on figure 5.24*A* represent 100% stage efficiencies. The McCabe-Thiele construction can also be used to develop a feel for the effect of the lower contacting efficiencies that nearly always occur in a continuous circuit. For example, instead of the horizontal and vertical lines being drawn to reflect 100% stage efficiency, draw the horizontal linescan be drawn to reflect only a 95% efficiency. Lower efficiencies can also be evaluated, but the number of stages indicated by the 95% construction often reflects that encountered in a continuous solvent-extraction circuit.

The McCabe-Thiele diagram shown in figure 5.24*B*, which is also the end product of an interactive process, is based on the copper-extraction isotherm shown in figure 5.20*B*. The construction is developed using the premise that the recycle solvent being fed to the system has been stripped with spent electrolyte from electrowinning cells and, therefore, is not barren; it contains approximately 2 g/L Cu (see figure 5.26*B*). Even though the recycle organic contains appreciable copper, the projected raffinate contains less than 0.2 g/L Cu.

Figure 5.25

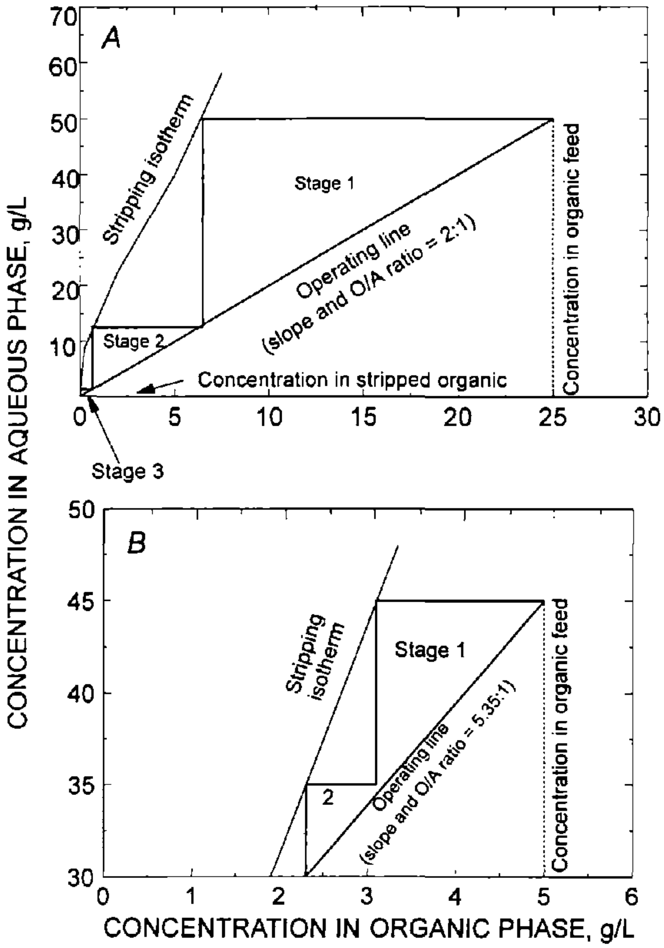


Modified McCabe-Thiele diagram for iron extraction (see figure 5.24A for original construction).

The general procedures outlined above can also be used to generate a McCabe-Thiele diagram that illustrates the number of stages required for stripping the metals from the loaded solvent. Figure 5.26*A* illustrates a McCabe-Thiele construction for stripping iron from the loaded solvent depicted in figure 5.24*A*. Similarly, figure 5.26*B* shows a McCabe-Thiele construction for stripping copper from the loaded solvent depicted in figure 5.24*B*.

Additional information related to the construction and interpretation of McCabe-Thiele diagrams is presented in references such as the following: Bennett and Myers (1962), Bridges and Rosenbaum (1962), (Bull and Celli (1949), Hazen (1985), McCabe and Thiele (1925), Ritcey and Ashbrook (1984, pp. 76-80), and Treybal (1968).

Figure 5.26



McCabe-Thiele diagram examples for stripping. A, Iron stripping (see figure 5.21A for stripping conditions); B, copper stripping (see figure 5.21B for stripping conditions).

5.4.4.6 Kinetics Testing

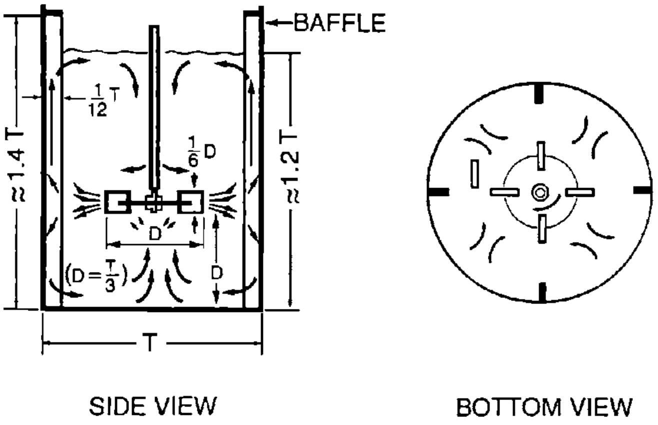
For a given throughput rate, the size of the mixers in a mixer-settler circuit depends on the time required to achieve equilibrium between the organic and aqueous phases. Therefore, determining the effective overall kinetics of the solvent-extraction system becomes important. Test work is required to determine the composite effect produced by interrelated system variables such as the chemical reaction rates, the degree of agitation, the viscosities, and operating temperatures.

A number of procedures can be used to develop kinetic data. For example, the shakeout test procedure described in section 5.4.4.2 will give a general feel for the contact time required to approach equilibrium in a large contactor, but the application is limited. This limitation arises because the type and degree of agitation influence the extraction and stripping rates. Agitation variables and other effects can be evaluated using a technique that consists of agitating the organic and aqueous phases together, thief sampling at appropriate intervals, and analyzing one or preferably both phases. Defining equilibrium contact time requirements is critical because equipment capacities vary. Various contactors such as sieve-plate columns, centrifugal contactors, etc. (Ritcey and Ashbrook, 1979, pp. 71-116) may apply for contact times of less than 60 s, but mixer-settlers may be the only units suitable for longer times.

A generalized description of the agitation and thief sampling procedure (for the extraction step) is outlined below.

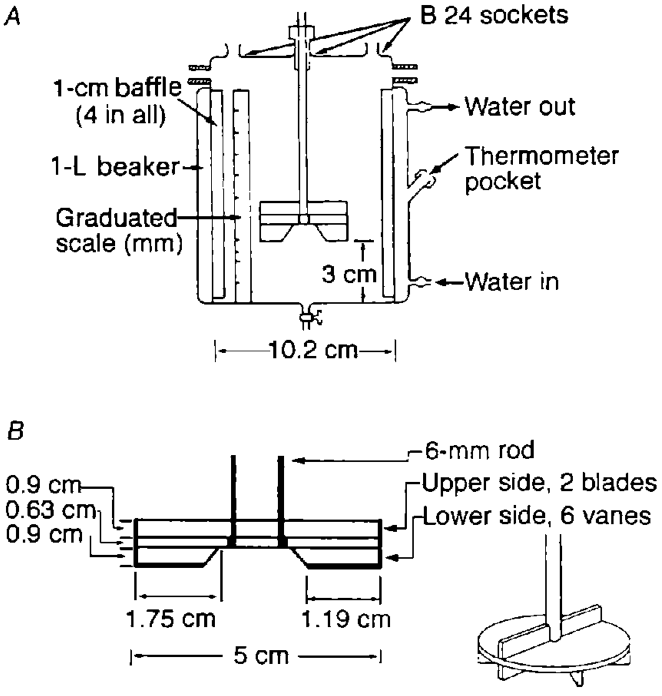
- Aliquots of the aqueous feed solution and the solvent mixture are taken for contacting in a suitable vessel. Typically, a 1:1 A/O ratio is a suitable starting point. Baffled beaker arrangements similar to that illustrated in figure 5.27 have been used successfully. Provisions for adjusting the vertical position of the impeller are needed. A somewhat more sophisticated contact device is illustrated in figure 5.28. This water-jacketed contactor, which has been described in a Zeneca Specialties brochure (1989), has apparently been particularly applicable for copper extractants, such as those produced by Zeneca Specialties.
- If a 1-L contactor is used, 400 mL of the organic solvent mixture is placed in the contactor and the agitator is started. If the contactor shown in figure 5.28 is used, the recommended stirrer speed is 1,270 rpm (preset when stirring an aqueous-organic mixture). Then 400 mL of the aqueous feed solution is quickly added. This procedure will almost always produce an organic continuous dispersion (i.e., droplets of the aqueous phase dispersed throughout a continuous organic phase). A conductivity tester can be used to determine which phase is continuous. An aqueous continuous dispersion will show conductivity, and an organic continuous dispersion is nonconducting. If temperature effects are being investigated, both solutions should be at the desired temperature, and this temperature should be maintained. The jacketed contactor is particularly suitable for temperature-effect studies. If the influence of stirring speed is being investigated, the equipment arrangement must include a variable-speed stirrer.

