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→ held in Casa Grande, Arizona on July 25, 1990 revealed several specific areas/subjects of potential environmental concern. These areas/subjects are: air quality; sulfuric acid handling and use; groundwater and hydrologic modeling; surface subsidence; attenuation; and recycle of fluids. Each of these areas/subjects will be addressed in a separate Bureau of Mines Open File Report (ofR) to be used as background documents in support of the ea. In addition, several other points of interest will be addressed in other background documents, including: the overall process description; geology and hydrology; mineralogy and petrology; rock quality and structure; and geophysics. → This report summarizes the results of the investigation into sulfuric acid handling and use. This material will then be incorporated by reference in the draft Environmental Assessment. ←

CONTENTS

	<u>Page</u>
Abstract.....	
Introduction.....	
Acid handling and use.....	
Sulfuric acid general information.....	
Acid handling.....	
Acid uses.....	
In situ leach mining.....	
Solvent extraction-electrowinning.....	
Extraction.....	
Stripping.....	
Electrowinning.....	
Environmental protection.....	
Acid transportation.....	
Acid spills.....	
Summary and recommendations.....	
References.....	

ILLUSTRATIONS

1. Map of Santa Cruz area.....	
2. MSDS for sulfuric acid.....	
3. Label required for sulfuric acid transport.....	
4. Copper ore zone and five-spots pattern.....	
5. Solvent extraction-electrowinning flow chart.....	

CONTENTS

Page

TABLES

1. NIOSH chemical hazard sulfuric acid information.....
2. How to use the emergency guidebook during an incident involving hazardous materials.....
3. Potential hazards guide for sulfuric acid (guide 39).....

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

ft	foot
gal	gallon
gpl	gram per liter
gpm	gallon per minute
h	hour
lbs	pound
mg/m ³	milligram per cubic meter
pct	percent
yr	year

OPEN FILE REPORT: SULFURIC ACID HANDLING AND USE RELATED TO
THE IN SITU COPPER LEACH MINING DEMONSTRATION PROJECT, ARIZONA

by Pamela J. Watson¹

*** ABSTRACT

The U.S. Bureau of Mines, under a cooperative agreement with ASARCO Santa Cruz, Inc. has started an investigation into the feasibility of in situ leach mining of a deep copper oxide deposit near Casa Grande, Arizona. Because this investigation involves a federal agency, all requirements of the National Environmental Policy Act (NEPA) must be observed. To meet these requirements, the Bureau intends to prepare an environmental assessment (EA) for this project to evaluate the significance of anticipated environmental impacts which may result. The EA briefly provides sufficient evidence and analysis for determining whether to prepare an environmental impact statement (EIS) or a finding of no significant impact (FONSI). An EIS is prepared if the action is determined to have a significant effect on the human environment. A FONSI is written if it is determined that a significant effect on the human environment will not result from the proposed action. Under a FONSI, the proposed action is exempt from requirements to prepare an EIS. Preliminary investigations, discussion between Bureau and industry researchers, and comments and concerns expressed at a public meeting held in Casa Grande, Arizona on July 25, 1990 revealed several specific areas/subjects of potential environmental concern. These areas/subjects

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are: air quality; sulfuric acid handling and use; groundwater and hydrologic modeling; surface subsidence; attenuation; and recycle of fluids. Each of these areas/subjects will be addressed in a separate Bureau of Mines Open File Report (OFR) to be used as background documents in support of the EA. In addition, several other points of interest will be addressed in other background documents, including: the overall process description; geology and hydrology; mineralogy and petrology; rock quality and structure; and geophysics. This report summarizes the results of the investigation into sulfuric acid handling and use. This material will then be incorporated by reference in the draft Environmental Assessment.

*** INTRODUCTION

The U.S. Bureau of Mines (Bureau) and ASARCO Santa Cruz, Inc. initiated the "Santa Cruz In Situ Copper Mining Research Project" on land owned by the Santa Cruz Joint Venture (ASARCO Santa Cruz, Inc. and Freeport Copper Co.) (SCJV) to evaluate the technical, economic, and environmental feasibility of in situ leach mining of copper oxide minerals. The research project is being conducted at the Santa Cruz site which is located approximately seven miles west of the city of Casa Grande, Arizona and one and three fourths miles north of Arizona State Highway 84. The Santa Cruz porphyry copper deposit has not been previously mined. The SCJV owns the surface and mineral rights of the test site. The land is retired agricultural land. The project is located in section 13, Township 6 South, Range 4 East. Location of the research project test site is shown in Figure 1.

The research project is separated into several interrelated tasks: site characterization to determine whether the geology and hydrology of the site are amenable to in situ leach mining; determination that the project is environmentally compatible; construction of a surface solvent extraction-electrowinning facility; and commencement of the actual in situ leach mining test.

The in situ leach mining process to be tested at the Santa Cruz site consists of injection of dilute sulfuric acid solution into a granitic bedrock complex containing soluble copper oxide minerals via wells constructed to protect the regional aquifer. Acid concentration of the injection fluid will be from 10 to 60 gpl (one to six pct by weight). The dilute acid solution, injected through a well into an otherwise undisturbed copper mineralized zone, migrates into and through the natural fractures and fissures which contain the mineralization and selectively dissolves the copper while leaving the rest of the rock relatively unchanged. This copper-bearing solution then flows toward a pattern of recovery wells which surround the injection well. It collects in the recovery wells, where it is pumped from the test zone to the land surface. Copper will be recovered from the solution by solvent extraction-electrowinning, resulting in the production of copper cathode sheets. After the copper is stripped from the solution, a small quantity of acid is added to the solution to correct for any acid naturally used or consumed by the rock. The solution is then pumped into the injection well and the process is repeated.

Before injection of the dilute acid solution, extensive testing was conducted to evaluate hydrogeologic conditions using wells

constructed at the test site. Groundwater monitor wells were constructed to monitor the basin fill aquifer. Pumping tests, injection tests using local groundwater, and a saline solution tracer test in the leaching zone were conducted to determine the hydrogeological condition of the ore body prior to testing with dilute acid solution.

The test program conducted prior to injection of dilute acid solution was authorized under a Temporary Groundwater Quality Protection Permit and a Temporary Aquifer Protection Permit issued by the Arizona Department of Environmental Quality (ADEQ). Test wells were drilled with authorization from the Arizona Department of Water Resources. In addition to being used to support the EA, test results will be incorporated into the Application for Aquifer Protection Permit and submitted to the Arizona Department of Environmental Quality (ADEQ). This Aquifer Protection Permit must be obtained from ADEQ before the in situ leach test with dilute acid solution can be conducted. In addition, the U.S. Environmental Protection Agency, under authority of the Federal Underground Injection Control Program, may require all injection wells to meet Class V well requirements, the primary restriction being no contaminant injected into an underground source of drinking water may cause a violation of any primary drinking water regulation under 40 CFR Part 142 or otherwise adversely affect the health of persons (7)².

