Bulletin 682

Recovery of Tungsten From Searles Lake Brines by an Ion-Exchange Process

By P. B. Altringer and others

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environment and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/ft^2	ampere per square foot
°C	degree Celsius
cm	centimeter
cm^3	cubic centimeter
cP	centipoise
d/yr	day per year
°F	degree Fahrenheit
ft	foot
ft^2	square foot
ft^3	cubic foot
ft/min	foot per minute
ft^3/lb	cubic foot per pound
g	gram
g/cm^3	gram per cubic centimeter
g/h	gram per hour
g/L	gram per liter
g/mL	gram per milliliter
gal	gallon
gpm	gallon per minute
gpm/ft^2	gallon per minute per square foot
gpm/ft^3	gallon per minute per cubic foot
h	hour
h/d	hour per day
in	inch
kW·h	kilowatt hour
L	liter
L/min	liter per minute
lb	pound
lb/d	pound per day
mg	milligram
mg/L	milligram per liter
Mgal	thousand gallon
mi	mile
mi^2	square mile
min	minute
mL	milliliter
mL/min	milliliter per minute
$mL/(min \cdot cm^2)$	milliliter per minute per square centimeter
Mlb	thousand pound
mm	millimeter
MM	million
MMBtu	million British thermal unit
MMlb	million pound
MMlb/yr	million pound per year
mV	millivolt
pct	percent
ppm	part per million
psi	pound per square inch
rpm	revolution per minute
vol pct	volume percent
wt pct	weight percent
yr	year

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

With Factors for Conversion to Units of the International System of Units (SI)

Abbreviation	Unit of Measure	To convert to–	Multiply by–
ft	foot	meters	0.30
ft^3	cubic foot	liters	0.035316
gal	gallon	liters	0.26417762
in	inch	centimeters	2.54
lb	pound	kilogram	0.4535

SCIENTIFIC AND TECHNICAL ABBREVIATIONS USED IN THIS REPORT

A–O	aqueous to organic ratio
BV	bed volume
BV/cycle	bed volume per cycle
COD	chemical oxygen demand
diam	diameter
$E°_A$	extraction coefficient
emf	electromotive force
ID	internal or inner diameter
M	molar mass
N	normal (concentration)

RECOVERY OF TUNGSTEN FROM SEARLES LAKE BRINES BY AN ION-EXCHANGE PROCESS

By P. B. Altringer[1] and others[2]

ABSTRACT

Searles Lake, CA, contains the largest known domestic tungsten resource. The brines in this near-dry lake bed, located in the Mojave Desert 130 mi northeast of Los Angeles, contain an estimated 135 MMlb of tungsten. However, the low concentration of tungsten (0.080 g/L WO_3) in the supersaturated brine makes selective tungsten extraction very difficult. Although many brine chemicals are extracted from the lake, tungsten recovery was an elusive goal prior to Bureau of Mines development of an ion-exchange technique. This publication describes the Bureau process. The following subjects are addressed:

- The Searles Lake tungsten resource.
- General problems associated with tungsten recovery.
- Bureau research objectives.
- Synthesis of ion-exchange resins.
- Development of a two-stage ion-exchange tungsten extraction and concentration procedure.
- Product recovery and purification.
- Economic evaluation.

Flowsheets for recovering three products (calcium tungstate, sodium tungstate, and tungstic oxide) are presented and evaluated, as well as a summary of the research effort and potential applications.

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[2]The other authors who contributed to this bulletin are identified in the chapters in which their work appears.

OVERVIEW

Tungsten is essential to the Nation's defense and critical to our industrial economy, yet the United States depended on imports for 68 pct of its annual tungsten requirements in 1985 (*1*).[3] To increase domestic supply, the Bureau of Mines has developed a tungsten recovery process for Searles Lake brines. These brines are estimated to contain 21 pct of the domestic 1985 reserve base (*1*) and constitute the largest known single tungsten deposit in the United States (*2*). Although tungsten production from this resource is marginally profitable at depressed tungsten prices (October 1984), the size of the deposit almost ensures that the reserve will be exploited in the future.

The Bureau process consists of three main operations: primary ion exchange for tungsten extraction, secondary ion exchange for tungsten concentration, and product recovery. The key to the process is selective extraction of the tungsten, present at dilute concentrations, from the supersaturated alkaline brines. Tungsten extraction is accomplished by using QRF ion-exchange resin, developed by Bureau researchers specifically for this purpose (*3–6*).

Untreated pH 10 Searles Lake brine is not a desirable process feed because the pH is too high for efficient tungsten extraction. Because lowering the pH is economically impractical for tungsten recovery alone, the proposed feed is an in-process stream from one or two of the three operating plants currently extracting other chemicals from Searles Lake brines. These two facilities lower brine pH by carbonation prior to salt extraction. Depleted brine, containing enough tungsten to satisfy one-fourth of the domestic annual consumption (1985 statistics), is returned to the lake (*1*).

Three alternative flowsheets were devised that could be used to recover tungstic oxide, sodium tungstate, and calcium tungstate (synthetic scheelite). All flowsheets were based on the premise that tungsten would be recovered as a byproduct at an operating salt-processing facility at Searles Lake and processed to an intermediate-grade chemical form, from which final tungsten products would be produced.

This bulletin presents research results on the development of resin and unit operations that contributed to development of the process. Key findings include the following:

- *Prior technology.*—Commercially available solvent extraction and ion-exchange technology did not solve the problem of selective tungsten extraction. Industrial efforts over the past 40 yr did not produce an economical process for tungsten recovery from Searles Lake brines.
- *Resin development.*—Bureau researchers synthesized several ion-exchange resins that selectively extract tungsten from Searles Lake brines. QRF beads, the resin selected for pilot-scale testing, demonstrated high tungsten capacity and exchange kinetics, coupled with physical stability. In addition, a high yield of usable resin was achieved during production.
- *Primary ion exchange.*—Basic primary ion-exchange technology for tungsten extraction, established from laboratory research, performed satisfactorily in the pilot plant at Kerr-McGee Chemical Corp.'s Westend facility at Searles Lake. Over 500,000 gal of pH 8.2 brine containing 0.080 g/L WO_3 (tungstic oxide) was treated in the pilot plant, and 84 pct of the tungsten was recovered in 15,000 gal of primary eluate containing an average of 1.3 g/L WO_3. Reducing brine alkalinity from pH 8.2 to 7.6, simulating a period of increased carbonation, increased extraction efficiency from a larger brine volume and raised the eluate grade. No serious resin degradation was apparent after a year of pilot-plant testing at Searles Lake.
- *Secondary ion exchange.*—Basic secondary ion-exchange technology for tungsten concentration, established from laboratory research, was successfully applied in the pilot plant at Searles Lake with minor modifications to the laboratory process. Almost 3,000 gal of primary eluate was processed in the field; 65 to 80 pct of the tungsten was recovered in 21 gal of secondary eluate containing 82 to 85 g/L WO_3. Later laboratory testing indicated that low field recoveries were due to resin agglomeration. Thorough resin fluidization with air prior to elution increased recoveries. Using ammonium hydroxide (NH_4OH) desorption, tungsten extraction was 96 pct, elution was 99 pct complete, and overall recovery was 95 pct. Using sodium carbonate (Na_2CO_3) desorption, tungsten extraction was 90 pct, elution was 92 pct complete, and overall recovery was 82 pct.

[3]Italic numbers in parentheses refer to items in the list of references preceding the appendixes.

- *Product preparation.* – A variety of intermediate tungsten compounds was prepared in the laboratory from secondary eluates, with tungstic oxide, sodium tungstate, and calcium tungstate (synthetic scheelite) showing promise for conversion to final tungsten products. Concentrations of inorganic impurities, arsenic and phosphorus, were decreased by precipitation with a magnesium salt to avoid potential product price penalties. Organic carbon impurities, apparently brine humates, interfered with product recovery and were effectively destroyed by roasting or oxidation treatments.

Implementation of the Bureau technology at the Westend facility could annually produce about 480,000 lb of anhydrous tungstic oxide analyzing, in weight percent, 99 WO_3, 0.12 As, 0.22 P_2O_5, and less than 0.4 B_4O_7; or about 830,000 lb of sodium tungstate analyzing, in weight percent, 58 WO_3, 0.11 As, 0.42 P_2O_5, and 0.18 B_4O_7; or about 590,000 lb of synthetic scheelite analyzing, in weight percent, 79 WO_3, 0.12 As, 0.33 P_2O_5, and 0.008 B_4O_7.

- *Cost evaluation.* – In October 1984, the Bureau performed a cost evaluation on a plant addition to recover tungstic oxide, sodium tungstate, and synthetic scheelite products from the soda-grainer overflow at the Westend facility. Using the interest rate of return method, only the tungstic oxide process is profitable. With the currently depressed tungsten market, this process would yield an estimated 1 pct rate of return after taxes; 15 pct is generally considered the minimum acceptable rate of return on investment for a new venture.

INTRODUCTION

Tungsten, a hard and heat-resistant metal, is essential to the Nation's economy and defense. The demand for tungsten in cemented carbides, mill products, and steel is increasing substantially; the rapidly growing use of tungsten carbide in well drilling and underground coal mining, and continuing uses in specialty steelmaking, superalloys, and chemicals make tungsten critical to our industrial economy. Domestic reserves, however, are not sufficient to meet projected demands.

This bulletin updates and summarizes research on recovering tungsten from Searles Lake brines, the largest known single domestic tungsten deposit. The research effort, which included cooperation with Kerr-McGee Chemical Corp. under a Memorandum of Understanding, encompassed synthesis of a physically stable tungsten-selective ion-exchange resin and development of a recovery process based on ion-exchange extraction.

Tungsten was first discovered in Searles Lake brines in 1937 when a condenser line clogged and the scale was analyzed (*2*). Since then, industry has invested considerable time, effort, and money in trying to develop a process to recover the tungsten (*7–9*). However, the processes developed were so far from economical that only one was piloted and none were seriously considered for full-scale implementation.

The Bureau of Mines began research to recover tungsten from Searles Lake brines in 1971 and completed the work in 1983. The Bureau first proposed a solvent extraction process in 1974 (*10*); this was followed by development of a more economical, ion-exchange process in 1979 (*4*) that was improved in 1980 (*3*). Several alternative flowsheets were developed during this research, the most feasible of which are presented along with detailed descriptions of the unit operations and their development. The advent of the Bureau's tungsten-selective ion-exchange resin coupled with the availability of suitable process feed streams prompted others to develop tungsten recovery processes for Searles Lake brines (*11–12*).

A description of the resource, research objectives, and problems encountered are presented in chapter 1. Detailed process descriptions, including flowsheets for recovering three marketable products, and a cost evaluation summary are presented in chapter 2. Chapter 3 addresses synthesis of the tungsten-selective ion-exchange resin, the key to the process. The remainder of the main body of the report discusses the development of unit operations: The primary ion-exchange extraction process is discussed in chapter 4, the secondary ion-exchange concentration process in chapter 5, and product recovery in chapter 6. Chapter 7 addresses the research remaining to be performed, and the potential for application of the basic technology at Searles Lake. The bulk of this research was performed on brine from Kerr-McGee Chemical Corp.'s Westend facility at Searles Lake; an economic evaluation of this process is presented in appendix A. Application of the research for recovering tungsten from brine in a second operating plant at Searles Lake, Kerr-McGee Chemical Corp.'s Argus facility, is discussed in appendix B.

CHAPTER 1.—RESOURCE DESCRIPTION AND RESEARCH OBJECTIVES

By P. B. Altringer

DESCRIPTION OF RESOURCE

The largest known single domestic tungsten deposit is contained in the brines of Searles Lake, CA. This nearly dry brine deposit is located in the Mojave Desert, 130 mi northeast of Los Angeles, CA. Mud and salt encrust almost all of the 35-mi² surface. It is theorized that tungsten accumulated in Searles Lake at the end of the last two ice ages, the Tahoe and Tiogra periods. Waters leached the Sierra Nevada Mountains, where numerous tungsten deposits are located, and flowed through the Owens Valley drainage system to Searles Lake where the exit was eventually blocked by volcanic ash and debris. This allowed the tungsten to accumulate in Searles Lake where the salt content was further enriched by numerous hot springs (*2*). Searles Valley is a now a closed structural basin filled with alluvium and nonmarine evaporites. The thickness of the fill ranges from zero at the periphery to over 700 ft in the deepest portions. The evaporite deposit consists of alternating mud beds and brine-saturated salt beds; about 50 pct of the deposit is brine. The principal beds are designated as the upper structure, the lower structure, and the mixed layer, which is the deepest bed. The brine contains an estimated 135 MMlb of tungsten (*2*), which represents 21 pct of the domestic 1985 reserve base[1]. Table 1 presents typical Searles Lake brine analyses. This supersaturated brine is unique because it is the only known natural brine resource that contains a hydrated tungsten species at dilute concentrations ranging up to 0.080 g/L WO_3.

The Kerr-McGee Chemical Corp. operates three brine treatment plants at Searles Lake; the Westend, Trona, and Argus facilities. The Westend facility processes approximately 1,800 gpm of brine from the lower structure with minor amounts of mixed layer and upper structure brine. The brine is carbonated to precipitate sodium bicarbonate ($NaHCO_3$), cooled to crystallize borax ($Na_2B_4O_7 \cdot 10H_2O$), cooled further to crystallize Glauber salt ($Na_2SO_4 \cdot 10H_2O$), and finally cooled still further to produce another crop of borax. The brine contains approximately 0.080 g/L WO_3; after carbonation, it has a pH of 7.5 to 8.5. The Argus facility processes approximately 10,000 gpm of brine from the upper part of the mixed layer. At present, the only product produced at the Argus facility is soda ash. The Argus brine contains approximately 0.040 g/L WO_3; after carbonation, it has a pH of 7.5. The Trona facility processes approximately 3,000 gpm of brine from the upper and lower structures to produce Glauber salt, potash, and borax. The brine contains approximately 0.070 g/L WO_3; carbonation is not used in this facility. Consequently, the Trona brine pH remains too high for good tungsten extraction. After extracting the salts, the depleted brine from the Westend and Argus facilities, containing nearly 2 MMlb of tungstic oxide per year, is returned to the lake (*13*).