Figure 5.27



Baffled contact vessel for kinetics studies.

Figure 5.28

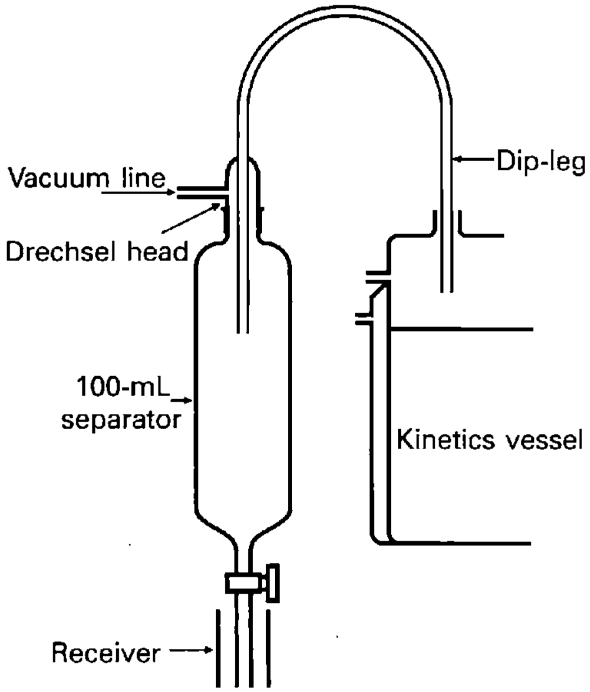


Zeneca design for contact vessel (A) and impeller (B). (Courtesy Zeneca Specialties)

For impellers, such as those shown in figures 5.27 and 5.28, tip speeds in the range between 200 and 700 ft/min are usually applicable.

- The starting time is normally considered to be the instant when all of the aqueous phase has been added. Applicable sampling intervals will vary with the solvent-extraction system being investigated. In general, however, sampling at 0.5, 1.0, 2.0, 4.0, and 16.0 min is a reasonable starting point for initial tests.
- Depending on the system being investigated and the analytical requirements, sample sizes in the 20- to 30-mL range usually prove to be adequate. The Zeneca procedure recommends a sampling apparatus such as that shown in figure 5.29 (Zeneca Specialties, 1989), but a variety of other devices including pipettes have also been used. Cutting off the pipette tip will permit faster collection of the sample. For very short contact times (e.g., 30 s or less), bracketing the sample time may be desirable. For example, if collecting the sample requires 2 s, start the sampling at 29 s.
- The phases should be separated completely and as quickly as possible, particularly for very short contact times. In some instances, immediate centrifuging of the thief sample may be desirable to quench mass transfer. It should be remembered, however, that even in a continuous mixer-settler circuit, the phase separation is not instantaneous, and some mass transfer may continue in the settler. Analyzing both phases is desirable. However, in some systems, such as the extraction of uranium from acidic sulfate liquors with an amine-type extractant, analysis of only the aqueous phase will produce satisfactory kinetics data. Figure 5.18 illustrates a plot obtained with this type of information. The effect of different degrees of agitation can be evaluated by procedures such as plotting a mass-transfer rate (e.g., weight of solute transferred per unit time) versus the stirring speed in revolutions per minute.

Figure 5.29



Sampling device for kinetics tests. (Courtesy Zeneca Specialties)

5.4.4.7 Phase-Separation Testing

Phase separation is a critical consideration in solvent-extraction operations because it influences a number of factors such as equipment type, equipment size, and solvent inventory. Chronologically, the overall phase-separation process can be classified as occurring in two stages: a primary break and a secondary break. For example, immediately after the agitation of an organic-aqueous dispersion is terminated, the mixture starts to separate into three distinct zones: a layer of the organic phase at the top, a layer of the aqueous phase at the bottom, and an intermediate layer containing the organic-aqueous dispersion. The term "primary break" designates the time required for the upper and lower layers to grow and meet at a sharply defined interface. At this point one or both phases may still appear cloudy because of the dispersion of very small droplets of one phase in the other. The time required for this remaining dispersion to coalesce and settle is designated as the "secondary break." Very slow or incomplete coalescence during the secondary break is often the primary cause of solvent loss from the system. The primary-break time determines the settler requirements in a mixer-settler contactor, and design requirements for a solvent recovery system are a function of the secondary-break characteristics of the dispersion.

A number of factors can influence the rate and completeness of phase disengagement; these include the droplet size in the dispersion, the density difference between the organic and aqueous phases, which phase is dispersed, the presence or absence of solids, the viscosity of the phases, the pH of the aqueous phase, and the system temperature. The experimental program is designed to determine the interrelated effects of these variables. Literature references, such as those listed at the end of section 5.4.1, should be consulted. The Ritcey and Ashbrook (1979, 1984) references are particularly valuable because both the theory and application of coalescence and phase disengagement are discussed in significant detail.

Bench-scale experiments can be used to develop the data and information needed for estimating the settler area requirements of a basic mixer-settler contactor such as that shown in figure 5.30. The bench-scale procedures discussed below apply to this type of contactor system. Generating scaleup information for other types of contactors including columns, centrifuge units, and even some mixer-settler refinements generally requires pilot-scale operations and close consultation with the respective manufacturers.

Both static and dynamic laboratory techniques have been used to investigate phase disengagement. The static test procedure involves vigorously agitating the organic-aqueous mixture and then allowing the dispersion to a separate in the same vessel or quickly transferring the dispersion to separate vessel such as a graduated cylinder. As coalescence proceeds, the position of the dispersion band is measured until the top and bottom edges of the dispersion band meet to form a single interface between the organic and aqueous phases. A plot of these disengagement measurements is used primarily to determine comparative phase-separation times for variables such as changes in O/A ratios, different diluents, degrees of agitation, etc. The data can also be used to make preliminary estimates of settler capacity requirements, but dynamic test procedures are recommended.