This report summarizes the results of the investigation of sulfuric acid handling and use raised by the NEPA process and/or by

²Underlined numbers in parentheses refer to the list of references at the end of the paper.

concerns expressed by the public through verbal or written comment at the Bureau's Public Meeting in 1990. This material is incorporated by reference in the draft Environmental Assessment.

*** ACID HANDLING AND USE

SULFURIC ACID GENERAL INFORMATION

Sulfuric acid is classified as a hazardous material, Class 8-- Corrosive, labeled UN 1830. As such, there are very specific rules and regulations for the handling, use, and transport of the acid.

Basically, sulfuric acid is an oily, colorless to slightly yellow, clear to turbid, odorless liquid. It is completely soluble in water. Sulfuric acid is not flammable but is highly reactive and capable of igniting finely divided combustible materials on contact. When contacting finely divided combustibles, it reacts violently with water and organic materials with evolution of heat. Contact of sulfuric acid with metals can also be explosive, and may produce sulfur dioxide and hydrogen gas (2). It is extremely hazardous when it comes in contact with many materials, particularly carbides, chlorates, fulminates, nitrates, picrates, powdered metals and other combustible materials. In addition, contact with sulfuric acid should be avoided for several inorganic and organic compounds, including: sodium carbonate, sodium hydroxide, elemental sodium, potassium permanganate, ammonium hydroxide, potassium chlorate, ethylene glycol, aniline, and ethylene diamine (16-17).

Long term exposure to high levels of acid fumes may cause erosion of teeth followed by jaw necrosis, bronchial irritation, coughing, and bronchial pneumonia, or gastrointestinal disturbances. Sulfuric acid is

acutely toxic to human tissue, the extent of tissue damage being directly dependent upon concentration and duration of exposure ranging from a mild, transient irritation, to corrosion, chemical burn, and in extreme and isolated cases, death (2). Acute and chronic respiratory diseases may be aggravated. Some studies indicate that sulfuric acid aerosol levels as low as 0.02 to 0.04 mg/m³ may cause significant effects on lung function in humans. In addition, concentrations as low as 0.04 mg/m³ may act synergistically with copollutants such as ozone, NO₂ and metal particulates (2). Sulfuric acid is not classified as a carcinogen. Table 1 more specifically describes the potential hazards of sulfuric acid (16). Tables 2 and 3 summarize the procedures to follow in the event of an accident, which is described more fully in the Transportation section, below. The Material Safety Data Sheet, figure 2, contains more thorough information about sulfuric acid. Recent legislation has however recommended deleting non-aerosol forms of sulfuric acid from the list of toxic chemicals subject to section 313 of the Emergency Planning and Community Right-to-Know Act of 1986, with no cause of adverse effects to human health or the environment being documented. Aerosol forms of acid are still subject to 313 rules, with aerosols defined as any generation of airborne sulfuric acid, including mists, vapors, gas, or fog without regard to particle size (2).

ACID HANDLING

The Occupational Safety and Health Administration (OSHA) has jurisdiction over any potentially hazardous material. Their rules and regulations would apply to the acid use and handling issue (5-6). The National Institute of Occupational Safety and Health (NIOSH) has

developed guidelines and standards for specific hazardous materials adopted by OSHA. Specific information has been identified with regard to sulfuric acid. That information is listed in table 1, along with the definition of the codes used by NIOSH (16). The handling of sulfuric acid will be regulated by Federal law as pertaining to hazardous materials as defined in the Code of Federal Regulations (CFR) under EPA, OSHA, NIOSH, and DOT rules (5-15). The label that must be prominently posted on trucks or tanker cars is illustrated in figure 3.

All employees will be required to take training in the safe handling and use of sulfuric acid as well as any other identified potentially hazardous materials, which would include OSHA Right-To-Know rules under their Hazard Communication Standards (5-6). This training must take place at initial assignment to an area with any potential hazardous materials present and/or when any new hazard is introduced to the workplace. The training should include:

- Requirements of the OSHA standard, which are a Permissible Exposure Limit (PEL) of 1 mg/m^3 for sulfuric acid and a Time Weighted Average (TWA) not to be exceed of 1 mg/m^3 . (5);
- Operations in the workplace where hazardous chemicals are used;

- Location of the written hazard communication program, material data safety sheets (MSDS), written hazard evaluation procedures, and lists of hazardous chemicals, including sulfuric acid and potentially some of the lixivants used in the solvent extraction-electrowinning (SX-EW) process;
- Procedures for determining the presence of a hazardous chemical;
- Specific hazards of the chemicals in the employee's work area, which are available on the MSDS;
- Personal protective measures and emergency procedures. Protective measures will be based on sulfuric acid hazards and emergency procedures will follow OSHA and NIOSH Guidelines. These have been developed by OSHA and NIOSH and the specific guidelines for sulfuric acid are given in tables 2 and 3;
- How to read and interpret information on labels and MSDS; and
- How to obtain and use available hazard information.

The U.S. Department of Transportation has developed the Emergency Response Guidebook for First Response to Hazardous Materials Incidents, the procedures developed would be used in the case of any spill or accident with a hazardous material (17). In general, the procedures to be followed are well described for anyone coming on an incident, accident, or spill. The Guidelines were developed for use by first

responders, to be used for initial action to be taken. The generic steps to take if an accident or spill has occurred are listed in table 2. The specific steps to take for dealing with sulfuric acid are listed in table 3. See Transportation section, below, for further information on handling of spills.

ACID USE

In Situ Leach Mining

During in situ leach mining, a dilute sulfuric acid solution, composed of 1 to 6 pct acid and 94 to 99 pct water, is injected through a well completed into an otherwise undisturbed ore zone. The dilute sulfuric acid solution will be made from a concentrated solution of 93 pct H_2SO_4 , delivered by tanker truck from sources in the area (18). At the Santa Cruz site, the copper oxide test zone is located at a depth of 1570 ft to 1770 ft below the land surface (fig. 4). The solution migrates into and through the fractures and fissures which contain the copper mineralization, and as it migrates copper is selectively leached from the ore leaving the rest of the rock relatively unchanged. The solution will be recovered through wells located along the perimeter of the well field (fig. 4). Copper will be removed from the solution using conventional solvent extraction-electrowinning methods. (See Solvent Extraction-Electrowinning section, below, for more thorough description of the processing.) Once stripped of its copper, the barren solution will be rejuvenated and recycled back into the ore zone. Movement of all fluids injected into the rock will be controlled through pumping. Approximately one to two pct of the rock in the test zone will be removed via the leaching process.