Bureau researchers tested brine from numerous process streams at the three facilities. The process stream selected for the body of testing was soda grainer overflow because it has the lowest pH of the available streams. Fresh brine is treated with carbon dioxide (CO_2) to lower the pH and precipitate $NaHCO_3$. The precipitate and brine are then separated in two stages using thickeners known as soda grainers. Overflow from the last thickener, with pH as low as 7.5, is treated to recover borax. Bureau research was conducted on brine from the last thickener overflow, prior to borax recovery.

[1]Includes economic and marginally economic reserves plus some subeconomic resources.

TABLE 1.—Analysis of raw Searles Lake brine

	Argus brine	Westend brine
Analysis, wt pct:		
NaCl	16.0	17.0
Na_2SO_4	6.7	7.6
KCl	1.3	4.3
Na_2CO_3	6.5	4.2
$Na_2B_4O_7$	0.5	1.2
Na_2S	0.06	0.2
$NaLi_2PO_4$	ND	0.07
Na_3PO_4	0.06	0.07
WO_3	0.0033	0.0062
WO_3, g/L	0.040	0.080
Density, g/cm³	1.220	1.305
pH	8.5	9.8

ND No data.

The Westend facility was chosen because its brine contained the highest concentration of tungsten, up to 0.080 g/L WO_3, although it had the lowest flow rate of 1,800 gpm. Brine from the newly constructed Argus facility was not available at the time of pilot testing. Research on Argus brine was conducted later and is summarized in appendix B.

The major complication encountered in solving the extraction problem was variation in brine composition. Representative brine samples were difficult to obtain since the lake is not homogeneous, and brine stream composition depended on which wells were used to provide brine. Brine characteristics at the lake also change from day to day and from season to season, fluctuating with the amount of moisture present. An additional problem arose when the brine was transported. During transportation, the brine cooled, the pH increased because of CO_2 evolution, and salts precipitated out due to the supersaturated condition of the brine. Recarbonation was necessary to reestablish the correct pH. When this pH adjustment was made, additional salts precipitated, further changing the brine composition.

RESEARCH OBJECTIVES

Tungsten recovery from lake brines has been an elusive target during 40 yr of industrial searching for economical extractive technology. This research sought to solve the problem of selectively extracting dilute tungsten from large volumes of supersaturated brines. Although several methods were devised for tungsten recovery in the past, including precipitation and solvent extraction techniques, none proved practical or economical (*7–10*) prior to Bureau ion exchange (*3–4*). Techniques that required chemically treating the brine failed because the huge chemical requirements necessary to adjust the alkalinity made operation prohibitively expensive. Solvent extraction techniques

were impractical because solvent losses exceeded the value of the recovered tungsten.

Early Bureau investigations showed that tungsten could be extracted from the brines by ion exchange. Results of these studies also indicated that a multistage recovery process might be necessary to concentrate the tungsten to a marketable product. Therefore, the goal of subsequent research was to identify and refine methods for accomplishing three major objectives:

1. Selectivity extract tungsten from the brines, the key to any recovery process.
2. Concentrate the tungsten.
3. Produce a marketable tungsten product.

A set of constraints based on the practicalities of commercial-scale recovery was adopted to guide the research program:

1. The tungsten extraction process would be designed to take place at the lake owing to the large volume of brine.
2. Brine characteristics would not be essentially changed before or after tungsten extraction to enable the process stream to continue to be used in the existing plant.
3. Pollution control would be observed in all phases of the process of meet environmental standards.
4. Tungsten extraction would be considered byproduct recovery from an existing plant for which infrastructure costs were already paid.

CHAPTER 2.—PROCESS DESCRIPTION AND ECONOMICS

By P. B. Altringer

The tungsten recovery process developed by the Bureau of Mines is based on selective sorption of tungsten from the alkaline Searles Lake brines with QRF resin (described in detail in chapter 3). QRF, an acronym for 8-hydroxyquinoline, resorcinol, and formaldehyde, is an ion-exchange resin that was synthesized by Bureau researchers specifically for this purpose (*3–4*).

The process consists of three main operations: primary ion exchange for tungsten extraction, secondary ion exchange for tungsten concentration, and product recovery. In this chapter, a general description of the processes to produce tungstic oxide, sodium tungstate, or calcium tungstate (synthetic scheelite) will be presented, followed by a detailed description of each unit operation; finally, highlights of an economic evaluation of the processes will be discussed.

PROCESS DESCRIPTION

Fresh brine from Searles Lake at pH 10 is not a desirable process feed because at this pH, the extraction of tungsten is not efficient. Lowering the pH to achieve more effective tungsten sorption is economically impractical for tungsten extraction alone. For this reason, a more attractive feed is an in-process stream from one or more of the three plants currently extracting other chemicals from Searles Lake brines. The proposed process is designed to recover tungsten products from a process stream of 1,800 gpm of brine containing 0.080 g/L WO_3, or 1,730 lb/d WO_3, from which soda has been extracted.

Tungsten is extracted from the brine using primary ion exchange with QRF resin beads. A series of ion-exchange columns, three to a unit, permits continuous processing. Test results indicate that 90 pct of the influent tungsten is extracted per cycle: 1,557 lb/d WO_3. Tungsten is eluted from the resin by desorption with a weak sodium carbonate (Na_2CO_3) solution with 96-pct recovery. This step selectively extracts and concentrates the tungsten about 20-fold, from 0.080 g/L WO_3 in the brine to 1 to 2 g/L WO_3 in the primary eluate, with an overall recovery of 86 pct.

Primary eluate is acidified to increase tungsten loading on QRF resin using a secondary ion-exchange circuit, and then heated to enhance CO_2 evolution, thereby degassing the solution to avoid channeling and pressure buildup in the ion-exchange columns. Sludge formed during acidification is settled and dissolved in a subsequent batch of alkaline feed (primary eluate).

Secondary ion exchange also employs QRF resin but operates on a smaller scale than does primary ion exchange. The step concentrates the tungsten from 1 to 2 g/L WO_3 in the primary eluate to 80 to 100 g/L WO_3 in ammonium hydroxide (NH_4OH) or Na_2CO_3 secondary eluate at a recovery of 97 pct.

Impurity levels in the secondary eluate are reduced using a magnesia precipitation step. The remaining tungsten is subsequently recovered as tungstic oxide (WO_3), sodium tungstate (Na_2WO_4), or synthetic scheelite ($CaWO_4$). Overall recovery from brine to product is about 84 pct, or 1,448 lb/d WO_3. Tungstic oxide and sodium tungstate are produced from secondary eluate by nearly identical methods. Spray drying forms tungsten salts, which are calcined to reduce organic impurities and produce tungstic oxide from NH_4OH secondary eluate, or sodium tungstate from Na_2CO_3 secondary eluate.

To produce commercial-grade synthetic scheelite, calcined sodium tungstate is dissolved in water and heated with the addition of calcium chloride ($CaCl_2$). Synthetic scheelite precipitates and is recovered from the remaining solution by filtration followed by drying.

UNIT OPERATIONS

A detailed description of the processes developed for recovering tungstic oxide, sodium tungstate, and synthetic scheelite follows. A flowsheet for these processes (fig. 1) allows for tungstic oxide or sodium tungstate production in stream 19 and synthetic scheelite production in stream 24. Material balances for the three systems are presented in tables 2, 3, and 4. A description of the plant design is included in appendix A.

Tungsten Extraction

Parallel series of three fixed-bed ion-exchange columns containing 3-ft-deep beds of QRF ion-exchange beads permit continuous tungsten extraction from process feed. Brine is pumped through two ion-exchange columns in series such that the second acts as a scavenger. When the resin in the first column is fully loaded with tungsten, it is disconnected from the series and a third column is added in the scavenger position. Tungsten in the first column is then eluted from the resin with a weak Na_2CO_3 solution. After elution is completed, the first column is ready to be returned to the extraction process in the scavenger position when the first of the other two columns has been fully loaded. In this manner, tungsten is extracted from the brine continuously.

Feed brine to the primary ion-exchange system (stream 1) is 1,800 gpm, pH 8.2, soda grainer overflow containing 0.080 g/L WO_3 from the Westend facility. Each 4.8-h cycle processes 65 BV of brine in a downflow mode and extracts 90 pct of the tungsten. The flow rate is 5 gpm/ft^2 of column surface area and brine temperature is ambient (usually 90° F). The resin loads to 4.4 g WO_3 per liter of wet-settled resin. Typical pressure drops of 15 and 10 psi are recorded across 3-ft-deep lead and scavenger load columns, respectively. The tungsten-depleted brine (stream 2) is returned to the process.

Tungsten is eluted (stream 3) in a downflow operation at a flow of 0.5 gpm/ft$_2$ of column surface area. The primary eluant is 5 BV of 5 g/L Na_2CO_3 in potable water at 90° F. Pressure drop across a 3-ft-deep bed is 1 psi. The first bed volume of eluate is displaced brine that contains 4 pct of the eluted tungsten. This waste eluate (stream 6) is returned to the process downstream. Bed volume 2, 3, and 4 of the eluate are saved as the primary eluate (stream 4) for further processing and are pumped to the acidification section. This product contains 92 pct of the eluted tungsten at a concen-

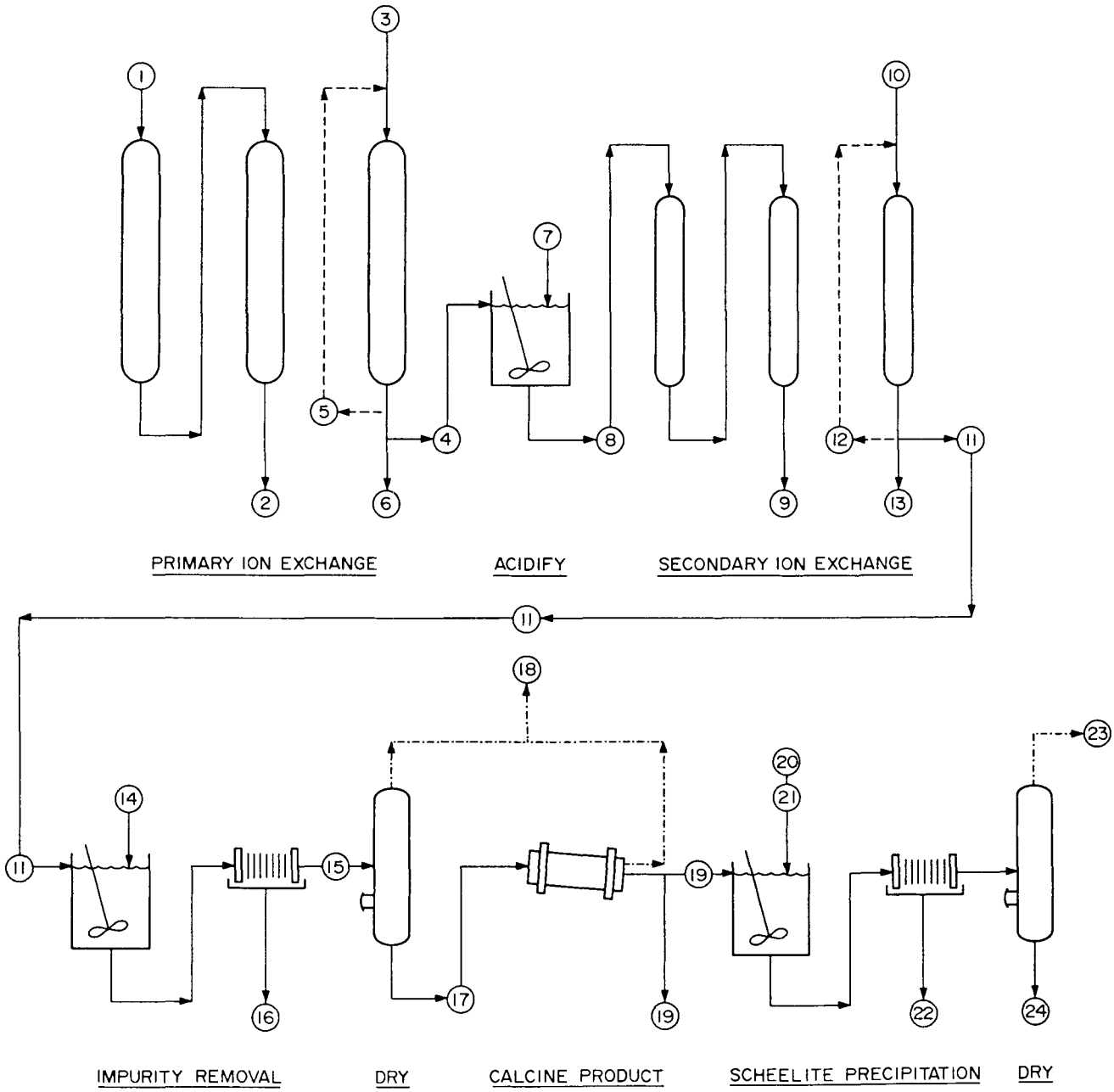

Figure 1.—Flowsheet for recovering tungsten products.