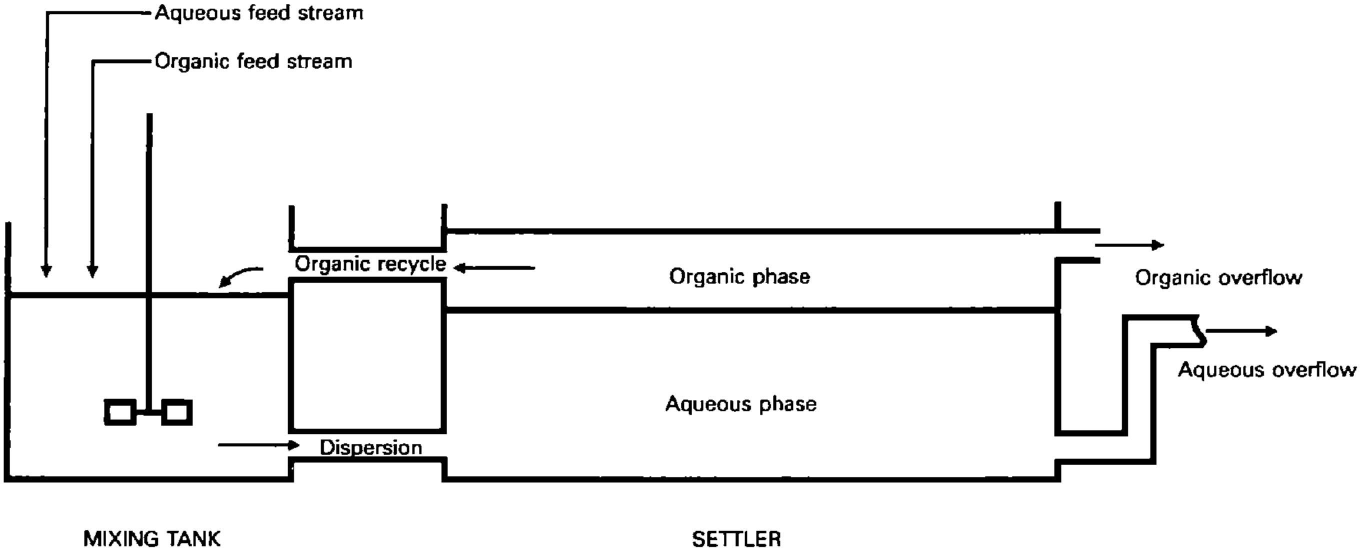
The bench-scale dynamic system uses a miniature mixer-settler. A continuous flow of the dispersion produced in the mixer is fed to the settler. The thickness of the dispersion band is measured for different flow rates, and the thickness is then plotted as a function of the flow rate. These data are then used to calculate specific flow rates. The term "specific flow" designates settler capacity in terms of the total flow of the organic plus aqueous phases per unit time per unit of cross-sectional area of the settler (e.g., gallons per minute per square foot or liters per minute per square meter). When consulting the literature, the researcher should be aware that some of the early solvent-extraction literature, particularly that related to uranium operations, expresses settler capacities in terms of only the individual aqueous or organic flows and not in terms of the total dispersion flowing from the mixer into the settler.

Other variables such as the degree of agitation, diluent effects, the effect of aqueous continuous and organic continuous dispersions, etc., can also be evaluated in the dynamic test apparatus.

Static test procedure—The following static test procedure is based on a technique described in a brochure distributed by Zeneca Specialties (1989). The procedure has been most widely used with copper extractants.

- Place 400 mL of the solvent mixture in a contact vessel such as that illustrated in figure 5.28, and adjust the temperature to the desired level. Hold this temperature constant during the test procedure.
- In a separate container, adjust 400 mL of the aqueous feed solution to the desired temperature. Start the stirrer at the desired preset speed, and transfer the 400 mL of aqueous feed to the contact vessel. The

Figure 5.30



Basic mixer-settler configuration.

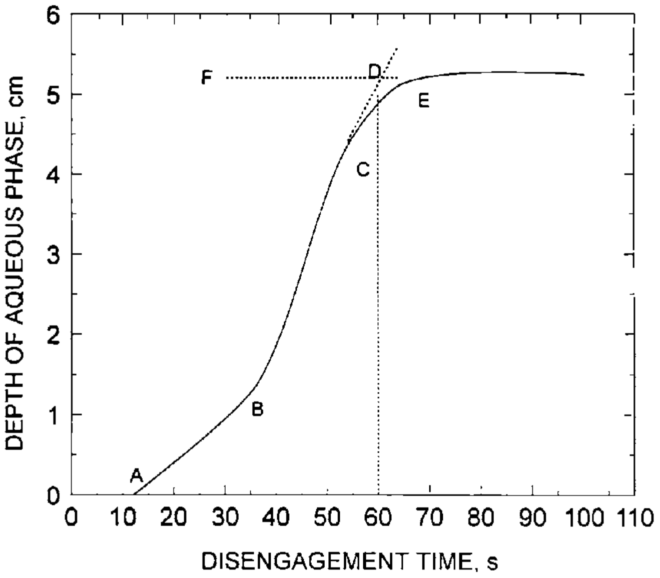
Zeneca procedure recommends a stirrer speed of 600 rpm for copper extraction, but other systems may require different degrees of agitation. When using the configuration and agitator position shown in figure 5.28, this technique produces an organic continuous dispersion. After 3 min, stop the agitation, allow the phases to separate, and drain off the aqueous phase. This sequence of operations produces a partially loaded organic phase.

- Restart the impeller at the desired speed, and add a second 400-mL charge of the temperature-adjusted aqueous feed solution to the contact vessel. Continue the agitation for the desired mixing time (typically 3 to 5 min).
- Turn off the agitator and simultaneously start a timer.
- Record the position of the bottom interface (i.e., the interface between the clear aqueous phase and the remaining dispersion band) versus time. A convenient technique is to record the time in seconds when the interface passes the 1.5-, 2.0-, 3.0-, 4.0-, 5.0-cm, etc., scale markings. Continue the measurements until the primary break is complete and record the final position of the interface.
- Carefully examine the appearance of the interface, and note the presence of any crud, residual bubbles, evidence of a skin formation, etc. Also inspect the clarity of the separated aqueous and organic phases, and record the presence of any cloudiness, color changes, or other conditions.
- Prepare a plot such as that of figure 5.31, which shows the depth of the clear aqueous phase versus the disengagement time for a copper solvent-extraction system. The Zeneca procedure recommends that the required disengagement time for the system be determined as follows:

1. Extrapolate the near-linear portion of the curve (section BC) until it intersects the horizontal line (FE), which defines the depth of the aqueous phase at complete phase disengagement.
2. The intersection (point D) can be taken as the disengagement time required for primary phase separation. In the curve shown, the section CE represents the time required for collapse of the final few drops. This region is disregarded for the system shown because it is variable and somewhat arbitrary. If other systems show a considerably flatter curve in the CE region, this difference should be taken into consideration and allowances made.

As mentioned above, the data from static phase-disengagement tests can be used to make preliminary estimates of specific flow requirements. For example, the static test procedure described above indicates a 1-min phase-disengagement time for 800 mL of total dispersion. Since the cross-sectional area of the unit is approximately 80 cm^2, the indicated specific flow is 10 (mL/min)/cm^2 (100 (L/min)/m^2 or 2.5 gpm/ft^2). This means that for the conditions tested, each square meter of settler area will handle 100 L/min of the total dispersion flowing from the mixer into the settler. These specific flows, however, should be used with caution. Experience in settler sizing, particularly for specialized designs, can be crucial; both dynamic phase-separation tests and discussions with equipment manufacturer are recommended.