Facilities on the surface include wellheads, pipes, tanks to hold solvent and acid, three evaporation and two storage ponds, and buildings. All surface storage areas will be underlain by impervious liners. Wells to be utilized during the term of the project include one injection well and four recovery wells. These wells are presently in place and were originally installed for use during a site hydrogeologic investigation. The four recovery wells are arranged in a square pattern on the ground surface with side dimensions of 127 ft. The single injection well is located in the center of the square. This arrangement is referred to as a "five-spot" well pattern (fig. 4). The total area of the research project is about 7.5 acres. Storage ponds will be designed on the average for a 24 h retention time at design flow rates. The ponds will all be double lined with a leak detection system in place. The sulfuric acid storage tanks will be designed to prevent discharge of liquids. Discharge control will include construction of a pad compatible with sulfuric acid. This pad will be surrounded by berms, walls, or dikes capable of containing 10 pct by volume of the total liquids stored or the volume of the largest liquid container, whichever is greater. All construction within the site area will be elevated 3 ft higher than the surrounding areas to eliminate potential damage from a 100-yr storm event.

Solvent Extraction-Electrowinning

The SX-EW process is a relatively simple method of removing dissolved copper from solutions produced by leaching of copper oxide ore. The process is widely used in connection with leaching of copper from previously-excavated or broken rock.

The pregnant leach solution containing dissolved copper is pumped via pipeline from the leaching operation to the SX-EW plant. The SX-EW process consists of three steps, which are described below and illustrated in figure 5.

Extraction

The first step in the SX-EW process is the removal of copper from the copper-bearing leach solution. The leach solution is vigorously mixed with an equal volume of kerosene-based solvent that contains an organic chemical specifically designed to extract the copper from the solution, leaving other dissolved metals and elements behind. After the solutions have been mixed for about two minutes, the mixture is allowed to settle.

The water-based leach solution, which has given up its copper to the organic chemical, is the heavier of the two solutions and sinks to the bottom. The barren leach solution is re-acidified to the proper leaching level and recycled through the injection wells into the leach zone in the ore body. The raffinate, which is the liquid product resulting from the extraction of a liquid with a solvent, will go from the SX circuit to the raffinate storage pond for storage prior to re-injection to the ore body. Excess raffinate and other plant solutions will be pumped to an evaporation pond.

The kerosene-based solvent containing the copper-laden organic chemical floats to the surface and is pumped to the next step in the solvent extraction process.

Stripping

In this, the second step in the process, the copper-bearing organic is mixed with a strong sulfuric acid solution (170 gpl H_2SO_4) called "electrolyte." The electrolyte solution strips the copper from the organic solution, leaving it barren of copper. These mixed solutions are allowed to settle. The kerosene-based organic, now barren of copper, again rises to the top and the electrolyte containing the copper, called "rich electrolyte" settles to the bottom. The barren organic solution is recycled to the extraction process and the copper-rich electrolyte solution is pumped to the electrowinning tankhouse.

Electrowinning

In the final step, electrowinning, the rich electrolyte is pumped through a series of tanks or "cells." Hanging in the tanks are anodes which are generally made of calcium, lead, and antimony alloy alternating with cathodes which are copper, stainless steel, or titanium. Each alloy plate serves as the anode pole of an electric circuit: each cathode pole begins as a "starter sheet" of titanium blanks utilizing plastic edge strips and a mechanical grooved bottom edge to permit ease of stripping. These plates hang in the tanks alternating anode with cathode. A direct current is passed through the electrolyte, reducing some of the copper ions to copper metal, which accumulates on the starter sheet. Cobalt sulfate will be added to the electrolyte as needed to prevent excess anode corrosion.

After several days in the cell, a starter sheet has grown to a slab of virtually pure copper weighing about 100 lbs. At that point, it is removed from the cell and replaced with a new starter sheet. The

harvested cathodes are ready for sale or for further processing into other copper products.

The electrolyte that has passed through the tankhouse, partially depleted of its copper, is recycled to the stripping process to have its copper content restored.

Environmental Protection

The solvent extraction-electrowinning process involves virtually no waste because all of the solutions are continuously recycled through three separate, closed-loop circuits. Sulfuric acid mist will be controlled in accordance with local air quality and OSHA regulations. The plant will have the appearance of a small-scale industrial facility.

*** ACID TRANSPORTATION

The acid will be transported to the SCJV by trailers made of stainless steel or blackened carbon steel, designed to carry up to 5000 gal. When transporting acid, they only carry 3200 gal. With other materials they can transport the full 5000 gal. The 3200 gallons translates to a fully loaded truck weight of 80,000 lbs (3-4, 18). The proposed leach solution injection rate is a range from 10 to 50 gpm. With an injection rate of 10 gpm and 1 pct acid, 2 trucks per month would be required, which would be the minimum. At an injection rate of 50 gpm and 5 pct acid, 34 trucks per month would be required, which would be the maximum.

All trucking firms must follow and adhere to Federal transportation regulations (1, 4, 9-15). Arizona follows Federal laws (13). The agency that would govern transportation is the Department of Transportation, both Federal and state (1, 9).

The Federal laws are promulgated under Code of Federal Regulations (CFR) Title 49, Transportation. The following chapters in Title 49 deal with the transport of sulfuric acid:

- Chapter I--Research and Special Programs Administration, Department of Transportation; Subchapter B--Materials Transportation Bureau; Part 107--Hazardous Materials Program Procedures (1);
 - Chapter I--Research and Special Programs Administration, Department of Transportation; Subchapter C--Hazardous Materials Regulations; Part 171--General Information, Regulations, and Definitions (1); Part 172--Hazardous materials tables and hazardous materials communication regulations (1); Part 173--Shippers--General Requirements for Shipments and Packagings (1); and Part 177--Carriage by Public Highway, especially Part 177.839--Corrosive liquids (1, 10);
- and
- Chapter III--Federal Highway Administration; Part 385--Safety Ratings (11); Part 386--Rules of Practice for Motor Carrier Safety Proceedings (12); Part 388--Cooperative Agreements with States (13); Part 394--Notification and Reporting of Accidents (14); and Part 397--Transportation of Hazardous Materials; Driving and Parking Rules (15).

The permit requirements are specified within these laws and rules. Safety regulations are found in Parts 385 and 394. Safety training regulations are found in 29 CFR 1910, described above (5-6).