TABLE 2.—Daily tungsten recovery from Searles Lake brines as tungstic oxide

Stream	Stream name	Volume, gal	Wet wt, lb									
			Total	WO_3	As	P_2O_5	B_4O_7	H_2SO_4	Na_2CO_3	NH_3	MgO	H_2O
1	Soda grainer overflow	2,592,000	28,200,403	1,730	4,109	20,574	229,263	0	NAp	0	NAp	NAp
2	Depleted brine	2,591,767	28,194,485	173	4,021	20,163	224,990	0	NAp	0	NAp	NAp
3	Primary eluant	199,385	1,673,589	65	2	4	13	0	8,319	0	0	1,665,186
4	Primary eluate product	119,631	999,358	1,491	27	130	1,402	0	4,991	0	NAp	991,317
5	Recycle primary eluate	39,877	333,119	65	2	4	13	0	1,664	0	NAp	331,371
6	Waste primary eluate	39,877	333,119	65	61	280	2,871	0	1,664	0	NAp	328,178
7	H_2SO_4 acidification	419	6,427	0	0	0	0	6,234	0	0	0	193
8	Feed to secondary	120,050	1,005,785	1,491	27	130	1,402	6,234	4,991	0	NAp	991,510
9	Depleted primary eluate	120,019	1,004,237	30	9	98	1,365	6,234	4,991	0	NAp	991,510
10	Secondary NH_4OH eluant	5,553	47,079	845	14	4	2	569	0	392	0	42,253
11	Secondary eluate product	1,201	10,513	1,448	18	30	22	0	0	355	0	8,640
12	Recycle secondary eluant	2,401	20,326	845	14	4	2	0	0	36	0	19,425
13	Waste secondary eluate	1,945	16,248	14	0	2	15	23	0	0	0	16,194
14	MgO precipitation	0	0	0	0	0	0	0	0	0	90	0
15	Feed to products (filtrate)	1,123	9,838	1,448	2	3	2	0	0	355	0	8,028
16	MgO precipitate	78	765	0	16	27	20	0	0	0	90	612
17	Dried tungstic oxide	NAp	1,661	1,448	2	3	2	0	0	94	0	112
18	Vapor	NAp	8,383	0	0	0	0	0	0	355	0	8,028
19	Calcined tungstic oxide	NAp	1,452	1,448	2	3	2	0	0	0	0	0

NAp Not applicable.

tration of 1 to 2 g/L WO_3. The fifth bed volume of eluate (stream 5) contains 4 pct of the eluted tungsten and is recycled to fresh eluant as makeup solution. Total tungsten recovery is 96 pct for this process step.

Tungsten Concentration

The secondary ion-exchange system can be operated with only one series of three columns containing 3-ft-deep QRF resin beds. In each 6.6-h cycle, 98 pct of the tungsten is recovered from 100 BV of clarified 90° F secondary feed (stream 8), which is pumped downflow through two fixed-bed columns in series. The flow rate is 5.7 gpm/ft² of column surface area. Spent secondary feed (stream 9), containing 2 pct of the influent tungsten, is sent to waste. A split-elution technique recovers 99 pct of the sorbed tungsten. Tungsten is eluted with a 90° F solution of $2N$ NH_4OH or $2N$ Na_2CO_3 (stream 10) and other recycled solutions (streams 11–13) at a flow rate of 0.87 gpm/ft² of column surface area. Eluant selection is determined by the desired product: Tungstic oxide is produced from NH_4OH eluate, and sodium tungstate and synthetic scheelite are produced from Na_2CO_3 eluate.

Primary Eluate Conditioning

Primary eluate is conditioned prior to use as feed to the secondary system to increase tungsten loading and eliminate operating problems created by evolution of CO_2 gas. Removal of the CO_2 is necessary to avoid bubble evolution in the columns during loading, which would result in pressure buildup. In each cycle, the 24,000 gal of primary eluate generated (stream 4) is acidified with sulfuric acid (H_2SO_4) (stream 7) to reduce the pH from 9.8 to 2.8, increasing tungsten loading on QRF resin to about 100 g WO_3 per liter of resin. Eluate acidification slowly releases CO_2. To increase the rate of CO_2 release, the acidified eluate (stream 8) is heated to 131° F, then cooled and settled prior to being pumped to the secondary ion-exchange section as feed. Precipitate formed during cooling remains in the bottom of the tank and is dissolved in the next batch of conditioned primary eluate, which is used as feed in the subsequent cycle. In this manner, steady-state concentrations are achieved in secondary feed.

Ammonium Hydroxide Elution

Elution using NH_4OH solution is a five-step procedure. The loaded resin is first washed in 1 BV of water to remove the remaining feed. Next, the tungsten is desorbed with 1 BV each of a strong recycle eluant, a weak recycle eluant, and a fresh $0.1N$ NH_4OH solution. Strong recycle eluant is $2N$ NH_4OH containing 40 to 60 g/L WO_3, and weak recycle eluant is $0.1N$ NH_4OH containing 10 to 30 g/L WO_3, both of which were produced in the previous cycle. Finally, the resin

TABLE 3.—Daily tungsten recovery from Searles Lake brines as sodium tungstate

Stream	Stream name	Volume, gal	Weight, lb								
			Total	WO_3	As	P_2O_5	B_4O_7	H_2SO_4	Na_2CO_3	MgO	H_2O
1	Soda grainer overflow	2,592,000	28,200,403	1,730	4,109	20,574	229,263	0	NAp	NAp	NAp
2	Depleted brine	2,591,767	28,194,485	173	4,021	20,163	224,990	0	NAp	NAp	NAp
3	Primary eluant	199,385	1,673,589	65	2	4	13	0	8,319	0	1,665,186
4	Primary eluate product	119,631	999,358	1,491	27	130	1,402	0	4,991	NAp	991,317
5	Recycle primary eluate	39,877	333,119	65	2	4	13	0	1,664	NAp	331,371
6	Waste primary eluate	39,877	333,119	65	61	280	2,871	0	1,664	NAp	328,178
7	H_2SO_4 acidification	419	6,427	0	0	0	0	6,234	0	0	193
8	Feed to secondary	120,050	1,005,785	1,491	27	130	1,402	6,234	4,991	NAp	991,510
9	Depleted primary eluate	120,019	1,004,237	30	4	68	1,337	6,234	4,991	NAp	991,573
10	Secondary Na_2CO_3 eluant	6,653	57,376	845	14	4	2	569	1,221	0	54,701
11	Secondary eluate product	1,201	10,413	1,448	23	60	50	0	1,062	0	7,770
12	Recycle secondary eluate	3,603	30,739	845	14	4	2	0	159	0	29,715
13	Waste secondary eluate	1,945	16,248	14	0	2	15	24	0	0	16,193
14	MgO precipitation	0	0	0	0	0	0	0	0	114	0
15	Feed to products (filtrate)	1,079	9,362	1,448	3	6	5	0	1,062	0	6,838
16	MgO precipitate	122	1,165	0	20	54	45	0	0	114	932
17	Dried sodium tungstate	NAp	3,237	1,448	3	6	5	0	1,062	0	713
18	Vapor	NAp	6,838	0	0	0	0	0	0	0	7,489
19	Calcined sodium tungstate	NAp	2,524	1,448	3	6	5	0	1,062	0	0

NAp Not applicable.

is conditioned for the next load cycle by pumping 1 BV of a 0.6*M* H_2SO_4 solution through the column. In this case, the flow is down and cocurrent. Each solution displaces the preceding solution from the column. The first solution to leave the column, primary eluate leftover from the loading cycle, is recycled to the secondary feed. The next solution, wash water, is discarded. Upon being displaced from the column, strong recycle eluant becomes the product eluate, containing 80 to 100 g/L WO_3, and is pumped to product recovery. Weak recycle eluant becomes the strong recycle eluant in the next cycle, and the fresh NH_4OH solution becomes the weak recycle eluant. The H_2SO_4 solution remains in the column until it is displaced at the start of the next loading cycle.

Sodium Carbonate Elution

Elution using Na_2CO_3 is similar to NH_4OH elution. First, the resin is washed with water. Then a strong recycle eluant, a weak recycle eluant, and a fresh eluant are pumped throught the resin bed. Finally, the resin is conditioned with a weak H_2SO_4 solution. There are two differences between the elution procedure using Na_2CO_3 and that using NH_4OH. For Na_2CO_3, the wash water is drained by forcing air into the top of the column, and the strong recycle eluant is introduced into the bottom of the column and pumped up through the resin bed instead of down. The CO_2 released during the upward elution procedure enhances the tungsten transfer by partially fluidizing the resin bed and increasing the contact between sorbed tungstate ions and eluant. This strong recycle eluant is retained in the column for 1 h, after which the elution proceeds downflow. The other difference is that 2 BV of weak recycle eluant is pumped through the column instead of 1 BV. When these are displaced from the column, the first bed volume becomes the strong recycle eluate, and the second is returned to the weak recycle eluate holding tank.

Impurity Removal

Arsenic and phosphorus concentrations are reduced in both eluates using a batch magnesium oxide (MgO) precipitation step prior to product recovery. These impurities are precipitated daily from the 1,200 gal of secondary eluate generated using 90 lb of MgO (stream 14) at a magnesium-to-arsenic ratio of 3:1. An addition of MgO is made to the secondary eluate at ambient temperature (77° F) and stirred for 60 min. The slurry is pumped through a pressure filter to separate the precipitate from the filtrate (stream 15), which serves as feed for tungsten chemical recovery. The MgO precipitate (stream 16) contains over 90 pct of the arsenic and the phosphate in a filter cake containing 20 pct solids, which is sent to waste.

TABLE 4.—Daily tungsten recovery from Searles Lake brines as synthetic scheelite

Stream	Stream name	Volume, gal	Weight, lb									
			Total	WO_3	As	P_2O_5	B_4O_7	H_2SO_4	Na_2CO_3	MgO	H_2O	$CaCl_2$
1	Soda grainer overflow	2,592,000	28,200,403	1,730	4,109	20,574	229,263	0	NAp	NAp	NAp	NAp
2	Depleted brine	2,591,767	28,194,485	173	4,021	20,163	224,990	0	NAp	NAp	NAp	NAp
3	Primary eluant	199,385	1,673,589	65	2	4	13	0	8,319	0	1,665,186	NAp
4	Primary eluate product	119,631	999,358	1,491	27	130	1,402	0	4,991	NAp	991,317	NAp
5	Recycle primary eluate	39,877	333,119	65	2	4	13	0	1,664	NAp	331,371	NAp
6	Waste primary eluate	39,877	333,119	65	61	280	2,871	0	1,664	NAp	328,178	NAp
7	H_2SO_4 acidification	419	6,427	0	0	0	0	6,234	0	0	193	NAp
8	Feed to secondary	120,050	1,005,785	1,491	27	130	1,402	6,234	4,991	NAp	991,510	NAp
9	Depleted primary eluate	120,019	1,004,237	30	4	68	1,337	6,234	4,991	NAp	991,573	NAp
10	Secondary Na_2CO_3 eluant	6,653	57,376	845	14	4	2	569	1,221	0	54,701	NAp
11	Secondary eluate product	1,201	10,413	1,448	23	60	50	0	1,062	0	7,770	NAp
12	Recycle secondary eluate	3,603	30,739	845	14	4	2	0	159	0	29,715	NAp
13	Waste secondary eluate	1,945	16,248	14	0	2	15	24	0	0	16,193	NAp
14	MgO precipitation	0	0	0	0	0	0	0	0	114	0	NAp
15	Feed to products (filtrate)	1,079	9,362	1,448	3	6	5	0	1,062	0	6,838	NAp
16	MgO precipitate	122	1,165	0	20	54	45	0	0	114	932	NAp
17	Dried sodium tungstate	NAp	3,237	1,448	3	6	5	0	1,062	0	713	NAp
18	Vapor	NAp	6,838	0	0	0	0	0	0	0	7,489	NAp
19	Calcined sodium tungstate	NAp	2,524	1,448	3	6	5	0	1,062	0	0	NAp
20	Calcine dissolution	856	7,141	0	0	0	0	0	0	0	7,141	NAp
21	$CaCl_2$ precipitation	157	1,730	0	0	0	0	0	0	0	1,038	692
22	Filtrate	1,034	9,293	15	1	0	5	0	1,062	0	7,765	3Ca, 442Cl
23	Vapor	NAp	414	0	0	0	0	0	0	0	414	0
24	Calcium tungstate	NAp	1,787	1,433	2	6	0	0	0	0	0	247Ca

NAp Not applicable.

Tungstic Oxide and Sodium Tungstate Recovery

Tungstic oxide can be produced from MgO-treated NH_4OH secondary eluate and sodium tungstate can be produced from MgO-treated Na_2CO_3 secondary eluate using almost identical techniques. The filtrate from MgO precipitation (stream 15) is pumped into a spray dryer. The tungsten salts (stream 17) that collect in the dryer are calcined at 1,100° F for 4 h to remove occluded organic materials coextracted with the tungsten from the brine and produce the calcined product (stream 19). When tungstic oxide is produced from the NH_4OH eluate, drying and calcining produce ammoniacal vapors (stream 18). Excess condensate is bled from the circuit and returned to the secondary ion-exchange step as fresh eluant. When sodium tungstate is produced from Na_2CO_3 eluate, vapors from the dryer and calciner are passed through a dust collector and then vented directly to the atmosphere. In both cases, solids leaving the calciner are cooled and then loaded into drums for shipment.

Each year this process would produce about 480,000 lb of anhydrous tungstic oxide analyzing, in weight percent, 99 WO_3, 0.12 As, 0.22 P_2O_5, and less than 0.4 B_4O_7, or 833,000 lb of sodium tungstate analyzing, in weight percent, 58 WO_3, 0.11 As, 0.42 P_2O_5, and 0.18 B_4O_7.