Figure 5.31



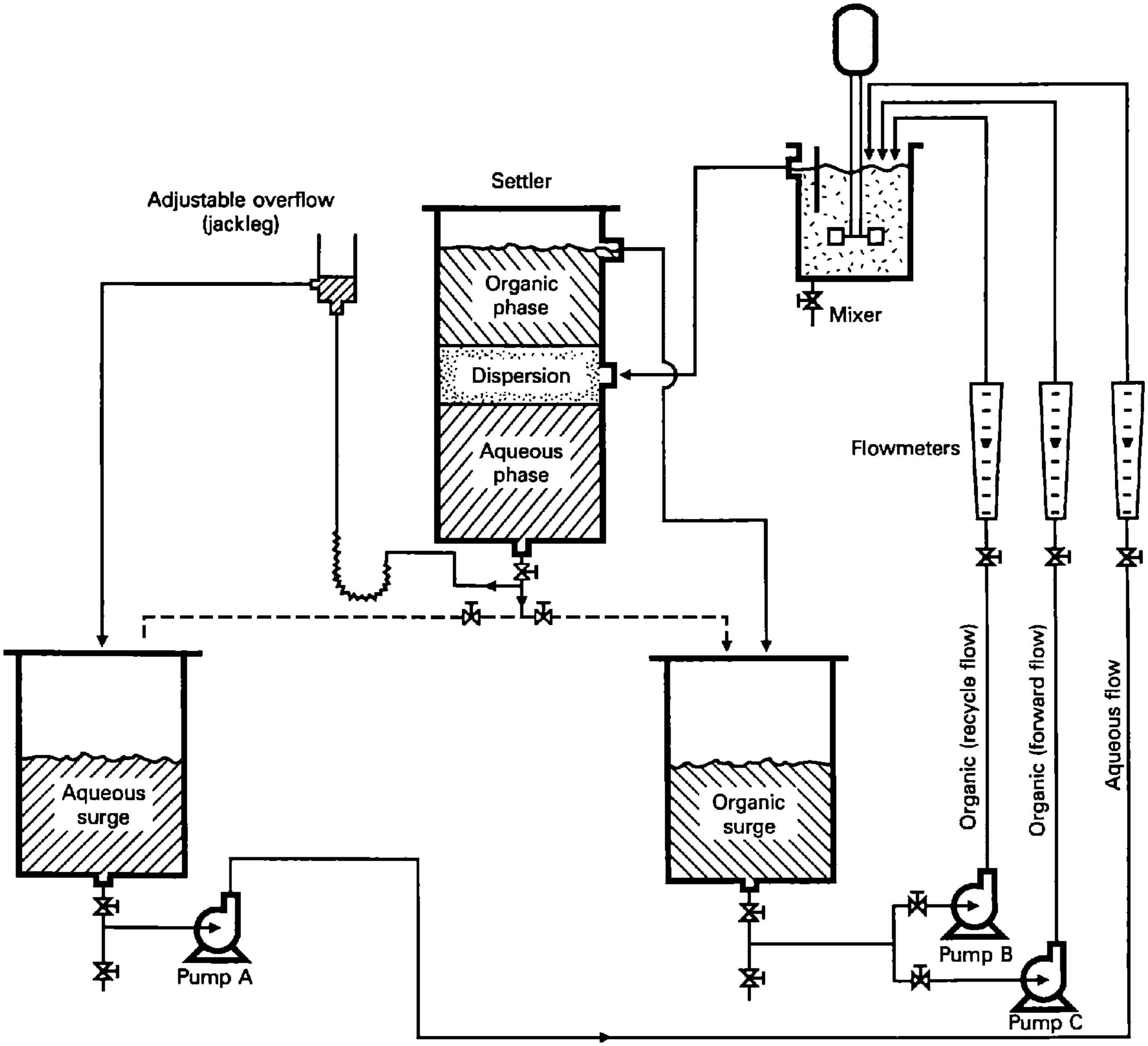
Typical plot of phase-disengagement data from static test measurements.

Dynamic test procedure—dynamic testing is usually conducted after static tests have identified near-optimum phase-disengagement conditions. The test procedure uses a miniature mixer-settler arrangement such as that shown in figure 5.32. This system is used to determine the relationship between the dispersion band depth and the specific flow (gallons per minute per square foot or liters per minute per square meter) attainable under various operating parameters or conditions.

The following general dimensions and capacities have been used for equipment arrangements such as that shown in figure 5.32.

- The mixer vessel configuration is equivalent to that illustrated in figure 5.27; a baffle is placed in front of the mixer overflow to minimize short circuiting. Feeding the organic and aqueous streams into the bottom of the mixing chamber has also been used. Mixer dimensions: ID = 10 cm, height = 14 cm, and solution depth = 10 - 12 cm. Impeller: Turbine such as that shown in

Figure 5.32



Dynamic system for measuring phase-separation characteristics.

figures 5.27 or 5.28, driven by an air motor or a variable-speed electric motor (500 to 1,500 rpm) that meets electrical code requirements for this type of service. The motor and impeller should be mounted so that the height of the impeller position can be adjusted.

- Settler dimensions: ID = 15 cm; total height = 35 cm; solution depth at overflow = 30 cm. The dispersion feed inlet is located at approximately 15 cm from the bottom of the settler.
- Surge vessels: ID = 15 cm; and height = ≈24 cm. The suggested total volume of the two surge vessels should be at least 1.4 times the total capacity held in the mixer and the settler. This capacity will normally permit complete drainage of the fluid contained in the mixer and settler into the surge tanks and still allow for a residual head of 6 to 8 cm in each surge vessel during system operations.
- All vessels are fabricated from glass or other transparent material and fitted with inlets, outlets, and drains

as shown. Each of the vessels should be fitted with a cover and appropriately vented.

- Except for the adjustable overflow system, the unit can be piped with rigid PVC pipe and valves. For most hydrometallurgical solvent-extraction operations, Tygon plastic tubing is suitable for both the adjustable overflow system and the remaining connections between vessels. After several months, however, some of the Tygon resin tubing may become brittle and should be replaced. For most applications, 1/4-in PVC pipe or 1/4 to 3/8-in-ID Tygon resin tubing will handle the required flows, but larger pipe or tubing is recommended for connections such as the gravity flow between the mixer and the settler.
- Either centrifugal or peristaltic pumps can be used. If peristaltic pumps are used, installation of a pulse damper between the pumps and the flowmeters will probably be necessary. Standard glass flowmeters, calibrated for the fluid being handled, are applicable for nearly all hydrometallurgical solvent-extraction investigations. Arrangements using only calibrated peristaltic pumps have also been used successfully. Pump A (figure 5.32) should be compatible with the aqueous feed solution, and pumps B and C should be compatible with the organic solvent mixture, but pumps that are compatible with both the organic and aqueous phases are more desirable. For most investigations, pumps with maximum capacities of about 1,500 mL/min will be satisfactory.

The following startup and operating techniques are generally applicable, but other procedures may also be suitable.

- Fill the aqueous and organic surge vessels with the desired aqueous feed solution and organic solvent mixture. In some instances it may be desirable or even necessary to work with varying degrees of loading and depletion in the organic and aqueous phases. This can occur, e.g., if the phase-disengagement rate is influenced by metal loading in the organic phase. If this type of variability is to be investigated, fitting the settler with a temporary agitator can be advantageous; the desired degrees of loading can be achieved by equilibration in the settler. The phases are then allowed to separate and are drained into the surge vessels.
- If an organic continuous dispersion is desired, transfer approximately 400 mL of the solvent mixture to the mixing vessel. Place the impeller at about the midpoint of the solvent in the mixer and start the impeller at the desired speed (often 600 to 1,000 rpm). Gradually add 400 mL of the aqueous feed solution, and adjust the impeller height to the desired operating position such as that shown in figures 5.27 or 5.28.

If an aqueous phase continuous dispersion is desired, both phases can be transferred to the mixer, and the impeller is started while positioned in the aqueous phase.

- Start the organic and aqueous feed flows at the desired initial rate, which will probably be the lowest rate in the planned test series. (The optimum specific flow for copper solvent-extraction operations is typically 2.0 gpm/ft^2 [$\approx$8 (mL/min)/cm^2], and the optimum for uranium solvent extraction with amine extractants is about 1.0 gpm/ft^2 [$\approx$4 (mL/min)/cm^2]).
- When the settler fills, and the top of the organic phase reaches the overflow level, open the bottom discharge valve and adjust the jack-leg position to give the desired organic-aqueous interface position.
- When the system stabilizes, record the thickness (if any) of the dispersion band and increase the organic and aqueous flow rates to the next desired specific flow. During the initial phase-disengagement studies, increasing the specific flow in increments equivalent to approximately 0.5 gpm/ft^2 is usually suitable. Repeat the procedure until the dispersion band thickness is about 9 in ($\approx$23 cm) or the settler approaches flooding, i.e., when a mixture of the organic and aqueous phases starts to discharge from one or both of the settler outlets. Figure 5.33 illustrates a plot of a typical dispersion band thickness versus the specific flow rates to a settler in a copper solvent-extraction circuit when operating with organic continuous and aqueous continuous dispersions. In commercial practice, settlers are often operated with specific flow rates that produce steady-state dispersion band thicknesses in the 4- to 6-in range.