Basically, the transportation of sulfuric acid must conform to these specific rules and regulations. More thorough investigations of all the aspects of sulfuric acid shipping and transportation can be found in the referenced CFR chapters. Sulfuric acid is required to be labeled "Corrosive", using the label illustrated in figure 3, UN 1830. It must be shipped in corrosive resistant containers, with a wall thickness no less than 8 mm mild steel. A corrosive liquid is defined as a liquid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact. If a liquid causes a severe corrosion rate on steel or aluminum, it is also classified as corrosive (2). Because the acid will be shipped to the Santa Cruz site in tanker trucks, no specific limitations on bulk shipment or packing requirements will apply.

ACID SPILLS

In the event of a spill, the ADEQ would coordinate the environmental side while the Department of Public Safety (DPS) would take charge of the safety and possible evacuation aspects (3). If a spill occurs and is less than 5 gal, the truck drivers are certified to handle it using soda ash or lime and water (See note about spills on any highway). Small spills (less than 3 gal) are handled by ventilating the area and flushing with large amounts of water, usually at least a 100 to 1 ratio. That is if you spill 3 gal of acid, you will need at least 300 gal of water to neutralize. The addition of water will react with the acid, creating heat and possible spattering. Therefore, all personal protective equipment must be worn while attending to a spill. Personal protective equipment required includes corrosive resistant coat, pants,

and gloves; steel-toe PVC boots; chemical goggles; hard hat with full face shield; and a respirator (NIOSH approved) (1, 10, 16-17).

If a spill is greater than 5 gal, it requires the application of a neutralizing agent. This application is a job for specially trained personnel. The truck drivers must notify the DEQ, DPS, and their home office. The responsible trucking firm will then send out their Emergency Response Team to supervise, cooperate with the DEQ and DPS, clean up the spill, and oversee the filling out of any and all required paperwork. If more than 1000 lbs (40 gal) is spilled, notification of CHEMTREC is also required. CHEMTREC, the Chemical Transportation Emergency Center, is a national organization of the Department of Transportation to coordinate and guide in the event of a spill of any magnitude. They provide, in conjunction with the National Response Center (the single Federal government center to which releases of hazardous substances must be reported), to provide 24-h assistance to emergency responders, carriers, shippers, and all others handling hazardous materials. The telephone number is 1-800-424-9300 (17).

*** SUMMARY AND RECOMMENDATIONS

Although classified as a hazardous material, sulfuric acid is a basic necessity to the operation of this in situ copper leaching demonstration project. Careful, thorough planning of the transportation, storage, and use of the acid will assure the safe handling at the project, which will minimize any environmental impacts from the surface handling activities. With a well-designed training and emergency response program in place, the project is committed to assuring the safeguarding of the environment. Results of this research

may open many new opportunities for in situ leaching of copper as well as other critical and strategic commodities.

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Table 1. - NIOSH Chemical Hazard Sulfuric Acid Information

Formula	H ₂ SO ₄
CAS, RTECS, and DOT UN/NA	7664-93-9; WS5600000; 1831/1830
Guide Number	39
Synonyms	Oil of vitriol
Exposure Limits	1 mg/m ³ (NIOSH) 1 mg/m ³ /10-hr TWA
IDHL Level	80 mg/m ³
Physical Description	Colorless to dark brown, oily liquid; odorless
Chemical and Physical Properties	MW: 98 BP: 518° F Sol: Miscible Not combustible, but highly reactive VP: <0.001 mm MP: 37° F
Incompatibilities	Organics; chlorates, carbides, fulminates, picrates, metals
Measurement Method	SiO ₂ ; NaHCO ₃ ; IC; III
Personal Protection and Sanitation	CLOTHING: > 1% AP/< 1% RP GOGGLES: Any poss WASH: Immed upon contam CHANGE: NA REMOVE: Immed contam non-imperv PROVIDE: > 1% eyewash, quick drench
Respirator Selection Upper Limit Devices Recommended	NIOSH 25 mg/m ³ : PAPRIHiEAG*/SA:CF* 50 mg/m ³ : CCRAGFHiE/SCBAF/SAF/GMFHiEAG 80 MG/M ³ : SAF: PD,PP Ω: SCBAF: PD,PP/SAF:PD,PP:ASCBA Escape: GMFHiEAG/SCBAE
Health Hazard: Route	Inh, Ing, Con
Health Hazard: Symptoms	Eye, nose, throat irrit; pulm edema, bron emphy; conj; stomatitis; dent erosion; trachbronc; skin, eye, burns; derm
Health Hazard: First Aid	Eye: Irr immed Skin: Water flush immed Breath: Art resp Swallow: Medical attention immed
Health Hazard: Target Organs	Resp sys, eyes, skin, teeth

KEY for Table 1

EXPLANATION OF ABBREVIATIONS ON NIOSH TABLE

TWA	time weighted average
IDHL	Immediately Dangerous to Life or Health
MW	molecular weight
BP	boiling point at 1 atmospheres, °F
So1	solubility in water at 68 °F, % by weight
VP	vapor pressure at 68°F, mmHg
MP	melting point, °F
SiO ₂	Silica gel adsorption tube
IC	Ion chromatography
III	NIOSH Manual of Analytical Methods - 3rd edition
CLOTHING	Wear appropriate equipment to prevent: >x%AP/y%RP: Any possibility of skin contact with liquids containing >x% of contaminant, and repeated or prolonged skin contact with liquids containing y%
GOGGLES	Wear eye protection to prevent: Any poss: Any possibility of eye contact
WASH	Employees should wash: Immed upon contam: Immediately when skin becomes contaminated
CHANGE REMOVE	Work clothing should be changed daily: NA: Not applicable Remove clothing: Immed contam non-imperv: Immediately remove non-impervious clothing that becomes contaminated
PROVIDE	The following equipment should be available: Eyewash, quick drench
Ω	Emergency of planned entry in unknown concentration or IDHL conditions
AG	Acid gas cartridge or canister
CCRAGFHiE	Any chemical cartridge respiratory with a full facepiece and acid gas cartridge(s) in combination with a high-efficiency particulate filter
GMFHiEAG	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted acid gas canister having a high-efficiency particulate filter
PAPRHiE	Any powered air-purifying respirator with a high-efficiency particulate filter
SAF	Any supplied-air respirator with a full facepiece
SAF:PD,PP	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
SAF:PD,PP: ASCBA	Any supplied-air respirator with a full facepiece and operated in pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
SA:CF	Any supplied-air respirator operated in a continuous flow mode
SCBAE	Any appropriate escape-type self-contained breathing apparatus

KEY for Table 1, continued

EXPLANATION OF ABBREVIATIONS ON NIOSH TABLE, continued

SCBAF	Any self-contained breathing apparatus with a full facepiece
SCBAF:PD,PP	Any self-contained breathing apparatus with full facepiece and operated in a pressure-demand or other positive pressure mode
Inh	Inhalation
Ing	Ingestion
Con	Skin and/or eye contact
bron	bronchitis
conj	conjunctivitis
dent	dental
derm	dermatitis
emphy	emphysema
irrit	irritation
pulm edema	pulmonary edema
trachbronc	tracheobronchitis
throat irrit	throat irritation
Irr immed	If this chemical comes in contact with the eyes, immediately wash the eyes with large amounts of water, occasionally lifting the lower and upper lids. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
Water flush immed	If this chemical comes in contact with the skin, immediately flush the contaminated skin with water. If this chemical penetrates the clothing, immediately remove the clothing and flush the skin with water. Get medical attention promptly.
Art resp	If a person breathes in large amounts of this chemical, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
Medical attention immed	If this chemical has been swallowed, get medical attention immediately. DO NOT INDUCE VOMITING.