Synthetic Scheelite Recovery

To produce commercial-grade synthetic scheelite, the calcined sodium tungstate is dissolved in sufficient water to produce a solution containing 95 g/L WO_3 (stream 20) by stirring moderately for 1 h at room temperature. A 40-pct solution of $CaCl_2$ in potable water (stream 21) is slowly added to the solution, precipitating scheelite. Stirring is continued for 1 h at 158° F. The precipitated scheelite is filtered, and the filtrate (stream 22) is returned to the calcine dissolution step. The product is dried, producing water vapors (stream 23). The synthetic scheelite product

(stream 24) contains, in weight percent, 79 WO_3, 13 Ca, 0.12 As, 0.33 P_2O_5, and 0.008 B_4O_7. This process would produce about 590,000 lb of synthetic scheelite annually.

ECONOMICS

The complete Bureau cost evaluation of a plant addition to recover tungstic oxide, sodium tungstate, and synthetic scheelite products from the soda-grainer overflow at the Westend facility is presented in appendix A. The evaluation includes a plant description, proposed equipment, and a cost estimation including capital and operating costs. The evaluation (conducted in October 1984) indicates that product costs would be \$5.03/lb WO_3 for tungstic oxide or sodium tungstate, and \$5.29/lb WO_3 for synthetic scheelite. Based on the currently depressed tungsten market, October 1984 values for the three products are \$5.14/lb WO_3 for tungstic oxide, \$4.32/lb WO_3 for sodium tungstate, and \$3.61/lb WO_3 for synthetic scheelite. Using the interest rate of return method, only the tungstic oxide process is profitable and would yield an estimated 1 pct rate of return on investment after taxes; 15 pct is generally considered to be the minimum acceptable rate of return on investment for a new venture.

CHAPTER 3.—ION-EXCHANGE RESIN DEVELOPMENT

By P. B. Altringer, W. N. Marchant,[1] R. O. Dannenberg,[2] T. H. Jeffers,[2] and P. T. Brooks[3]

An objective of this research was to minimize processing costs and ensure compatibility with current processing operations by recovering tungsten without essentially altering the chemistry of the brine. Ion exchange achieved this objective. In the past, industrial research tested several methods; however, none of the methods proved economical (*2, 7–9*). Techniques for chemically treating the brine, such as attempts to precipitate tungstic acid from acidified brine, failed because the huge chemical requirements necessary to change the characteristics of the alkaline brines made operating expenses prohibitive. Known solvent extraction techniques had been proven uneconomical because of excessive solvent losses (*10*). Ion-exchange techniques generally do not involve comparable material losses, but existing ion-exchange materials did not extract tungsten effectively (*14–20*).

INITIAL TUNGSTEN RECOVERY RESEARCH (21)

Initial tungsten recovery research consisted of three stages, testing commercial ion-exchange resins, examining novel solvent extraction systems, and synthesizing tungsten-selective ion-exchange resins.

Promising results were first achieved by extracting tungsten from pH 10 untreated lake brine with the resin Amberlite IRA 400[4] after dissolving catechol, or dihydroxybenzene, in the brine (*10*). This approach was suggested by the work of Halmekoski who found the converse; that is, anion-exchange resins saturated with tungsten extracted catechol and similar organic compounds from aqueous solutions (*22*). This procedure was too expensive for large-scale use; therefore, efforts were directed toward improving process economy by decreasing catechol consumption.

Tungsten extraction required less catechol when brine was extracted with a kerosene solution containing catechol, the quaternary amine Aliquat 336, and isodecanol. Both the rate and amount of tungsten extracted by the kerosene solution were proportional to the catechol content. Tungsten was stripped from the organic phase with a 1*M* sodium hydroxide (NaOH) solution. Although good tungsten extraction was achieved, an excessive loss of catechol occurred during solvent stripping.

The solvent extraction technique was improved by replacing catechol with a less soluble derivative, 4-tert-butyl catechol. This solvent system extracted both boron and tungsten from brine; however, the catechol derivative proved unstable. Improved results were achieved using 2,3-naphthalenediol in place of the catechols. However, an economic appraisal showed that the technique was impractical because chemical costs exceeded the value of the recovered tungsten.

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[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

The need for eliminating solvent losses typical of solvent extraction procedures prompted research to develop an insoluble, tungsten-selective ion-exchange resin capable of sorbing tungsten directly from brine, without the use of costly complexing agents or other chemicals required to change the nature of the brine. Because the affinity of dihydroxybenzene and trihydroxybenzene derivatives for tungsten was demonstrated in early testing, phenol-formaldehyde-type resins containing polyhydroxy compounds appeared likely to have tungsten affinities. Procedures described in the literature (*14, 23–24*) were employed for resin synthesis. A variety of resins was prepared and tested by mixing 10 g of resin for 1 h with 100 mL of Searles Lake brine. Results of these screening tests, shown in table 5, demonstrated the superiority of a copolymer of 3,4,5-trihydroxybenzoic acid (gallic acid), resorcinol, and formaldehyde. This polymer was referred to as GRF resin. Typically, 90 pct of the tungsten and 12 pct of the boron were removed from the brine and recovered in the resin column eluate. Prolonged cycling, however, caused both chemical and physical degradation of the resin.

TABLE 5.—Tungsten extraction from Searles Lake brines using experimental ion-exchange resins[1]

Resin composition	*Tungsten extraction, pct*
8-hydroxyquinoline, formaldehyde	0
Cinchonine, resorcinol, formaldehyde	0
0-aminophenol, formaldehyde	2.8
Phenylpyrocatechol, resorcinol, formaldehyde	5.2
2,4-dihydroxybenzoic acid, resorcinol, formaldehyde	11
3,4-dihydroxybenzoic acid, phenol, formaldehyde	11
Catechol, formaldehyde	11
Anthranilic acid, formaldehyde	28
2,3-naphthalenediol, resorcinol, formaldehyde	39
3,4,5-trihydroxybenzoic acid, resorcinol, formaldehyde (GRF)	90

[1]Tests were performed by mixing 10 g of resin for 1 h with 100 mL of Searles Lake brine.

HERF GRANULAR RESIN[5]

Promising leads, developed as the result of GRF resin synthesis and testing, were pursued with the objective of producing a resin with improved chemical and physical stability, tungsten capacity, and selectivity for tungsten over boron. This objective was met by utilizing 8-hydroxyquinoline, also known as 8-quinolinol, or oxine, because of its well-known affinity for tungsten and many other heavy metals. The 8-hydroxyquinoline was polymerized with resorcinol as well as formaldehyde and a polyamine. This material was used to synthesize the second-generation resin, HERF, developed by the Bureau specifically for tungsten extraction from alkaline solution (*4*). Testing also began on Kerr-McGee plant effluents that were less alkaline than the pH 9 to 10 raw lake brine. The less alkaline brine was a more attractive feed, because tungsten sorption increased with decreased brine alkalinity.

[5]Adapted from reference 21.

Ion-exchange resins incorporating 8-hydroxyquinoline have been known for over 25 yr, and have been used to extract various heavy metals from acidic media. There are no reports of using them to recover tungsten from alkaline solution. The properties of these resins have never been completely satisfactory, and no resin suitable for this purpose is commercially available in the United States. Most of the 8-hydroxyquinoline resin preparations described in the literature are modifications of two methods: condensation of 8-hydroxyquinoline, resorcinol, and formaldehyde (*15–16*), and coupling a diazotized poly (aminostyrene) resin with oxine (*17*). The problems with both of these types of resin were that the capacities and exchange rates were low. Condensation resins with higher capacities were subsequently synthesized (*14*), but other researchers were unable to reproduce the results (*18*). High-capacity resins were produced by preventing the loss of water during curing, and kinetics were improved by incorporating sulfonic acid groups in the matrix (*19*). Researchers claimed to have synthesized condensation resins from oxine, but these resins were limited to use in acidic and neutral solutions (*20*). The Bureau developed a resin in granular form capable of selectively extracting tungsten from alkaline solutions.

The general procedure used for preparing a batch of resin granules entailed mixing 8-hydroxyquinoline in 2*N* NaOH followed by adding ethylenediamine and one-half of the required formaldehyde. The reactants dissolved during 1 h of stirring at room temperature to from a viscous, amber-colored solution. Resorcinol dissolved in 2*N* NaOH was added, followed by the remaining formaldehyde, and a firm, transparent gel formed within 20 min. The gel was cured at 105° C for 16 h, crushed, and screened. The resin granules were first washed with water, next with dilute H_2SO_4, and finally with dilute NaOH to remove soluble unreacted components and to convert the resin to the sodium form.

The resins were tested initially by mixing 5 g of moist resin for 30 min with 50 mL of brine containing 0.07 g/L WO_3 plus a trace of radioactive tungsten added as gamma-emitting tungsten-181. Tungsten sorption was rapidly and conveniently measured radiometrically, and results were later confirmed by conventional colorimetric analysis. Boron sorption was determined by atomic absorption spectrophotometry. Table 6 shows the superior performance of HERF resin granules relative to GRF resin ganules.

TABLE 6.—Tungsten and boron extraction by HERF and GRF resin[1]

Resin composition, molar proportion of monomers[2]	Extraction, pct	
	Tungsten	Boron
1H:0.6E:1R:8F	82	6.2
1G:0.1R:2.5F	57	22

[1]Testing was performed by mixing 5 g of resin for 30 min with 40 mL of pH 8.5 carbonation plant effluent.

[2]H = 8-hydroxyquinoline, E = ethylenediamine, R = resorcinol, F = formaldehyde, G = gallic acid.

QRF BEAD RESIN

Nearly half of the granular GRF and HERF resin produced in the initial research was lost during stage grinding of resin blocks and subsequent sizing. Production of resin beads, rather than resin granules, was advantageous in achieving a much higher yield of usable resin; a 90-pct yield of usable beads in the 20- to 48-mesh size range was achieved using suspension polymerization. Ethylenediamine was not used in the new resin formulation, since it demonstrated no benefits in bead synthesis; there was no evidence of increased strength, exchange kinetics, or tungsten capacity. The new resin bead, composed of 8-hydroxyquinoline (also referred to as 8-quinolinol), resorcinol, and formaldehyde was termed "QRF."

QRF beads exhibited more rapid loading kinetics and a greater tungsten capacity than did HERF granules. Figure 2 shows that QRF beads load tungsten faster than do HERF granules. For example, after 30 min, QRF beads loaded to 2.40 g/L WO_3, but HERF granules loaded to only 1.60 g/L WO_3. After 60 min, QRF beads loaded to 2.75 g/L WO_3, but HERF granules loaded to only 1.75 g/L WO_3. Equilibrium was achieved after about 180 min. These kinetic data were obtained from batch shaker tests using 1,000 mL of pH 7.5 soda grainer overflow brine containing 0.075 g/L WO_3 and 10 mL wet-settled resin sized to 20 to 48 mesh.

QRF beads also exhibited greater tungsten capacity than did HERF granules, as shown in figure 3. At an aqueous-to-resin ratio of 100, QRF beads loaded to 3.9 g/L WO_3 compared with 2.9 g/L WO_3 for HERF granules. These equilibrium loading results were obtained in batch shaker tests where varying amounts of pH 7.5 soda grainer overflow brine were contacted with 10 mL of 20- to 48-mesh wet-settled resin for 4 h.

Laboratory development of QRF resin in bead form required extensive review of the literature followed by investigation of several critical factors influencing resin bead production. These factors included molar ratio of components, dispersion media, prepolymerization time and temperature, agitator speed, and curing time.

Resin Chemistry

Various researchers have described producing cationic and anionic resins in bead form by suspension polymerization of water-soluble organic compounds in a water-immiscible solvent (*14*, *20*, *25–29*). A high-boiling-point, water-immiscible organic solvent, such as dichlorobenzene, was used as the suspending medium and water of condensation was removed from the reaction mixture by distillation.

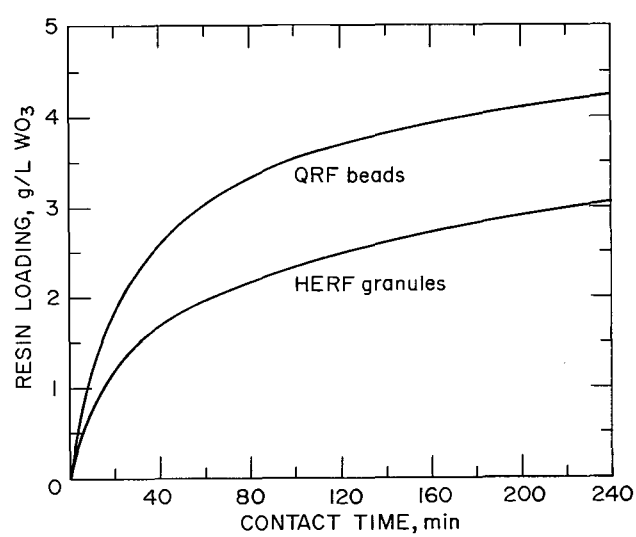

Figure 2.—Kinetics of loading HERF granules and QRF beads.

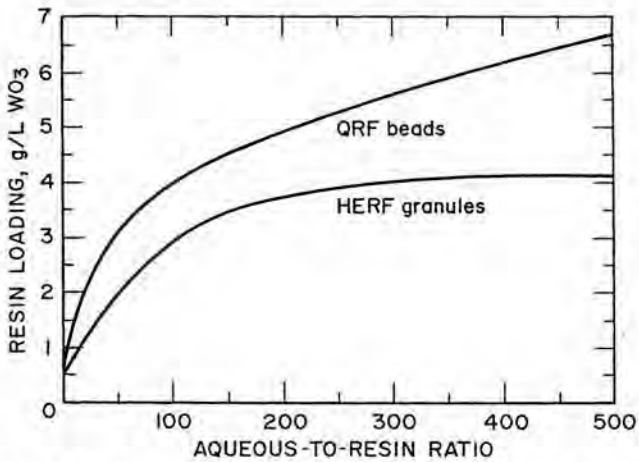

Figure 3.—Loading capacity of HERF granules and QRF beads.