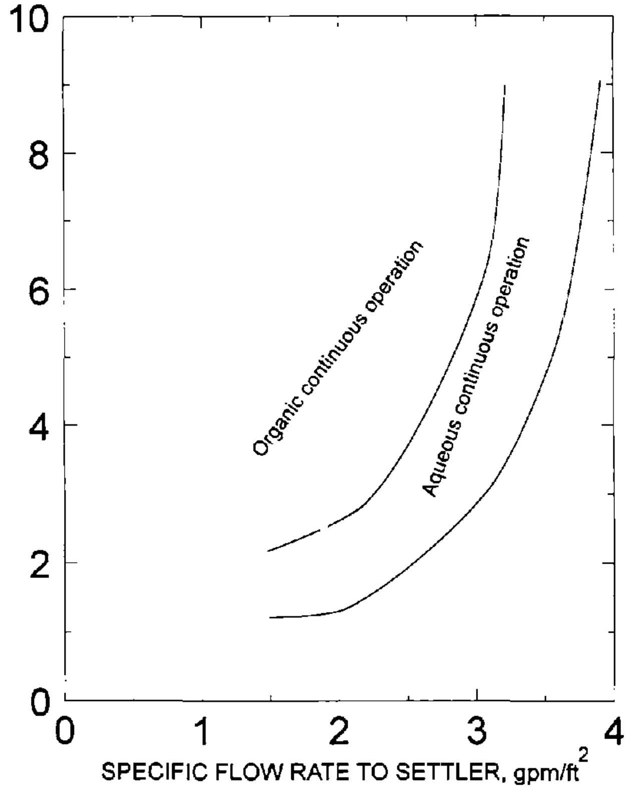
Dynamic phase-disengagement tests can also be used to investigate the effect of other circuit variables on settler capacities. For example, both visual observations and quantitative measurements can be made on the effect of variables such as the degree of agitation in the mixer, phase ratios, diluents and modifiers pH, etc. If the system is refined and fitted for temperature control, the effect of temperature variations can also be investigated.

5.4.5 Small-Scale Continuous Tests

5.4.5.1 Introduction

If the batch-test studies have indicated that the proposed solvent-extraction separations are technically feasible and have provided the information required for a conceptual flowsheet, the next probable step is to investigate the concept in a small-scale continuous countercurrent solvent-extraction system. One of the main reasons for conducting these small-scale continuous tests is to establish the stage-efficiency relationships required for scale-up calculations. This correlation defines, e.g., the difference between the theoretical extraction per stage as indicated by a McCabe-Thiele analysis of batch-test data (see figure 5.24) and the actual extraction realized in a given continuous countercurrent system. Typically, the actual distribution curve or extraction isotherm is displaced in some degree to the right of the theoretical isotherm as defined by the shakeout tests. Some of the variables that can influence this displacement include mixing time, pH effects, and short circuiting. Short circuiting in a copper-extraction circuit, e.g., may reduce the extraction in a continuous mixing stage to only about 75% of that obtained for the same residence time in batch mixing (Hazen, 1985, p. 13-41). Small-scale continuous solvent-extraction tests are also applicable for investigating additional factors including the degree of mixing, crowding, crud buildup, reagent stability, solvent losses, scrubbing requirements, and other recycling effects. Once near-optimum operating conditions have been established, the small-scale continuous systems can be used to produce the feed solutions needed for investigating downstream operations.

Figure 5.33



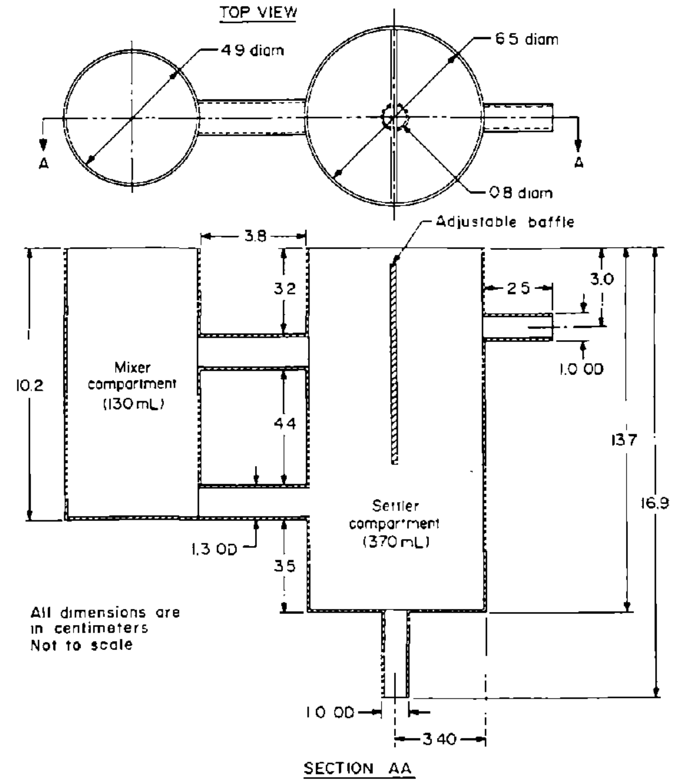
Typical variation of dispersion band thickness with changes in specific flow rates (copper extraction).

5.4.5.2 Equipment

Hydrometallurgical investigations have typically used a series of bench-scale mixer-settler stages for these continuous countercurrent solvent-extraction studies. A wide variety of equipment arrangements have been used, and individual researchers have often developed specific preferences. The following paragraphs describe and discuss the general layout and operation of a system that has been used successfully in a number of USBM solvent-extraction studies. The system consists of a series of miniature mixer-settler units such as that shown in figure 5.34.

This interconnected mixer-settler unit has two parallel tubes that join the mixer and settler compartments. The upper passage is used to recycle organic phase from the settler to the mixer. In some solvent-extraction operations, maintaining a continuous organic phase (i.e., a water-in-oil dispersion) requires this recycle. To obtain an organic recycle, the impeller is positioned in the lower half of the mixer, and under these conditions the dispersion flows from the mixer to the settler through the bottom tube. Conversely, by suitable positioning of the impeller, flow can be reversed to transfer aqueous phase from the settler

Figure 5.34



Interconnected mixer-settler unit.

into the mixer through the lower tube. This type of operation is adopted when an aqueous continuous dispersion is desired. If no recycle is desired, the upper tube is plugged with a suitable stopper.