Table 2. - How to Use the Emergency Guidebook During an Incident Involving Hazardous Materials

APPROACH CAUTIOUSLY	Resist the urge to rush in; you cannot help others until you know what you are facing. Approach from upwind, if possible. Stay clear if all spills, vapors, fumes, and smoke.
IDENTIFY THE HAZARDS	<p>ONE--Identify the material by finding one of the following: the 4-digit ID number on a placard or orange panel; or the 4-digit ID number (after UN/NA) on a shipping paper or package; or the name of the material on a shipping paper; placard, or package.</p> <p>TWO--Look up the materials 2-digit guide number in either: the ID number index (yellow pages) or the name of material index (blue pages) or the list for all explosives.</p> <p>THREE--Turn to the numbered guide (orange pages) and read that guide.</p>
SECURE THE SCENE	Without entering the immediate hazard area, do what you can do to isolate the area and assure the safety of people and the environment. Move and keep people away from the scene and the perimeter. Allow room enough to move and remove your own equipment.
OBTAIN HELP	Advise your headquarters to notify responsible agencies and call for assistance from trained experts through CHEMTREC and the National Response Center (NRC) which can be reached through CHEMTREC or dialed directly. 1-800-424-9300
DECIDE ON SITE ENTRY	Any efforts you make to rescue persons, protect property or the environment must be weighed against the possibility that you could become part of the problem. Enter the area with the appropriate protective gear. Above all--do not walk into or touch spilled material. Avoid inhalation of fumes, smoke and vapors, even if not hazardous materials are known to be involved. Do not assume that gases or vapors are harmless because of lack of a smell--odorless gases or vapors may be harmful.

FOR SULFURIC ACID THE GUIDE TO FOLLOW IS NUMBER 39.

Table 3. - Potential Hazards Guide for Sulfuric Acid (Guide 39)

HEALTH HAZARDS

Poisonous if inhaled or swallowed
 Contact causes severe burns to skin and eyes.
 Runoff from fire control or dilution water may cause pollution.

FIRE OR EXPLOSION

Some of these material may burn, but none of them ignites readily.
 May ignite other combustible materials.
 Violent reaction with water.
 Flammable/poisonous gases may accumulate in tank or hopper cars.
 Runoff to sewer may create fire or explosion hazard.

EMERGENCY ACTION

- Keep unnecessary people away; isolate hazard area and deny entry.
- Stay upwind, out of low areas, and ventilate closed spaces before entering.
- Positive pressure self-contained breathing apparatus (SCBA) and chemical protective clothing which is specifically recommended by the shipper or manufacturer may be worn. It may provide little or no thermal protection.
- Structural firefighters' protective clothing is not effective for these materials.
- Isolate the leak or spill area immediately for at least 150 feet in all directions.
- Call CHEMTREC at 1-800-424-9300 for EMERGENCY ASSISTANCE.

FIRE

Do not get water inside container.
 Small Fires: Dry chemical or CO₂.
 Large Fires: Flood fire area with water from a distance.
 Do not get solid stream of water on spilled material.
 Move container from fire area if you can do it without risk.
 Apply cooling water to sides of containers that are exposed to flames until well after fire is out. Stay away from ends of tanks.

SPILL OR LEAK

Do not touch or walk through spilled material; stop leak if you can do it without risk.
 Fully-encapsulating, vapor-protective clothing should be worn for spills and leaks with no fire.
 Use water spray to reduce vapor; DO NOT put water directly on leak, spill area or inside container.
 Keep combustibles away from spilled material.
 SPILLS: Dike for later disposal; DO NOT APPLY WATER unless directed to do so.
 Cleanup only under supervision of an expert.

FIRST AID

Move victim to fresh air and call emergency medical care; if not breathing, give artificial respiration; if breathing is difficult, give oxygen.
 In case of contact with material, immediately flush skin or eyes with running water for at least 15 minutes.
 Speed in removing material from skin is of extreme importance.
 Remove and isolate contaminated clothing and shoes at the site.
 Keep victim quiet and maintain normal body temperature.