The reaction between 8-hydroxyquinoline (quinolinol, oxine), resorcinol, and formaldehyde is base-catalyzed and involves condensation and cross-linking as proposed in the following reaction.

A conceptual reaction product of resin and anionic tungsten is indicated by the following compound, where $W_xO_yH_z$ represents a hydrated tungsten species.

Bench-Scale Resin Synthesis

Small resin batches were prepared in an electrically heated, smooth-walled glass reaction kettle equipped with a centrally located agitator (fig. 4). Typically, 32 g of quinolinol were slurried with 150 mL of 2*M* NaOH followed by adding 72 mL of 37 pct formaldehyde maintaining the temperature at 24° C. This mixture was combined with a solution of 24 g resorcinol in 150 mL of 2*M* NaOH and 72 mL of 37 pct formaldehyde. The mixture was stirred at 24° C for 5 h. The solution, at nearly 10-cP viscosity, was poured into 500 mL of refluxing, 87° C monochlorobenzene stirred at 150 rpm using a 3-in-diam, four-blade, turbine impeller. A dispersant, SPAN 80, was used at a concentration of 6.6 g/L chlorobenzene. After curing for 20 h, the suspension was filtered, and the resin beads were washed with methanol, rinsed with water, and wet-screened at 20 to 48 mesh.

The beads were stored in a moist condition to prevent irreversible dehydration, shrinkage, and a consequent reduction in tungsten sorption capacity. In one test, for example, dried resin extracted only 15 pct as much tungsten as an equal volume of moist resin.

Molar Ratios of Reactants

QRF resin was routinely made at an 8-hydroxyquinoline-to-resorcinol-to-formaldehyde molar ratio of 1:1:9. In an effort to increase the kinetics and tungsten capacity of QRF resin, the 8-hydroxyquinoline-to-resorcinol molar ratio was varied, keeping a constant volume of monomer and formaldehyde; no advantage was gained by increasing the ratio from 0.5 to 4.0. In fact, at ratios greater than 2.0, it was necessary to increase the ratio of 8-hydroxyquinoline-to-formaldehyde from 1:9 to at least 1:5 before any beads were produced. At ratios lower than 1:5, a semisolid mass of unreacted monomer was produced.

Dispersion Medium

Water-immiscible monochlorobenzene was a satisfactory medium for dispersing an aqueous solution of resin components. The densities of the organic and aqueous phases were nearly equal at 1.1 g/mL. A more dense medium, such as bromobenzene at 1.5 g/mL, caused the aqueous dispersion to crowd into an upper layer and form bead agglomerates that were difficult to separate. Monochlorobenzene, a liquid at room temperature, was easily washed from the beads. The dispersant SPAN 80 was used

Figure 4.—Bench-scale reactor for producing 500-mL resin batches.

at a concentration of 6.6 g/L of monochlorobenzene to aid in bead forming. Poor dispersion caused large globs to form when no dispersant was used and excessive dispersant caused a high yield of very fine beads.

Prepolymerization Time and Temperature

Retention time and temperature, following the combining of both resin component solutions prior to dispersion in refluxing monochlorobenzene, influenced bead yield, hardness, and tungsten capacity. During this period, called prepolymerization time, the chemical reaction is proceeding but at a slower rate than the rapid and extensive polymerization that occurs in the refluxing monochlorobenzene. Results in table 7 show both yield of 20- to 48-mesh beads and tungsten loading at several prepolymerization times. These small batch tests were conducted, as previously described, using a 1-L reactor stirred at 150 rpm. Tungsten loading was measured after mixing 10 mL of resin beads for 60 min with 200 mL of pH 8 sodium tungstate solution containing 1 g/L WO_3. Temperature during prepolymerization was controlled using a water bath to remove the heat of reaction. Tungsten loading decreased with increased prepolymerization time, whereas bead yield improved. Bead elasticity decreased as prepolymerization time increased; firm beads were produced after 300 min of prepolymerization time, whereas elastic, easily deformed beads were produced at shorter prepolymerization times. Highly elastic beads would deform and inhibit brine flow within the ion-exchange columns at operating pressures.

During the prepolymerization phase, cooling is required to prevent the heat of reaction from increasing mixture viscosity from an easily poured 10 cP to a viscous 1,000 cP and finally to a gel. For example, in initial tests at 50° C, the resin mixture reached 1,000 cP in 4 min, whereas in later tests, a viscosity of 1,000 cP was reached in 42 min at 30° C. The optimum resin production conditions of 300 min prepolymerization time at 24° C were estimated from test results presented above; these conditions provided long crosslinking time and prevented premature gelling by low temperature, which enabled the mixture to be transferred at 10 cP.

Agitator Speed

The degree of agitation used to disperse the resin mixture in monochlorobenzene-SPAN 80 governed the size distribution of resin beads. The trend is shown in figure 5, where tip speed of a 7.6-cm-diam, flat-blade agitator within a 10.2-cm-diam reactor is related to the yield of 20- to 48-mesh resin beads. Many coarse beads were produced at 100 rpm, whereas fine beads predominated at 200 rpm. Equivalent tip speeds for scaleup studies were 80 ft/min for 100 rpm and 160 ft/min for 200 rpm.

Curing Time

Resin polymerization was accomplished in refluxing chlorobenzene and polymerization degree varied with retention time at 87°C. Increasing amounts of water were expelled as the resin polymerized. Part of the water was a product of the condensation reaction and part was water contained in the resin component mixture. Resin hardness, as determined by a bead-crushing device, increased and tungsten capacity decreased with curing time. Resin beads were routinely cured for 20 h, after which QRF beads were similar in elasticity to commercially available Rohm and Haas Amberlite IRA 410 resin.

TABLE 7.—Effect of retention time on resin bead yield and tungsten sorption capability

Retention temp, ° C	Retention time, min	Yield of 20- to 48-mesh beads, pct	Tungsten loading, g WO_3 per liter of resin
24	1	57	9.2
	100	54	9.2
	200	74	8.4
	300	91	5.6
20	400	90	5.6

LARGE-SCALE QRF SYNTHESIS

Following successful laboratory development of the tungsten recovery technique, pilot tests were planned to obtain engineering data under actual conditions at Searles Lake. This necessitated escalating resin synthesis from 500-mL laboratory batches (equivalent to 0.02 ft^3) to semicommercial-scale batches of 1 ft^3 or more to supply the necessary 20 ft^3 for the resin columns. Escalation proceeded to an unbaffled stainless steel reactor with a 9.5-in ID and a working depth of 13 in. This reactor and the basic resin-making procedure resulted in 0.2-ft^3 resin batches and provided an intermediate point for further escalation. The primary objective of the studies was to relate agitator size, blade-tip speed, and bead size distribution.

Impellers used in larger scale testing were turbine types with four, square, flat blades, and a blade width equal to 25 pct of the turbine diameter. Two impellers were fixed to a single shaft such that impeller spacings were one-third and two-thirds of the liquid depth measured from the bottom of the reactor. Identical bead yields of 90 pct in the 20- to 48-mesh range were achieved at impeller tip speeds of 128 ft/min using impeller diameters of either 3.13 or 6.0 in. Thus, good bead yields were achieved in two tests at identical impeller tip speeds using two different impeller diameters.

Final escalation was made using an unbaffled, glass-lined, steam-jacketed reactor with an inner diameter and working depth of 17.75 in each (fig. 6). The centrally located, variable-speed agitator shaft held two four-blade, 11.2-in-diam turbine impellers geometrically similar to the im-

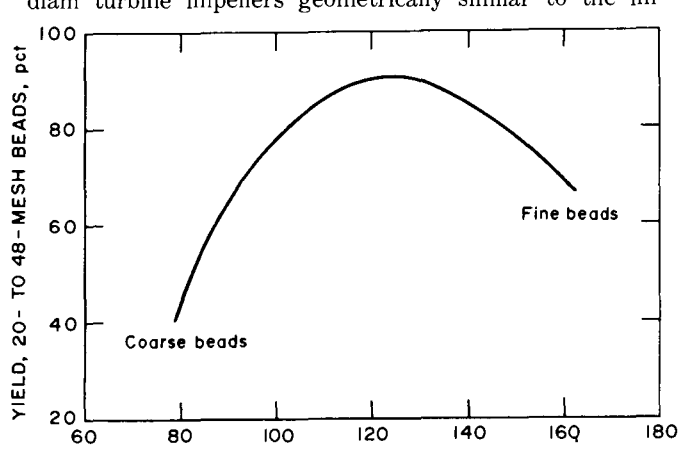

Figure 5.—Resin bead yield as function of impeller tip speed.

Figure 6.—Semicommercial reactor for producing 1-ft³ resin batches.

pellers used in the 9.5-in reactor. The equation shown below, which relates impeller speed and diameter for two geometrically similar vessels and agitators, was helpful for estimating agitator speed necessary for producing a high yield of 20- to 48-mesh beads in the large reactor (*30*). Time and materials were conserved by minimizing the number of tests required to achieve a 90-pct yield of usable resin beads.

$$N_2 = N_1\left(\frac{D_1}{D_2}\right)^n,$$

where N_1 = agitator speed in reactor 1,
N_2 = agitator speed in reactor 2,
D_1 = impeller diameter in reactor 1,
D_2 = impeller diameter in reactor 2,
and $n = 0.75$ for suspended solids.

Based on good results achieved at a tip speed of 128 ft/min in the 9.5-in reactor, the estimated speed for 11.2-in impellers in the 17.75-in reactor was 150 ft/min, equivalent to 51 rpm. This speed resulted in an 82-pct yield of 20- to 48-mesh beads. Increasing agitator tip speed to 162 ft/min, equivalent to 55 rpm, increased the yield to 90 pct. Thus, the equation provided a useful estimated agitator tip speed even though the two reactors differed in width-to-depth ratios.

Chemicals used to produce 1 ft³ of resin beads were 2,207 g 8-hydroxyquinoline, 1,655 g resorcinol, 5.5 gal 2*M* NaOH, and 2.6 gal of 37-pct formaldehyde. The resulting mixture occupied a volume of 9.0 gal and, after prepolymerization at 75° F for 300 min, was dispersed in 9.0 gal of chlorobenzene containing 6.6 g/L SPAN 80.

Laboratory resin was initially washed with methanol followed by a water rinse; later tests showed the methanol wash was not advantageous, and only a thorough water wash was used to remove soluble, unreacted materials.

Nearly 20 ft³ of 20- to 48-mesh QRF resin beads were prepared at a 90-pct yield after escalating resin synthesis from a laboratory reactor to a semicommercial scale.

SUMMARY

- Resinous ion-exchange granules synthesized from 8-hydroxyquinoline, ethylenediamine, resorcinol, and formaldehyde (HERF) effectively extracted tungsten from Searles Lake brines.
- A more sophisticated, suspension-polymerization technique enabled the production of resin beads with a much higher yield of usable resin than that attainable by granule production. The new type of resin (QRF) thus synthesized exhibited faster tungsten loading kinetics and higher capacity than did HERF granules.
- QRF beads, synthesized from 8-hydroxyquinoline, resorcinol, and formaldehyde, were produced in laboratory batches of 500 mL, equivalent to 0.02 ft³; production was successfully escalated to batches of 1 ft³ at yields of 90 pct in the 20- to 48-mesh range. Nearly 20 ft³ of QRF resin beads was produced on a semicommerical scale.

CHAPTER 4.—TUNGSTEN EXTRACTION BY A PRIMARY ION-EXCHANGE PROCESS

By P. B. Altringer and P. T. Brooks

A primary ion-exchange process comprising a system for sequential loading and elution of QRF resin in columns was selected for tungsten extraction because it enables continuous processing. Two columns are connected in series for tungsten sorption; while the third column is eluted. Once the lead column is loaded, it is disconnected and eluted. The second, or scavenger, column is then connected in the lead column position, and the eluted column is connected in the scavenger position. Results showed that the basic primary ion-exchange technology established from laboratory research performed satisfactorily under conditions encountered at Searles Lake.

BENCH-SCALE RESEARCH USING HERF RESIN GRANULES[1]

Research to develop processing technology began prior to the development of QRF resin; consequently, much of the early processing technology testing was conducted using HERF resin. Tests were conducted to determine the effects of resin particle size, brine pH, temperature, and flow rate on tungsten sorption and elution using static resin beds ranging in diameter from 15 to 51 mm and ranging in depth from 440 to 914 mm, respectively. A typical experimental setup is shown in figure 7.

[1]Adapted from reference 21.