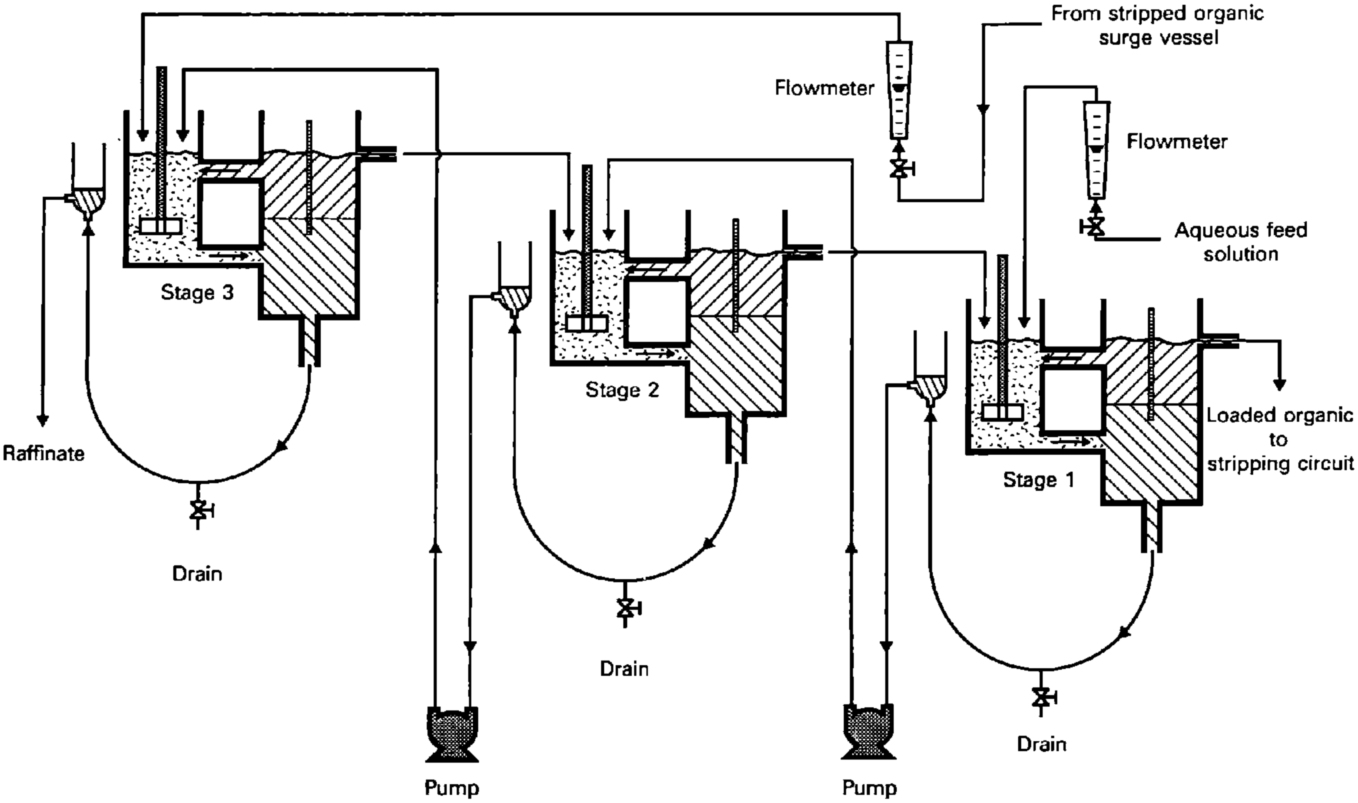
The mixer unit shown has a mixing volume of approximately 130 mL. If the total flow through the mixer is 20 mL/min, the effective mixing time will be approximately 6.5 min. Agitation is typically provided by a 2.5-cm-diameter by 1-cm-high, four-bladed, paddle-type impeller operating at about 800 rpm. Suitable agitators have been produced by machining the impeller from a polypropylene block, press-fitting the impeller onto a stainless steel shaft, and then coating the shaft with a length of heat-shrinkable polyolefin tubing. A threaded connection between the impeller and the shaft could also be used. In most instances, adequate mixing has been obtained with the mixer configuration shown in figure 5.34, but if desired, the mixer can be fitted with baffles. The agitator should be driven by either a currently approved variable-speed electrical motor or an air motor.

The settler chamber of the interconnected unit has an active volume of 370 mL. For a 20-mL/min total flow to the settler, the unit is considerably oversize for most solvent-extraction systems. Therefore, the settler is useful for effective phase separation and general observations of conditions such as crud buildup, but will not define a realistic settler capacity. Independent phase-separation studies, such as those described in section 5.4.4.7, are necessary for settler sizing.

The individual mixer-settler units are assembled in the combinations needed to provide the separations as defined by the conceptual flowsheet developed from the batch-test data. Figure 5.35 portrays the arrangement of a three-stage extraction system. The stage numbers correspond to the stages designated on the McCabe-Thiele construction of figure 5.24. The same general arrangement is also applicable for scrubbing and stripping circuits.

Precise control of the aqueous and organic feed rates is required. Requisite control has been achieved using either steady-head tanks and flowmeters or calibrated peristaltic pumps. Peristaltic pumps are used for interstage transfer of the aqueous phase. Airlifts have also been used successfully for this pumping operation. The pumps are adjusted to pump ahead all of the flow coming from the

Figure 5.35



Three-stage mixer-settler extraction circuit (Pyrex glass with Teflon polymer baffle plate).

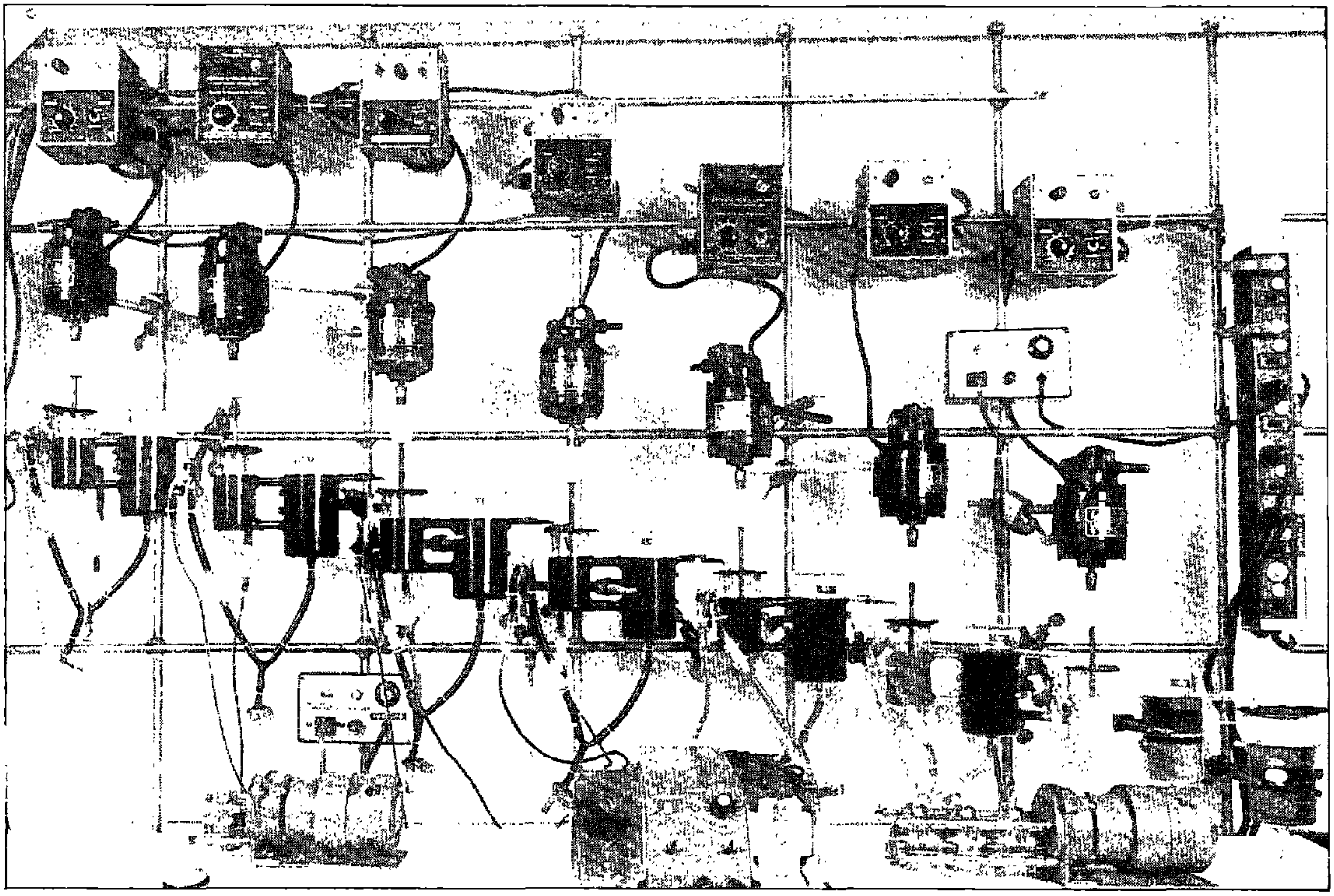
jackleg, which is essentially an adjustable overflow weir. Raising or lowering the jack leg controls the position of the organic-aqueous interface in the settler. The interstage organic flow in the circuit is by gravity. Providing covers for both the mixers and the settlers is recommended to minimize evaporation loss from the solvent mixture. Tygon-type plastic tubing is satisfactory for the interstage connections in most solvent-extraction systems, but this tubing may become brittle upon aging and will require periodic replacement. A number of hydrometallurgical researchers have found that Viton plastic tubing is one of the most durable for pumping the organic phase with peristaltic pumps that have roller-type pump heads. It is suggested, however, that pump manufacturers be consulted for specific recommendations concerning the particular aqueous and organic phases being handled.