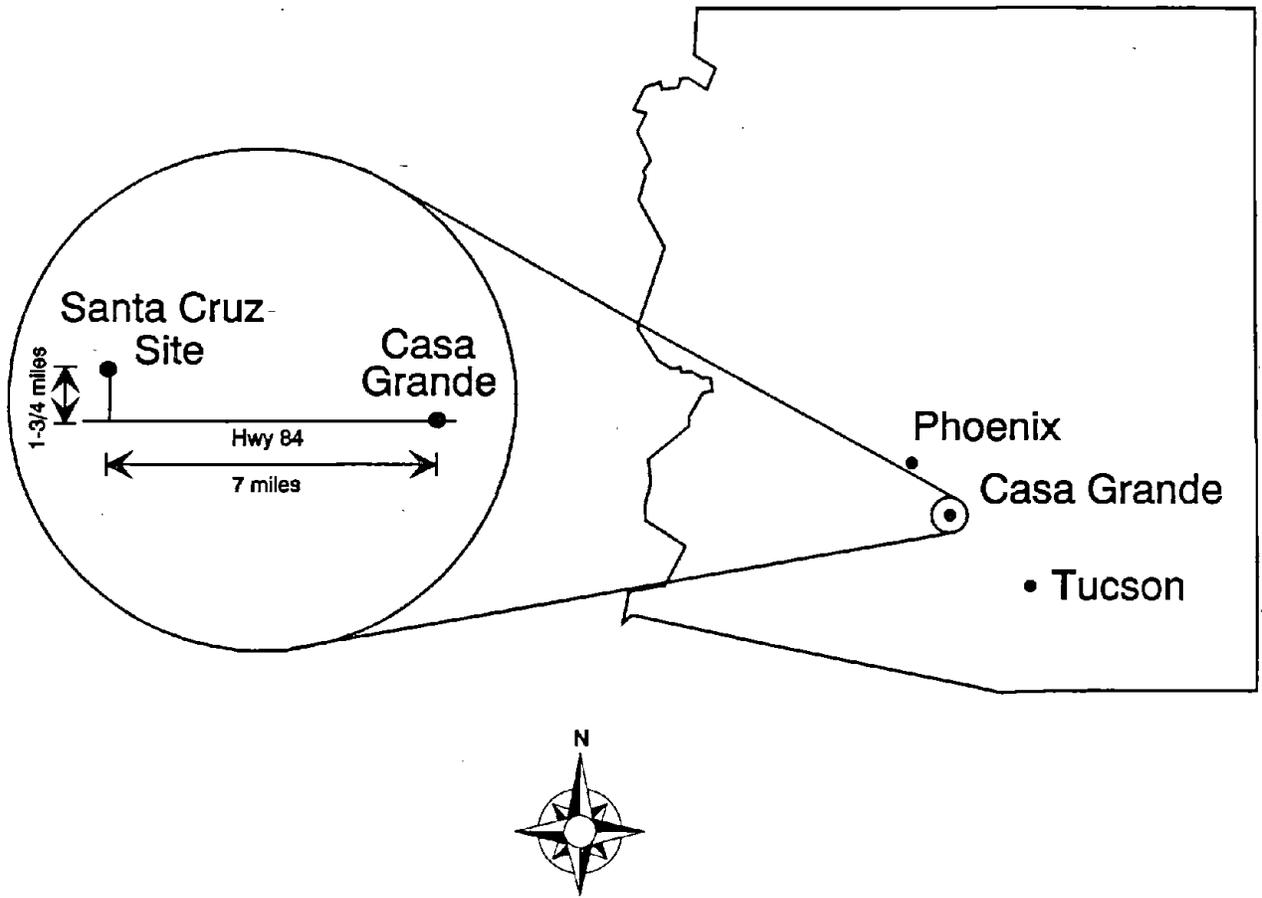


FIGURE 1. - Location map of the Santa Cruz in situ copper mining research project test site.

ASARCO **SULFURIC ACID** **MATERIAL SAFETY DATA SHEET**

A. GENERAL INFORMATION

TRADE NAME (COMMON NAME OR SYNONYM) Sulfuric Acid, Oil of Vitriol		ASARCO PRODUCT CODE # 1860	
CHEMICAL NAME Sulfuric Acid	FORMULA H2SO4	MOLECULAR WEIGHT 98.08	
ADDRESS (No., STREET, CITY, STATE AND ZIP CODE) ASARCO Incorporated 180 Maiden Lane New York, New York 10038 Phone: 212-510-2000			
CONTACT General Information— Department of Environmental Sciences		PHONE NUMBER DAY 801-262-2459 NIGHT 801-943-4551	ISSUED DATE 1/7/83
First Aid Information—(Dr. C. H. Hine) Transportation Emergencies—CHEMTREC		415-777-2213 800-424-9300	REVISED DATE 12/8/88

B. INGREDIENTS

MATERIAL OR COMPONENT	C.A.S. #	WT. %	PERMISSIBLE AIR CONCENTRATION (mg/cu.m.)		SARA Title III Sec. 313 Chem.
			OSHA	ACGIH	
Sulfuric Acid	7664-93-9	93-99	1.0	1.0	Yes

C. FIRST AID MEASURES

Inhalation: Remove to fresh air. If breathing has stopped, give artificial respiration. If breathing with difficulty, give oxygen.
 Ingestion: Drink large amounts of water (or milk, if available) to dilute the acid. DO NOT INDUCE VOMITING!
 Skin or Eye: Immediately flush with plenty of water for at least 15 minutes. Remove contaminated clothing.
GET PROMPT MEDICAL ATTENTION!

D. HEALTH HAZARD INFORMATION

PRIMARY ROUTES OF ENTRY INGESTION <input type="checkbox"/> INHALATION <input checked="" type="checkbox"/> SKIN <input type="checkbox"/>	CARCINOGENECITY Not listed as a carcinogen by NTP, LARC, OSHA
ACUTE OVEREXPOSURE (SYMPTOMS AND EFFECTS) 1. Inhalation of fumes or mists can cause irritation or corrosive burns to the upper respiratory system. Lung irritation and pulmonary edema can occur. 2. Ingestion can cause irritation and corrosive burns to throat, mouth, and stomach. Can be fatal if swallowed. 3. Causes severe burns or irritation on skin contact. 4. Liquid contact with the eyes can cause irritation, corneal burns, and blindness. Mist contact may irritate or burn	
CHRONIC OVEREXPOSURE (SYMPTOMS AND EFFECTS) Long term exposure to high levels of acid fumes may cause erosion of teeth followed by jaw necrosis, bronchial irritation, coughing, and bronchial pneumonia, or gastrointestinal disturbances.	
MEDICAL CONDITIONS POSSIBLY AGGRAVATED Acute and chronic respiratory diseases.	

E. FIRE AND EXPLOSION

FLASH POINT Not Applicable	AUTO IGNITION TEMPERATURE Not Applicable	FLAMMABLE LIMITS IN AIR (% BY VOL.) Not Applicable
UNUSUAL FIRE AND EXPLOSION HAZARDS Flammable and explosive hydrogen gas can be generated inside metal drums and storage tanks. Concentrated acid can ignite combustible materials on contact. Acid plus active metal can also form explosive concentrations of hydrogen.	FIRE EXTINGUISHING AGENTS RECOMMENDED If involved in a fire, use water spray; avoid spraying water into containers. If only a small amount of combustibles is present, smother fire with dry chemical.	FIRE EXTINGUISHING AGENTS TO AVOID Direct stream of water may cause spattering.
SPECIAL FIRE FIGHTING PRECAUTIONS Use NIOSH/MSHA approved self-contained breathing apparatus and full protective clothing if involved in fire. At high temperatures, sulfuric acid or sulfur trioxide mists can be released from vented or ruptured containers. If water is added to concentrated sulfuric acid, violent spattering can occur and considerable heat may be evolved.		