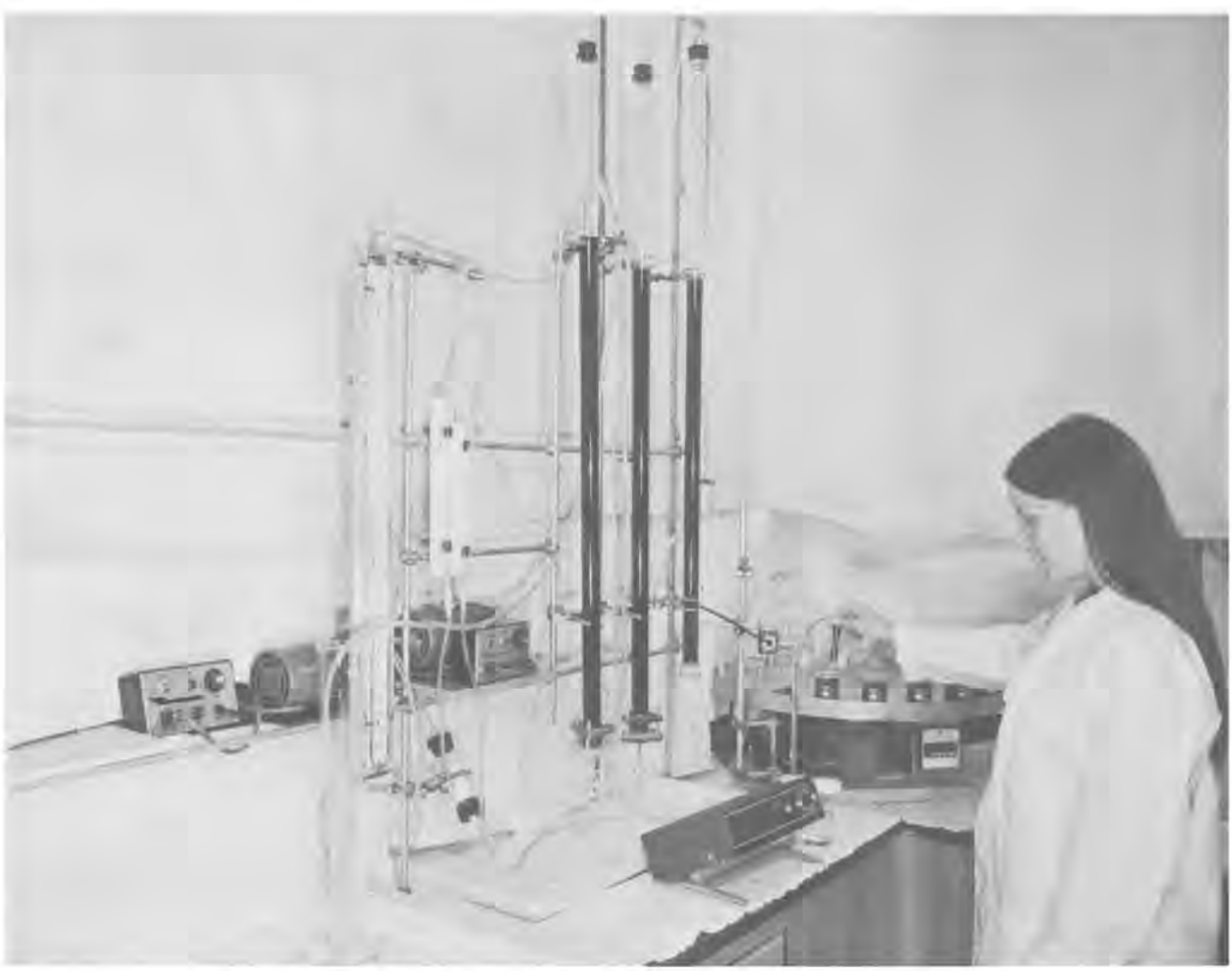

Figure 7.—Bench-scale ion-exchange columns used for testing HERF resin.

Effect of Resin Particle Size on Tungsten Sorption Rate and Capacity

Blocks of HERF resin were crushed, sized, and tested to determine the effect of particle size on tungsten sorption using batch tests in which 5 g of resin was shaken in 100 mL of pH 8.5 carbonate plant effluent. Results in table 8 show the increased rate of tungsten sorpotion by the smaller resin granules. Equilibrium was essentially reached in 24 h for all particle sizes. Most subsequent testing was done using resin particles sized 20 to 48 mesh, the size range used in most industrial static-bed operations.

Effect of Brine pH on Tungsten Extraction and Elution

Tungsten extraction became more effective as brine alkalinity decreased; test results are shown in table 9. These results prompted use of the pH 7.5 soda grainer overflow. Conversely, tungsten elution with water became less effective when tungsten was sorbed from less alkaline brines. This suggests that the sorbed tungsten species varies with brine pH.

Laboratory test solutions were prepared from the carbonation plant effluent stream by acidification with CO_2 followed by filtration to remove precipitated $NaHCO_3$. Tests were performed in a 75-mL resin bed, 440 mm deep, at a loading flow rate of 20 mL/(min · cm²) [5 gpm/ft² of column cross-sectional area]. Eighteen bed volumes of feed were used to load the resin. Tungsten was eluted from the resin bed using 4.5 BV of water at a flow rate of 4 mL/(min · cm²) [1 gpm/ft² of bed area].

Resin Elution Using Sodium Salts

Since water elution was not effective for tungsten loaded from the soda grainer overflow brine, a variety of eluants was tested to enable complete tungsten desorption using a minimum volume of solution. Minimizing eluant volume maximizes the tungsten concentration and aids subsequent tungsten recovery; also, minimizing solution volume conserves the scarce water supplies in the Searles Lake desert area. Sodium salts at concentrations of 10 g/L were tested to compare relative effectiveness for eluting a 75-mL column of resin containing 67 mg of tungstic oxide sorbed from pH 7.5 soda grainer overflow. Tungsten was completely eluted using 4.5 BV of either Na_2CO_3 or NaOH solution. Solutions of $NaHCO_3$, sodium chloride (NaCl), or sodium sulfate (Na_2SO_4) removed only 55 to 70 pct of the tungsten. Although the NaOH solution was an effective eluant, the strongly basic pH 12 solution degraded the HERF resin, and a more dilute pH 11 solution of NaOH eluted only 68 pct of the tungsten. A solution of Na_2CO_3 was preferable for eluting tungsten sorbed from carbonated brine because elution was effective with no resin deterioration.

Further testing was performed to define more clearly the effectiveness of Na_2CO_3 solutions for eluting tungsten from loaded resin. No advantage was gained using eluants containing more than 5 g/L Na_2CO_3. Comparative elution tests were conducted using 2.5-cm-diam and 90-cm-deep resin beds. The resin beds contained 2.2 g WO_3 that had been sorbed from 100 BV of pH 7.5 brine. Elutions with 6 BV of eluant containing 10, 5, 2.5, and 1 g/L Na_2CO_3 were 100, 96, 82, and 55 pct, respectively. Fifty percent of the tungsten was eluted using 6 BV of water containing no added Na_2CO_3.

TABLE 8.—Tungstate soption rate from carbonation plant effluent as function of HERF resin granule size[1]

Particle size range, mesh	Tungsten extraction, pct			
	10 min	60 min	120 min	24 h
−10, +16	41	73	81	91
−16, +20	53	81	87	94
−20, +35	64	86	89	94
−35, +48	71	87	90	94

[1]Batch tests where 5 g of resin was shaken in 100 mL of pH 8.5 carbonation plant effluent.

TABLE 9.—Tungsten extraction and elution using HERF resin as function of brine alkalinity[1]

Brine pH	Tungsten, pct	
	Extracted[2]	Eluted[3]
8.5	43	95
8.0	73	88
7.5	74	84
7.0	99	52

[1]Tests were performed in a 75-mL resin bed, 440 mL deep.
[2]Loaded from 18 BV of feed at 20 mL/(min · cm²) [5 gpm/ft²].
[3]Eluted with 4.5 BV of water at 4 mL/(min · cm²) [1 gpm/ft²].

Effect of Temperature on Tungsten Sorption and Elution

Tungsten sorption was more effective with lower feed temperatures; conversely, tungsten elution was more effective with higher temperatures. Tungsten loading from soda grainer overflow in 200-min batch shaker tests at a solution-to-resin ratio of 100 was 3.2, 1.8, and 1.2 g WO_3 per liter of resin at temperatures of 20°, 40°, and 60° C, respectively. The temperature of soda grainer overflow normally is 32° C.

Elution of resin loaded to 3.2 g WO_3 per liter of resin increased from 48 to 60 pct when the temperature of 0.5-pct-Na_2CO_3 solution was increased from 20° to 40° C in 200-min batch shaker tests at a solution-to-resin ratio of 100. The effect of elevated temperature on resin over an extended period was not tested at this time.

Effect of Flow Rate on Tungsten Sorption and Elution

Tungsten sorption from brine flowing through a column of HERF resin was more complete at low solution flow rates, whereas increased flow rates enabled a greater rate of tungsten transfer. This relationship is typical of diffusion-controlled operations. For example, 71 pct of the tungsten was sorbed from 100 BV of pH 7.5 brine flowing through 90 cm of resin at a rate of 20 mL/(min · cm²). Eighty-nine percent of the tungsten was sorbed from the brine when the flow rate was decreased to 4 mL/(min · cm²). The average rates of tungstic oxide removal were 0.32 and 0.074 g/h at the high and low flow rates, respectively. The higher of the two feed rates (equivalent to 5 gpm/ft²) is typical of many ion-exchange operations and appears more practical. The data plotted in figure 8 show tungsten sorption from the 90-cm bed containing 425 mL of resin.

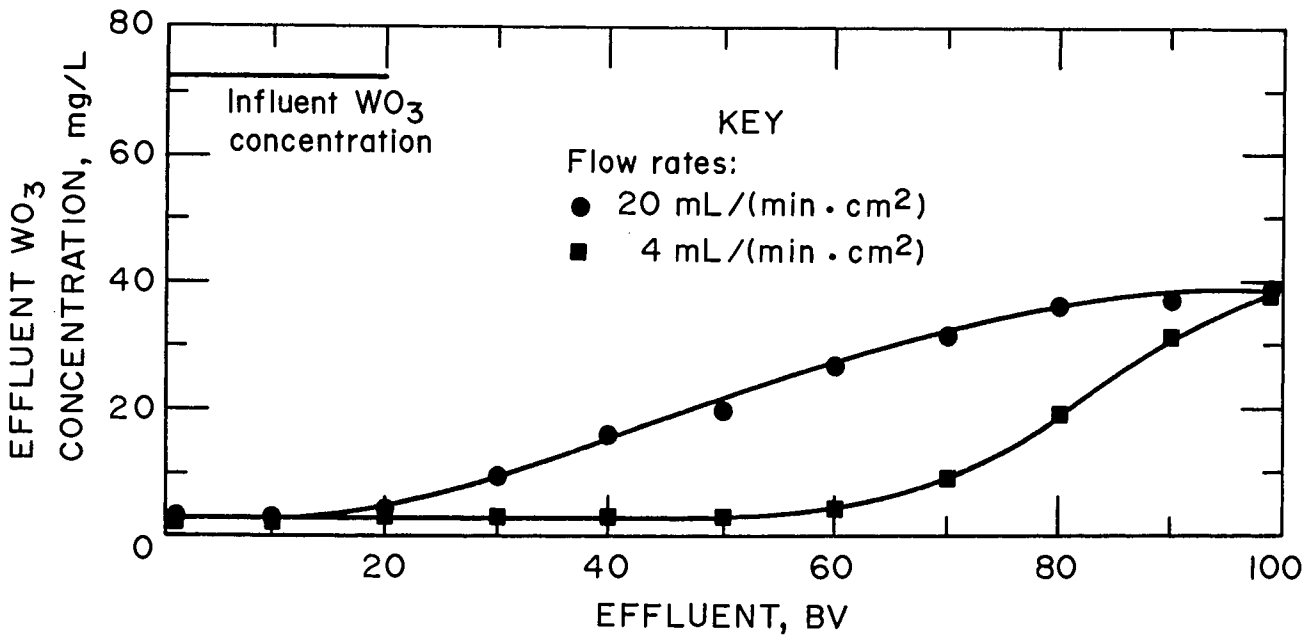

Figure 8.—Tungsten extraction from pH 7.5 brine at two flow rates.

Tungsten elution from the 425-mL resin bed was determined as a function of eluant flow rate using solutions containing 5 g/L Na_2CO_3. Data plotted in figure 9 show that the most concentrated eluate was produced at the two lowest flow rates tested. From 85 to 90 pct of the tungsten was desorbed using 5 BV of eluate at flow rates of 2 to 4 mL/(min · cm²) of column area, whereas only 65 pct of the tungsten was desorbed at a flow rate of 20 mL/(min · cm²). Elution at 2 mL/(min · cm²) [0.5 gpm/ft²] was preferable because subsequent tungsten recovery improved with increased tungsten concentration, and elution was still completed within the time required for loading.

HERF Resin Durability

The resistance of HERF granular resin to chemical and physical degradation during prolonged use, an important economic factor, was tested by alternately loading and eluting a 75-mL resin bed. Tungsten sorption, initially 70 pct, decreased to 60 pct after 581 loading and eluting cycles. A thin film of elemental sulfur that collected on the surface of the resin granules during cycling interfered with tungsten sorption. The film, which formed by oxidation of brine sulfides, was loosely adherent, and much of it was removed by washing the resin with a stream of water,

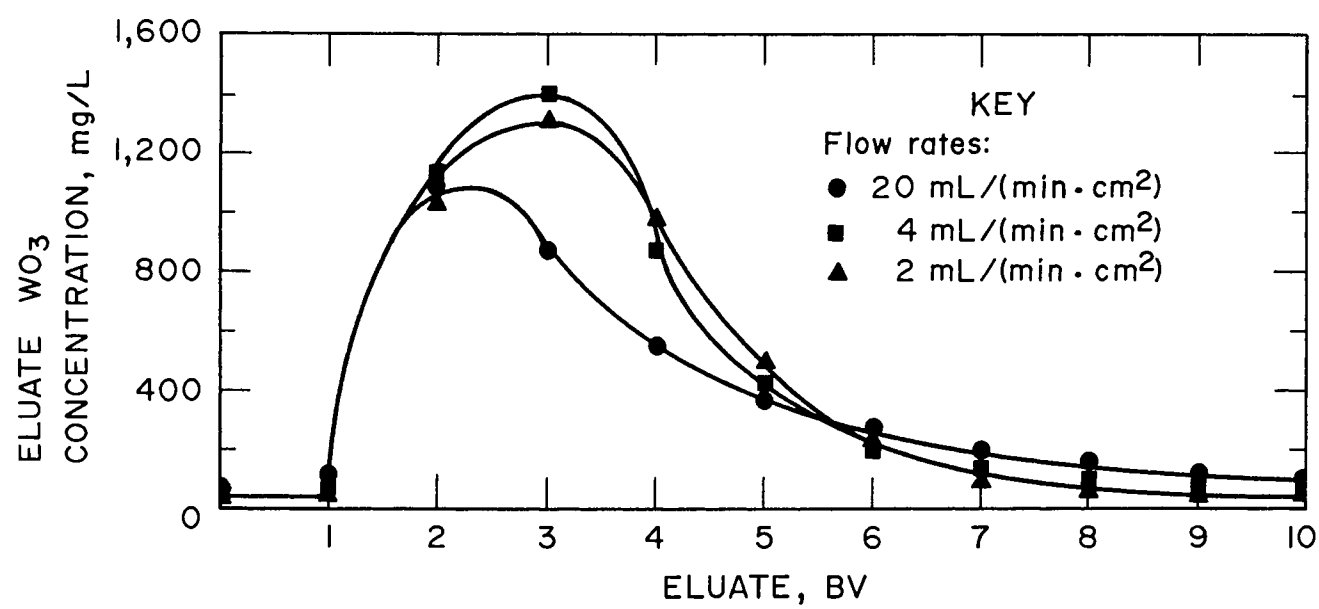

Figure 9.—Tungsten elution from HERF resin using 5-g/L Na_2CO_3 solution.

restoring resin effectiveness. No physical deterioration of the resin was apparent after prolonged cycling. Physical breakdown, caused by resin expansion and contraction during cycling, was not expected to be appreciable because HERF resin undergoes less than a 5-pct change in volume during cycling. The sulfur accumulation problem was not encountered in later testing using subsequent brine samples and QRF beads.