All continuous solvent extraction systems should be set up in an adequately ventilated area. Installing the system in a walk-in hood unit is recommended. All electrical motors, etc., should be of a type currently approved for service in the conditions that will be encountered for the particular solvent-extraction system being investigated.

The photograph of figure 5.36 illustrates the layout of a solvent-extraction system setup used for investigating the removal of iron from a chloride leach solution prior to subsequent cobalt, manganese, and nickel separations (Redden and others, 1988). The system contains four extraction stages and three stripping stages. The flowsheet concept was based on the McCabe-Thiele analyses shown in figures 5.24 and 5.26. Even though figure 5.24 indicates that three extraction stages would be adequate, a fourth stage was added to provide a factor of safety and to obtain more precise control and evaluation of conditions affecting the iron content of the final raffinate. Subsequent downstream separations required nearly complete iron removal.

Other types of bench-scale contactors have been described by Bridges and Rosenbaum (1962) and by Ritcey and Ashbrook (1979, pp. 28-40). Several different types of laboratory-scale mixer-settler units have been produced commercially. Reagent manufacturers and distributors can often supply the names of companies currently producing these units.

Figure 5.36



Layout of bench-scale solvent-extraction system.

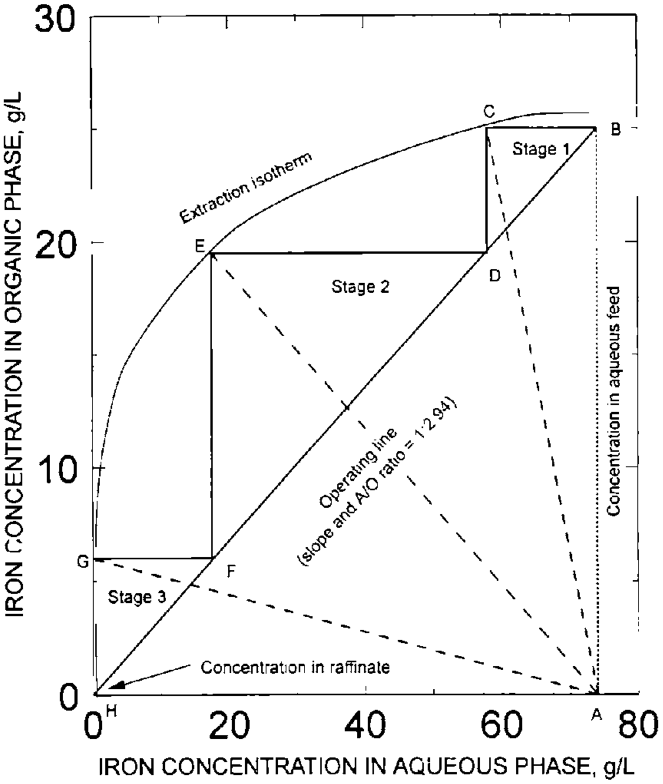
5.4.5.3 General Operating Considerations

To some degree every solvent-extraction separation is unique. This is true even when relatively similar systems are being used. Therefore, fully standardized test procedures for bench-scale continuous solvent-extraction separations are not feasible, but some generalizations are possible. Commercial operating techniques and procedures described in the literature can often provide guidance for operating bench-scale solvent-extraction circuits. The following paragraphs discuss a number of generalizations for mixer-settler systems such those as illustrated in figures 5.35 and 5.36.

- *Startup*—The initial startup of a mixer-settler solvent-extraction unit can be conducted using at least two different techniques. The first involves filling each mixer-settler unit of the extraction section with the desired phase ratio of the fresh aqueous feed and unloaded solvent mixtures. The system is then operated until steady-state conditions are reached. Typically this approach requires the operating time needed for four or five replacements of the circuit volume. The same general technique can be applied for startup of the stripping section. The second procedure involves filling each unit of the extraction system with aqueous and organic phases that have been equilibrated to simulate the anticipated steady-state conditions. The equilibrations are based on applicable McCabe-Thiele diagrams developed from shakeout test data. Figure 5.37 illustrates the procedure for a three-stage extraction system such as that previously depicted in figures 5.24 and 5.35. The mixer and settler of stage 1 are filled with the product of an organic-aqueous dispersion obtained by equilibrating fresh aqueous feed and the solvent mixture using the phase ratio defined by the slope of line AC. Similarly, equilibrated combinations prepared based on phase ratios defined by the lines AE and AG are used to fill stages 2 and 3, respectively. When this technique is used, steady-state operation is typically reached in less than 1 h of continuous operation. This startup procedure is particularly applicable when only limited quantities of feed liquor are available.

- *Jackleg adjustment*—The jackleg adjustment depends on the desired position of the interface in the settler. For example, if the impeller position and other factors equivalent to those shown in figure 5.35 are applicable, the jackleg height would be adjusted to give the interface position shown. If, however, the impeller position was adjusted so that the dispersion flow from the mixer to the settler was through the upper connecting tube, the interface position shown would result in an aqueous recycle. To achieve an organic recycle with this impeller position, it would be necessary to lower the interface below the lower connecting tube. These variations and other factors such as the degree of recycle desired usually depend upon trial-and-error positioning of the impeller and adjustment of the interface while observing the response in the mixer-settler unit.

Figure 5.37



Phase-ratio combinations for equilibrated startup procedure.

- *Dispersion conditions*—As mentioned previously, conductivity measurements can be used to determine which phase is continuous. Aqueous phase continuous dispersions (organic droplets dispersed in a homogeneous aqueous phase) are conductive, and organic phase continuous dispersions are relatively nonconductive. Any type of conductivity measuring device can be used. A simple device can be made by using a milliammeter (or even a flashlight bulb) and a suitable battery connected to probes that can be immersed in the dispersion.

The A/O ratio in the dispersion can be measured by sampling the dispersion with a calibrated syringe or similar device. The syringe tip is inserted into the dispersion in the mixer, and a sample withdrawn. The phases are allowed to separate, and the relative volumes noted. The contents of the syringe are then discharged back into the mixer. This type of measurement is used, e.g., when adjusting the recycle flows to achieve the desired phase ratio in the mixer.