F. PRECAUTIONS/PROCEDURES

NORMAL HANDLING Do not get in eyes, on skin, or on clothing. Do not breathe vapor or mists. Use protective equipment as outlined in Section G. Do not add water to acid. When diluting, always add acid to water cautiously and with agitation. Use with adequate ventilation.	ENGINEERING CONTROLS Adequate ventilation to maintain acid mist below permissible exposure limits. Packaging, unloading areas, or open processing equipment may require mechanical ventilation.
SPILL OR LEAK Dilute small spills or leaks cautiously with plenty of water. Neutralize with alkali such as soda ash or lime. Adequate ventilation is required for soda ash due to release of CO2 gas. No smoking in spill area. Major spills must be handled by a predetermined plan. Diking with soda ash is recommended. Attempt to keep out of sewer.	STORAGE Protect from physical damage. Store in cool, well ventilated area away from combustibles and reactive chemicals. Keep out of sun and away from heat. Keep containers in upright position. No smoking in storage area.

Figure 2. - MSDS for Sulfuric Acid

F. PRECAUTIONS/PROCEDURES (Continued)

PERSONAL HYGIENE Avoid inhalation, skin contact, or ingestion. Practice good housekeeping and personal hygiene procedures.	SPECIAL: PRECAUTIONS/PROCEDURES/LABEL INSTRUCTIONS Loosen closures carefully. LABEL SIGNAL WORD: DANGER
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G. PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY PROTECTION Where airborne exposures may exceed OSHA/ACGIH permissible air concentrations, the minimum respiratory protection recommended is a negative pressure air purifying respirator with cartridges that are NIOSH/MSHA approved against dusts and mists having a TWA not less than 0.05 mg/cu.m.	EYES AND FACE Chemical goggles or face shield required.
OTHER CLOTHING AND EQUIPMENT Rubber gloves and aprons or equivalent required when handling sulfuric acid. Full protective clothing recommended when handling large quantities of sulfuric acid.	

H. PHYSICAL DATA

MATERIAL IS (AT NORMAL CONDITIONS) Liquid		APPEARANCE AND ODOR Oily, colorless to slightly yellow, clear to turbid liquid. Odor threshold is -1 mg/cu.m.	
MELTING POINT (DEGREES C) 93.19% at -29 C, 98% at -1C	BOILING POINT (DEGREES C) 276-281	SPECIFIC GRAVITY (H2O = 1) 1.835-1.844	VAPOR DENSITY (AIR = 1) Not Applicable
SOLUBILITY IN WATER (% BY WEIGHT) Complete	pH 1% solution: pH = 0.9	VAPOR PRESSURE (mm Hg) 90% = 0.005 at 20 C 95% = 0.0015 at 35 C	EVAPORATION RATE Not Applicable

I. REACTIVITY DATA

STABILITY Stable	CONDITIONS TO AVOID Not Applicable		
INCOMPATIBILITY (MATERIALS TO AVOID) Sulfuric acid is not flammable but highly reactive and capable of igniting finely divided combustible materials on contact. Reacts violently with water and organic materials with evolution of heat. Extremely hazardous in contact with many materials, particularly carbides, chlorates, fulminates, nitrates, picrates, powdered metals and other combustible materials. Attacks many metals releasing hydrogen. Examples of common inorganic chemicals that should be avoided include: sodium carbonate, sodium hydroxide, elemental sodium, potassium permanganate, ammonium hydroxide, and potassium chlorate. Common organic chemicals that have been reported as being incompatible with sulfuric acid include: ethylene glycol, aniline, and ethylene diamine.			
HAZARDOUS DECOMPOSITION PRODUCTS Sulfur Trioxide Mist	HAZARDOUS POLYMERIZATION Will not occur	CONDITIONS TO AVOID Not Applicable	

J. ENVIRONMENTAL

REGULATED BY DOT? Sulfuric Acid is regulated as a Corrosive Material. UN1830.	
WASTE DISPOSAL METHODS (DISPOSER MUST COMPLY WITH FEDERAL, STATE, AND LOCAL DISPOSAL OR DISCHARGE LAWS) If hazardous under 40 CFR 261, Subparts B and C, material must be treated or disposed in a facility meeting the requirements of 40 CFR 264 or 265. If non-hazardous, material should be disposed in a facility meeting the requirements of 40 CFR 257.	
RCRA STATUS OF UNUSED MATERIAL EPA Hazardous Waste No. D002(Corrosive) if discarded.	40 CFR 261

K. REFERENCES

PERMISSIBLE CONCENTRATION REFERENCES OSHA regulations for airborne contaminants 29 CFR 1910.1000; ACGIH Threshold Limit Values for Chemical Substances	
HAZARD INFORMATION REFERENCES <i>Documentation of the Threshold Limit Values</i> , 5th Ed., ACGIH <i>Patty's Industrial Hygiene and Toxicology</i> , Vol. 2A, 3rd Rev. Ed., 1981	<i>NFPA Fire Protection Guide on Hazardous Materials</i> , 8th Ed., 1984 <i>Handbook of Toxic and Hazardous Chemicals</i> ; Sittig, Marshall: 1981
GENERAL <i>Handbook of Chemistry and Physics</i> , 57th Ed., 1976-77, Weast, R.C., Editor, CRC Inc.	

L. ADDITIONAL INFORMATION

INFORMATION (HAZARDS, PRECAUTIONS, FIRST AID, ETC.) IS ABBREVIATED. MORE DETAILED INFORMATION IS CONTAINED IN REFERENCES FOUND IN SECTION K Additional Information Contact: ASARCO Incorporated Sulfuric Acid Sales Department P. O. Box 5747 Tucson, AZ 85703-0747 (602) 629-0214	
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Figure 3. - Label required for sulfuric acid transport