Results of Bench-Scale Research Using HERF Resin Granules

Results from small-scale laboratory testing using HERF granules indicated the following preferred operating conditions:

- Resin particle size 20 to 48 mesh.
- pH 7.5 soda grainer overflow feed.
- Eluant of 5-g/L Na_2CO_3 solution.
- Ambient extraction and elution temperature.
- Flow rate of 20 mL/(min·cm²) [5 gpm/ft²] for loading, and 2 mL/(min·cm²) [0.5 gpm/ft²] for elution.

HERF resin demonstrated durability under these conditions.

BENCH-SCALE RESEARCH USING QRF RESIN BEADS

Continued resin-development investigations produced methods for synthesizing QRF resin beads having improved exchange kinetics and increased tungsten capacity superior to those of HERF granules. Tests using QRF beads were conducted to determine resin loading and feed volume per cycle and to bracket the operating pH range of soda grainer overflow feed. Various elution systems were also tested in an effort to accomplish the following:

- Concentrate tungsten in the eluate because subsequent tungsten product recovery is easier as the tungsten concentration in the eluate increases.
- Minimize eluant water consumption because potable water is scarce and expensive in the desert environment at Searles Lake.
- Determine the suitability of local brackish water for eluant makeup water because brackish water used for chemical plant process water is much more plentiful and less expensive than potable water.
- Selectively desorb impurities from the resin because marketability and value of the tungsten product improve as the impurity levels decrease.

The apparatus used for testing (fig. 10) was scaled up to three 7.6-cm-diam, 91-cm-deep acrylic columns each con-

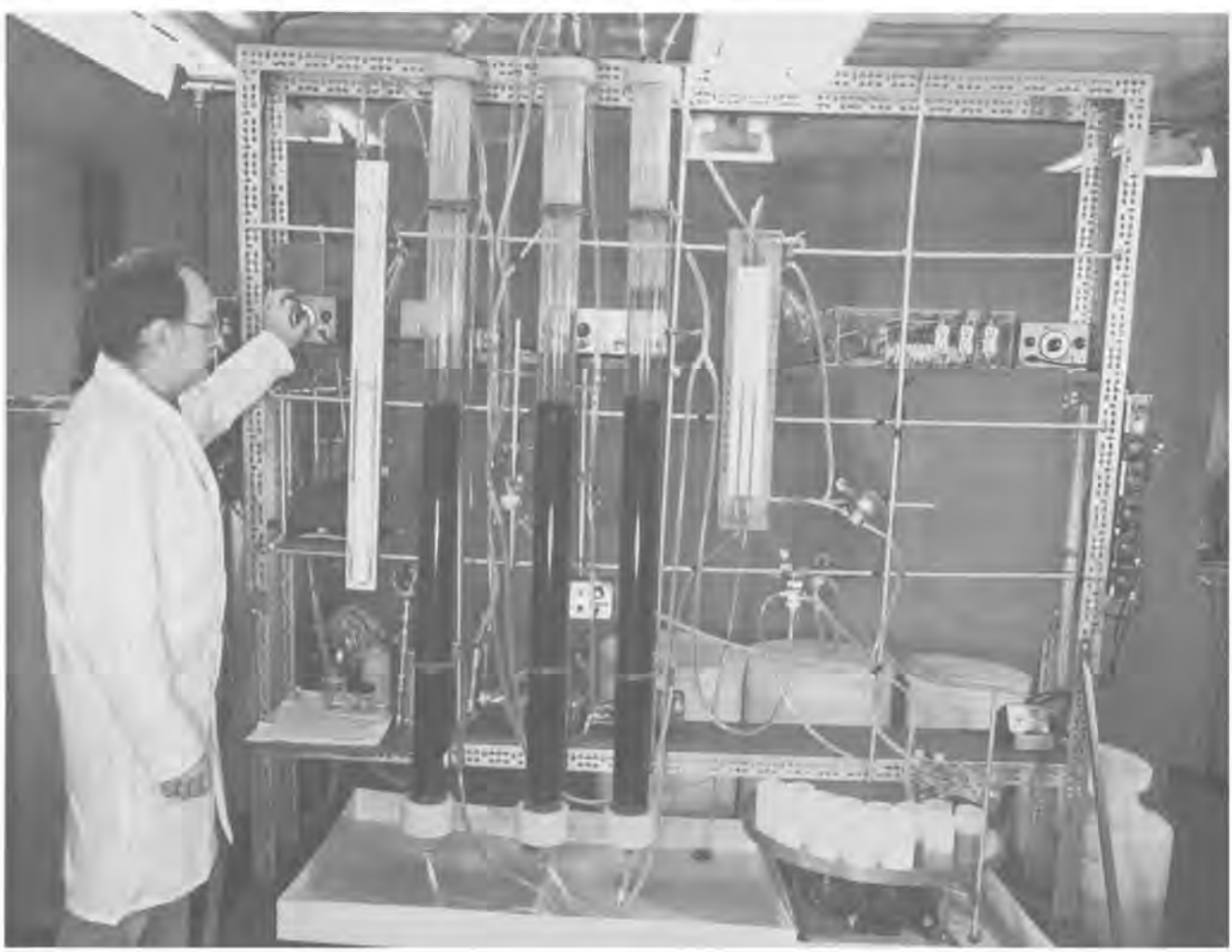

Figure 10.—Bench-scale ion-exchange apparatus used for testing QRF resin beads.

taining 4.2 L of QRF beads, unless otherwise noted. Almost 20,000 L of soda grainer overflow was shipped to the Salt Lake City Research Center for testing. Results were used to determine the parameters for pilot plant testing at Searles Lake.

Effect of Brine pH

To determine the saturation loading of QRF resin as a function of feed volume and pH, tests were conducted at a loading flow rate of 930 mL/min (equivalent to 5 gpm/ft² of column surface area), using 80 to 200 BV of brine at pH 7.5, 7.8, and 8.2. Increasing the brine pH decreased tungsten extraction, as expected from results of earlier testing. The capacity of QRF bead resin decreased from 7.0 to 5.0 to 3.8 g/L WO_3 of wet settled resin as the brine pH increased from pH 7.5 to 7.8 to 8.2, respectively (fig. 11). By comparison, HERF resin granules used in earlier work had a capacity of only 3.5 g/L WO_3 of wet settled resin from pH 7.5 brine. Calculations for QRF resin, based on equilibrium and kinetic data, showed that for 90-pct extraction 104, 74, and 56 BV of feed containing 0.075 g/L WO_3 should be processed per cycle at pH 7.5, 7.8, and 8.2, respectively.

Eluate tungsten concentrations also decreased with increased brine pH. Ninety percent of the eluted tungsten was concentrated to 1.7 and 0.97 g/L WO_3 in 3 BV of eluate as the brine alkalinity increased from pH 7.5 to 8.2. Subsequent laboratory testing used pH 7.5 brine.

Elution as Function of Flow Rate

Lower elution flow rates were tested in an effort to increase tungsten concentration in the eluate and minimize eluant consumption. Results showed no appreciable advantage in lowering the flow rate below 93 mL/min (0.5 gpm/ft²). For example, 90 pct of the eluted tungsten was concentrated in 3.1, 3.0, and 3.2 BV of 5-g/L-Na_2CO_3 eluate as the flow rate was decreased from 93 to 47 to 19 mL/min (0.5, 0.25, and 0.1 gpm/ft²), respectively. The 93-mL/min flow rate is advantageous because the elution cycle is complete before the simultaneous loading cycle is over. This allows scheduling a backwash cycle during elution downtime to break loose accumulated debris without interrupting operations. An elution flow rate of 93 mL/min (0.5 gpm/ft²) was used in additional testing.

Elution as Function of Eluant Type and Temperature

Since potable water is scarce and expensive at Searles Lake, brackish water from Trona, CA, was shipped to the Salt Lake City Research Center to test its usability as eluant makeup water. A typical analysis is shown in table 10. All the loaded tungsten was eluted by 5 BV of 5 g/L Na_2CO_3 in the brackish process water, but only 20 g WO_3 loaded in the subsequent extraction cycle in the 7.6-cm-diam columns. When potable water was used, 30 g WO_3 loaded in the subsequent extraction cycle. Some interfering constituents in the brackish water, possibly silica or an organic compound, blocked one-third of the sites normally available for tungsten sorption, and subsequent tungsten loading decreased by one-third. The use of brackish water for eluant makeup was discontinued in the laboratory because of its adverse effect on tungsten sorption.

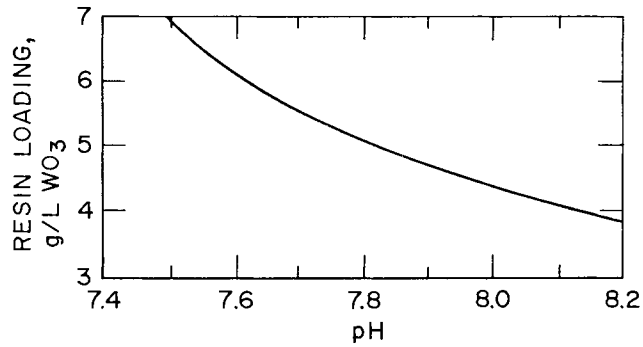

Figure 11.—QRF resin loading as function of pH.

TABLE 10.—Typical analysis of brackish process water from Trona, CA

Constituent	Analysis, g/L
Cl	3.2
Na	2.2
SO_4	.83
HCO_3	.26
K	.1
CO_3	.086
Br	.02
SiO_2	.015
S=	.007
As	.005
B_4O_7	.002
I	.001

Two series of tests were conducted using heated eluants because earlier testing had suggested a trend of increased elution rate with elevated temperature. The purpose of these tests was to decrease eluant consumption, increase tungsten concentration in the eluate, and eliminate the need for the Na_2CO_3 addition. Early testing had demonstrated that as the pH of the brine feed decreased, complete tungsten elution with water became more difficult at ambient temperature (see table 9). A solution of 5 g/L Na_2CO_3 was found effective for complete tungsten elution at 25° C as the brine feed approached pH 7. Eluants tested were a 5-g/L Na_2CO_3 solution, distilled water, and potable water. The following two series of tests were conducted in a single 2.5-cm-diam glass column 91-cm deep containing 467 mL of 20- to 48-mesh QRF resin beads. The resin was loaded with 160 BV of pH 7.5 Westend soda grainer overflow brine containing 0.075 g/L WO_3 at a flow rate of 103 mL/min (5 gpm/ft²). The resin loaded to an average of 6.2 g/L WO_3 of wet-settled resin. Elution was conducted using 3.9 BV of eluant at a flow rate of 10.3 mL/min (0.5 gpm/ft²).

In the first series of tests, increasing the elution temperature for the standard 5-g/L-Na_2CO_3 eluant increased tungsten concentration and decreased eluant consumption (fig. 12). For example, 35, 68, and 84 pct of the tungsten loaded in the previous cycle was desorbed in the second bed volume of eluate at 25°, 50°, and 75° C, respectively, with average tungsten concentrations of 2.1, 4.4, and 5.4 g/L WO_3. The first bed volume of eluate was displaced brine. Complete tungsten elution was achieved in each case using 3.9 BV eluant.

In the second series of tests, the rate of tungsten desorption increased with increased temperature for all three eluants, as shown by the results in table 11. While there was a marked increase in tungsten elution by increasing the temperature from 25° to 50° C, little advantage was gained by a further increase in temperature to 75° C. For example, the percent tungsten desorbed in 3.9 BV increased

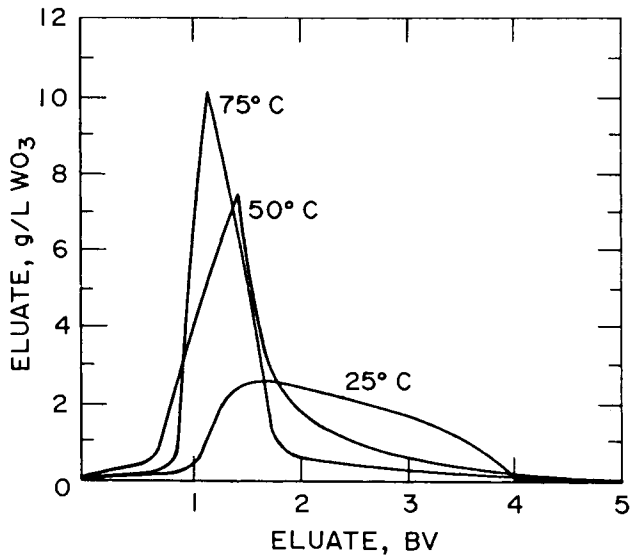

Figure 12.—Tungsten elution from QRF resin at different temperatures using 5-g/L Na_2CO_3 solution at 10.3 mL/min.

from 87 to 92 to 100 pct for 5 g/L Na_2CO_3, from 61 to 94 to 95 pct for distilled water, and from 73 to 86 to 84 pct for potable water at 25°, 50°, and 75° C, respectively.