- ***Sampling***—Syringes are also appropriate devices for sampling the mixer dispersions to determine mass-transfer conditions in each mixing stage. When steady-state operating conditions are reached, a sample is withdrawn from each mixer in the circuit. The phases are allowed to separate and then discharged into suitable sample containers. The sample size depends on the volume required for the desired analyses. Plotting these values on the theoretical extraction isotherm graph developed from the shakeout tests reflects the stage efficiency obtained in the mixer-settler units under the test conditions used. Typically, the extraction isotherm defined by this procedure is displaced to the right of the theoretical isotherm. The relative position of the two curves in combination with a McCabe-Thiele construction indicates the stage efficiency in each mixer-settler stage. This efficiency measurement can be used when developing scaleup relationships for cost evaluation studies.
- ***Shutdown***—Each stage of the mixer-settler circuit illustrated in figures 5.35 and 5.36 is hydraulically isolated. Therefore, when the circuit is shut down, there is no transfer of either the organic or aqueous phase between mixer-settler units. This means that when the circuit is restarted, steady-state conditions are established immediately. Also, when the circuit is shut down and the phases are allowed to separate, samples of the organic and aqueous phases can normally be used for stage-efficiency measurements. Comparison of the results from these samples and the syringe samples discussed in the sampling section above is recommended, particularly during the initial phases of an investigation,

5.4.6 Safety

Although commercially available solvent-extraction reagents, diluents, and modifiers are not generally classed as hazardous materials, the MSDS for each material should be carefully studied before the material is used. This caution would be particularly applicable for any experimental reagents. Some extractants, such as di-2-ethylhexyl phosphoric acid (DEHPA), may contain small percentages of organic compounds that are classified as hazardous or even carcinogenic.

The MSDS indicate that eye contact with solvent-extraction reagents, diluents, and modifiers can produce various degrees of irritation. Skin contact may also produce significant irritation. Other cautions include the following:

- Flammability or explosive characteristics are associated primarily with the diluents. When indicated by MSDS information, approved electrical equipment, including motors and switch gear, should be used. Recommended fire-extinguishing media include carbon dioxide, dry chemical agents, and foam. Upon combustion, most solvent-extraction reagents can produce hazardous fumes or decomposition products.
- In general, solvent-extraction reagents, diluents, and modifiers are stable under normal conditions, but are not compatible with strong oxidizing agents.
- The MSDS indicate that the vapors from solvent-extraction reagents may be harmful, particularly if inhaled in large amounts or for prolonged periods. Adequate ventilation, therefore, is important.
- Spills may present significant hazards and require containment. For example, all bench-scale solvent-extraction equipment should be installed over a collection system that has the capacity to confine and contain any spills or leaks.
- The MSDS should be consulted for general waste disposal requirements. Local regulations may also dictate special disposal criteria.
- Before solvent-extraction experiments are conducted, preparation of a JSA is always prudent (see chapter 1, section 1.2.5.3). For example, toxic ions, such as arsenates, chromates, and other heavy metals, may be present in the feed solutions. The solvent-extraction process may concentrate these ions significantly. Also, the acidic or basic stripping solutions are usually corrosive and should be handled in a manner that will prevent any skin or eye contact.

Each solvent extraction operation is unique in that it may involve specific hazardous materials or equipment. The researcher must evaluate these hazards and establish appropriate safety and health practices that adhere to current regulatory requirements.

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ACKNOWLEDGMENTS

The author thanks the following for the constructive advice, comments, suggestions, and support provided during the preparation of this report.

- USBM personnel at the Salt Lake Research Center, the Rolla Research Center, the Reno Research Center, the Albany Research Center, and the Tuscaloosa Research Center for extensive technical consultations and detailed reviews of both preliminary and revised draft manuscripts for all components of the document.
- Robert C. Emmett, EIMCO Process Equipment Co., Salt Lake City, UT, for comprehensive technical consultations and manuscript reviews related to chapter 4 on solids-liquid separations.
- Charles Maes, Zeneca Specialties, Phoenix, AZ, for consultations and technical information related to section 5.4 of chapter 5 on solvent extraction.
- George A. Wolfe, Henkel Corp., Tucson, AZ, for consultations and technical information related to section 5.4 of chapter 5 on solvent extraction.
- David Gefvert, Sherex Chemical Co., Inc., Dublin, OH, for consultations and technical information related to section 5.4 of chapter 5 on solvent extraction.
- James P. Bowersox, Dorr-Oliver, Inc., Milford, CT, for consultations and technical information related to section 4.3 of chapter 4 on filtration separations.

APPENDIX.—OTHER ABBREVIATIONS, ACRONYMS, AND SYMBOLS

Chapter 1

CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CFR	Code of Federal Regulations
EPA	Environmental Protection Agency
JSA	job safety analysis
LEL	lower explosive limit
MSDS	material safety data sheets
NIOSH	National Institute for Occupational Safety and Health
NRC	National Research Council
OSHA	Occupational Safety 'and Health Administration
PEL	permissible exposure levels
SARA	Superfund Amendments and Reauthorization Act
TLV	theshold limit values
TWA	time-weighted average
UEL	upper explosive limit

Chapter 2

ASTM	American Society for Testing and Material
OSHA	Occupational Safety and Health Administration

Chapter 3

DO	dissolved oxygen
EDTA	ethylenediaminetetra-acetic acid
Eh	oxidation potential
emf	electromotive force
ID	inside diameter
JSA	job safety analysis
MSDS	material safety data sheets
NDT	nil-ductility temperature
NFPA	Nation Fire Protection Association
OEA	oxygen-enriched atmosphere
ORP	oxidation reduction potential
SS	stainless steel
TCLP	toxicity characteristic leaching procedure

Chapter 4

A	area below settling curve (4.2.3.1); unit area (4.2.3.2); area of filtering surface (4.3.1)
C	concentration of flocculable solids at time t (4.2.3.3)
C_c	concentration of solute in final washed cake (4.3.4.5)
C_f	concentration of solute in feed-slurry liquid (4.3.4.5)
C_o	concentration of initial pulp (4.2.3.1); concentration of flocculable solids at time t_o (4.2.3.3)
C_u	desired underflow concentration (4.2.3.1)
C_w	concentration of solute in wash liquid (4.3.4.5)
D	specific gravity of solution (4.2.3.1); weight ratio of liquid to solids at desired underflow density (4.2.3.2)
D/U	dewatered but unwashed (cake) (4.3.4.5)

F	dilution or weight ratio of liquid to solids for rate R (4.2.3.2)
G	specific gravity of dry solids (4.2.3.1)
g_L	grams of liquid (4.2.3.2)
g_s	grams of dry solids (4.2.3.2)
H	average pulp height in compression zone (4.2.3.1)
h	area below settling curve divided by settling time (4.2.3.1)
H_o	initial pulp depth (4.2.3.1)
H_u	underflow pulp height (4.2.3.1)
K	solution decant volume (4.2.3.2); rate constant (4.2.3.3)
n	exponent (4.2.3.1); wash ratio (4.3.4.5)
P	total pressure drop across cake and filter medium (4.3.1)
R	settling rate (4.2.3.2)
r	resistance of filter medium and equipment restrictions (4.3.1)
$Sp.Gr._{,L}$	specific gravity of liquid (4.2.3.2)
t	time (4.2.3.3)
t_o	time at start of flocculation reaction (4.2.3.3)
t_u	time for pulp to settle (4.2.3.1)
V	volume of filtrate (4.3.1)
V_w	volume of cake wash (4.3.4.5)
W	weight of dry solids (4.2.3.1); mass of dry-cake solids (4.3.1); weight of dry cake (4.3.4.5)
α	average specific cake resistance (4.3.1)
ΔP	pressure drop across cake (4.3.4.5)
θ	time (4.3.1)
θ_d	dry time (4.3.4.5)
μ	viscosity of filtrate (4.3.1); viscosity of liquid phase (4.3.4.5)

Chapter 5

A/O	aqueous to organic (ratio)
aq	aqueous
BDST	bed-depth/service-time
C_f	final concentration
C_o	concentration in feed liquor
E	extraction coefficient
ID	inside diameter
JSA	job safety analysis
M	metal
MSDS	material safety data sheets
O/A	organic to aqueous (ratio)
OD	outside diameter
org	organic
PVC	polyvinyl chloride
WSR	wet-settled resin
X/M	equilibrium capacity

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☆ U.S. Gov. Printing Office: 1995-709-088/20,009