WELL FIELD DIAGRAM

In Situ Copper Mining Research Project

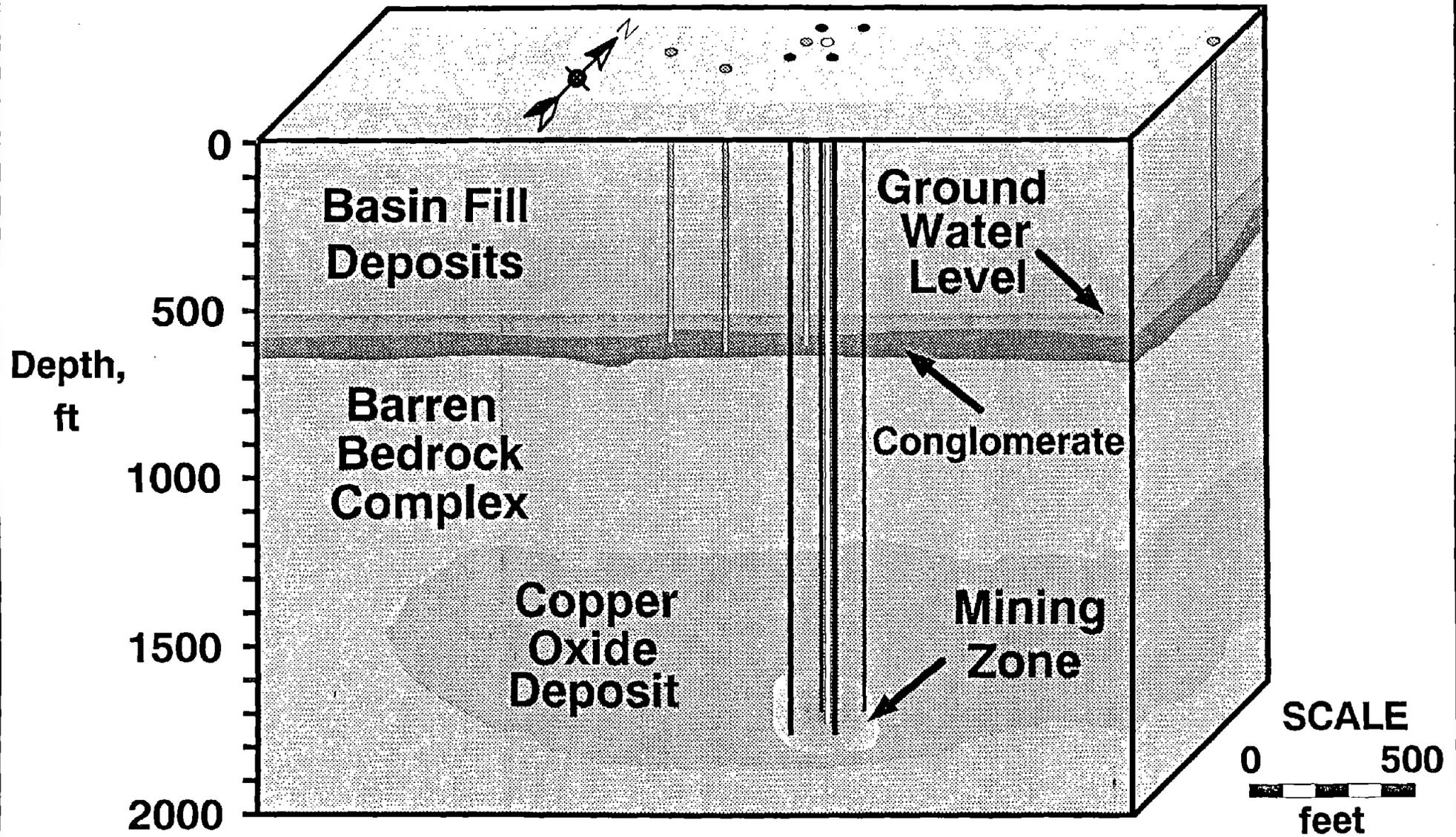


Figure 4. - Copper ore zone and 5-spot pattern

SX/EW PROCESS FLOW DIAGRAM

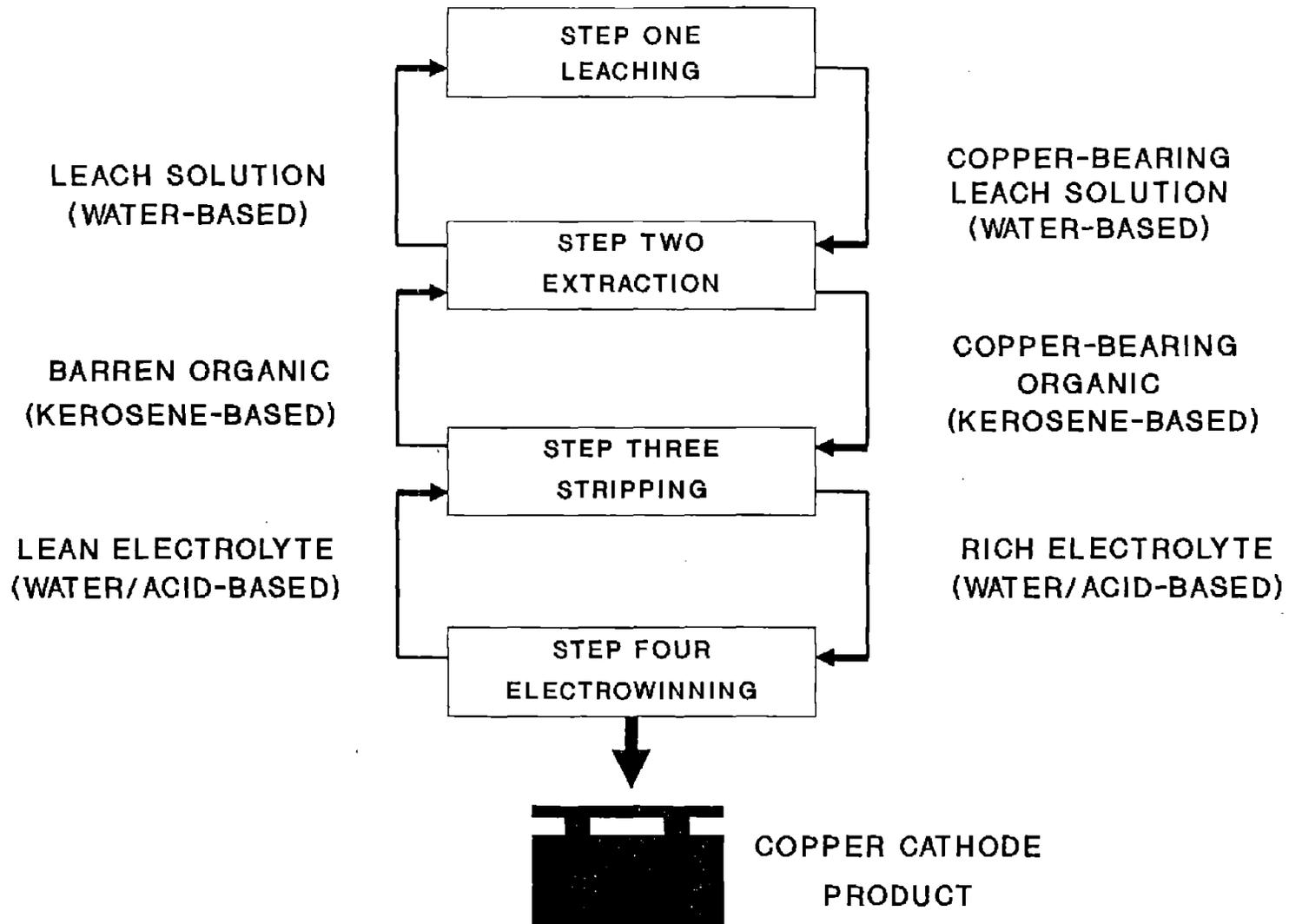


Figure 5. - Solvent extraction-electrowinning flow chart