In an effort to determine what effect elution at elevated temperature would have on the durability of QRF resin, a small 2.5- by 15.3-cm glass column containing 375 mL of QRF resin beads was exposed to elevated temperatures. Distilled water at 60° C was pumped through the column of resin at 10.3 mL/min (0.5 gpm/ft²) for 100 days. Although heating the resin caused it to shrink to 79 pct of its original volume, the 296 mL of heat-treated resin loaded more tungsten than did the 375 mL of fresh resin. This demonstrated that the resin retained its effectiveness, as shown by the data in table 12. Due to the concern regarding the effects of resin shrinkage on continuous operation, heated elution was not tested in the pilot plant at Searles Lake.

Selective Impurity Elution[2]

Two series of preliminary tests were conducted to evaluate a system for selectively removing impurities from the resin prior to tungsten elution in order to increase the marketability and value of the tungsten product. Organics interfere with product recovery and dilute the product grade, and inorganic impurities such as arsenic and phosphorus contaminate the product, reducing its value.

Batches of QRF resin were loaded for selective elution tests by pumping pH 7.5 soda grainer overflow through a series of two 15-mm-diam columns, each containing 48 mL of wet-settled resin at 17 mL/min (2.6 gpm/ft²). The first column was considered loaded after passing 100 BV of solution through the system.

Elution of Inorganics

In the first test series, various solutions were tested to determine the effect of pH values on the elution of inorganic impurities. Loaded resin was removed from the first column, mixed, and a 12-mL sample placed in a 15-mm-diam column, and eluted at a flow rate of 1.7 mL/min (0.26 gpm/ft²). Two bed volumes of eluant were used followed by 8 BV of 5-g/L Na_2CO_3 solution for tungsten elution. All of the inorganic eluate was collected in one-third bed-volume increments for analysis.

The results presented in table 13 show that 2 BV of a combined ammonium chloride and ammonium hydroxide (NH_4Cl-NH_4OH) solution was the most selective eluant for these impurities followed closely by a potassium sulfite (1*M* K_2SO_3) solution. Two bed volumes of the NH_4Cl-NH_4OH solution eluted 86 pct of the arsenic and 96 pct of the phosphorus with less than 1 pct tungsten loss (*31*); 2 BV of 1*M* K_2SO_3 solution eluted 87 pct of the arsenic and 93 pct of the phosphorus with a 3-pct tungsten loss. The remaining tungsten was then completely desorbed with 5 BV of a 5-g/L-Na_2CO_3 solution.

The other solutions resulted in 14 to 46 pct tungsten loss in 2 BV of eluate. Smaller volumes of carbonic acid and benzoic acid were also effective. Using 1.66 BV of carbonic acid solution removed 83 pct of the arsenic and 91 pct of the phosphorus with a 2-pct tungsten loss. Using 1.33 BV of benzoic acid solution removed 76 pct of the arsenic and 88 pct of the phosphorus with less than a 2-pct tungsten loss. Distilled water was not a suitable selective eluant because it eluted 46 pct of the tungsten as well as arsenic and

TABLE 11.—QRF tungsten elution as function of temperature in 3.9 BV of eluant[1]

Temp, °C	Tungsten eluted, pct		
	5 g/L Na_2CO_3	Distilled water	Potable water
25	87	61	73
50	92	94	86
75	100	95	84

[1]Tests were performed in a 2.5-cm-diam, 91-cm-deep bed of QRF resin beads loaded from 160 BV of pH 7.5 brine at 103 mL/min (5 gpm/ft²). Elution was performed at 10.3 mL/min (0.5 gpm/ft²).

TABLE 12.—QRF tungsten sorption before and after heat treatment[1]

	Fresh resin	Treated resin
Tungsten load:		
Weight, g	0.461	0.482
Recovery, pct	82	85
Elution, pct	100	100
Eluate (2d, 3d, and 4th BV):		
WO_3, g/L	1.44	1.49
Pct of total	90	91

[1]Heat tests were performed in a 2.5-cm-diam, 15.3-cm-deep bed of QRF resin beads through which 60° C distilled water was pumped at 10.3 mL/min (0.5 gpm/ft²) for 100 days.

TABLE 13.—Selective elution of inorganic impurities in 2 BV of eluant

Eluant	pH	Elution, pct		
		WO_3	As	P_2O_5
1*M* NH_4Cl + 0.1*N* NH_4OH	8.3	0.9	86	96
Carbonic acid	3.8	14	84	96
Benzoic acid	2.9	35	85	95
1*M* K_2SO_3	10.4	3	87	93
pH 4 buffer	4.0	14	85	89

[2]The authors acknowledge S. R. Borrowman, P. J. McDonough, and R. O. Dannenberg for the primary research in this subsection.

phosphorus in 2 BV; 10 pct of the tungsten was eluted in the first bed volume of distilled water. The pH 4 buffer solution was less selective and had the grave disadvatage of suppressing subsequent tungsten elution using the standard Na_2CO_3 solution. Two bed volumes of pH 4 buffer solution eluted 85 pct of the arsenic and 89 pct of the phosphorus with a 14-pct tungsten loss. These results indicate that using 2 BV of a combined NH_4Cl-NH_4OH or a 1*M* K_2SO_3 solution followed by 5 BV of Na_2CO_3 has the potential for effective separation of the major inorganic impurities from the tungsten. Further testing, including economic evaluation, would be necessary to judge the desirability of the technique.

Elution of Organics

In the second series, conducted as batch tests, water was adjusted to various pH values with acid or base to determine the effect of pH on elution of organic impurities. Twelve milliliters of loaded QRF resin was mixed with 25 mL of distilled water. The pH of the resin-water mixture was adjusted to the desired pH value from 3 to 11 by adding either NaOH or H_2SO_4. After stirring for 10 min, 5-mL samples of solution were withdrawn for analysis of tungsten and determination of chemical oxygen demand (COD). This determination provides a measure of the oxygen equivalent needed to oxidize organic matter that is susceptible to oxidation by hot dichromic acid (*32*). The degree of organic destruction was determined by comparing the initial and final COD.

Results from these experiments show that the tungsten and the organic carbon elute simultaneously. The existence of an organometallic complex is strongly indicated by the elution data, in which the ratio of tungsten-to-carbon in the eluate is constant. A plot of COD versus tungsten (fig. 13) is two straight lines. The slopes of these lines are equal to the weight of oxygen needed to oxidize the organic carbon per unit weight of WO_3. The COD-to-WO_3 ratio for the main organometallic complex remains constant at 12 g COD per gram of WO_3 throughout the range of the test, indicating that the organometallic complex is a discreet compound. A second organometallic complex was eluted in the same manner with a slope of 6. These data demonstrate that separation of the organics from the tungsten by selective elution is not possible by pH control alone.

Durability of QRF Bead Resin

The durability of QRF bead resin was tested under various conditions in the laboratory; the resin held up well, physically and chemically, during storage, and under long-term exposure to pressure.

After extracting tungsten from 16,000 L of Searles Lake brines in three 7.6-cm-diam columns containing 20- to 48-mesh QRF resin beads, the QRF beads exhibited essentially no physical or chemical degradation. Less than 2-pct breakage and 2-pct apparent loss had occurred. Up to 2-pct breakage can occur during resin transfer and screening. Microscopic analysis revealed that 2 pct minus 48-mesh material resulted from broken hollow resin beads produced during resin synthesis, not from solid resin beads. The size distribution of QRF resin, originally 87 pct 20 to 35 mesh and 13 pct 35 to 48 mesh, changed little during testing; it was 86 pct 20- to 35-mesh, 12 pct 35- to 48-mesh, and 2 pct minus 48-mesh material at the completion of the series (see table 14). In comparison, 100-mL samples of 20- to 48-mesh

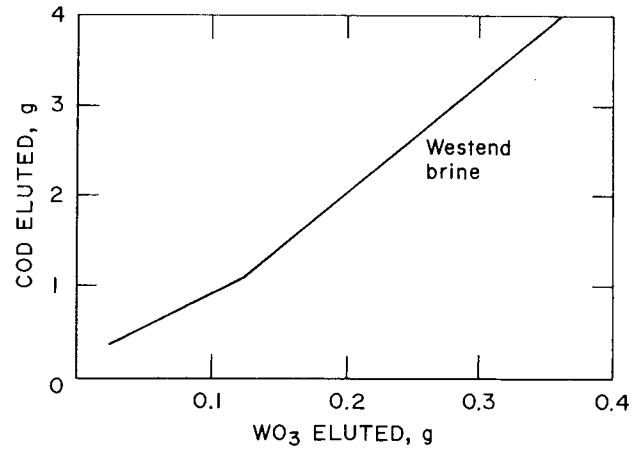

Figure 13.—Elution of organic material and tungsten from QRF resin loaded from soda grainer overflow.

TABLE 14.—QRF resin size distribution before and after 6 months of use and storage, percent

Resin	−20, +35 mesh	−35, +48 mesh	−48 mesh
Before test series	87	13	0
After test series	86	12	2
Stored in distilled water	84	16	1
Stored in brine	85	14	1
Stored in eluant	85	15	1

unused QRF beads stored in distilled water, soda grainer overflow brine, or eluant comprised of 5 g/L Na_2CO_3 for 6 months (since the beginning of the test series) contained 0.9, 0.7, and 0.6 pct minus 48-mesh beads, respectively, when rescreened at the completion of the test series, half of which resulted from hollow resin beads that broke during rescreening. Both fresh and used resin loaded essentially the same amount of tungsten in comparative tests, indicating no chemical degradation.

Tests were conducted to determine the effect of cyclic column pressurization on QRF resin. A laboratory device was built for determining QRF resin breakdown after prolonged cycling between atmospheric pressure and 60 psi, the range of pressure encountered during field testing. Wet resin was cycled between low and high pressure every 10 min, or 144 times daily, in the laboratory. QRF resin suffered only 18 pct attrition after 9,255 cycles of alternating between 60 psi and atmospheric pressure. That is, 18 pct of the original 20- to 48-mesh resin beads passed through a 48-mesh screen after the cyclic treatment. These results extrapolate to a projected lifetime of about 6.5 yr of plant operation using 4-h cycles. Results in table 15 show that the remaining 20- to 48-mesh QRF resin extracted just as much as tungsten as did fresh resin.

Results of Bench-Scale Research Using QRF Bead Resin

- QRF bead resin demonstrated superior exchange kinetics and tungsten capacity over HERF granular resin; QRF was selected for use in scaled-up process research.

TABLE 15.—QRF tungsten sorption before and after pressure treatment[1]

	Fresh resin	Treated resin
Tungsten load:		
Weight ..... g	0.458	0.458
Recovery ..... pct	83	83
Elution ..... pct	100	100
Eluate (2d, 3d, and 4th BV):		
WO_3 ..... g/L	1.51	1.36
Pct of total	92	90

[1]Pressure tests were conducted by cycling resin between atmospheric pressure and 60 psi each 10 min for 9,255 cycles in the laboratory.

- A feed rate of 930 mL/min (5 gpm/ft²) and feed volumes between 56 and 104 BV of brine were selected for larger scale tests from tests in 7.6-cm-diam, 91-cm-deep columns.
- Elution conditions of 5 BV of 5 g/L Na_2CO_3 solution in potable water at ambient temperature and at a flow rate of 93 mL/min (0.5 gpm/ft²) were selected from tests in 7.6-cm-diam, 91-cm-deep columns.
- A promising system for selectively desorbing arsenic, and phosphate impurities from loaded resin with ammonium salt solutions was devised.
- QRF bead resin demonstrated good physical and chemical durability in the laboratory under extended loading-elution testing, under storage, and under accelerated long-term exposure to heat and pressure.

PILOT-SCALE RESEARCH TO OBTAIN ENGINEERING DATA

Tests needed to be conducted at Searles Lake to obtain the engineering data necessary for large-scale process design. A cooperative research plan was devised by the Bureau and Kerr-McGee Chemical Corp. with the following objectives:

- Confirm previous laboratory results using fresh brine and local water supplies.
- Produce sufficient quantities of tungsten-rich solutions for product recovery.
- Provide engineering data.
- Determine resin life under actual plant conditions.
- Demonstrate the technology to industry personnel.

This section presents performance data obtained from tests conducted at the Westend plant of the Kerr-McGee Chemical Corp. starting in July 1979.

The primary ion-exchange system (fig. 14) consisted of three 10-ft-tall, 11.25-in-ID acrylic columns plus associated piping. The transparent columns proved advantageous for observing and diagnosing operating problems. Nearly 20 ft³ of QRF resin beads were synthesized by the Bureau to provide 20- to 48-mesh beads for charging primary and secondary ion-exchange systems. Essential piping details (fig. 15) enabled flexibility in column operations. Plastic piping and valves were generally used to avoid corrosion. Feed and eluant flows were regulated with electronic flow-indicator controllers.

Equipment arrangement for feeding and eluting the primary system is shown in figure 16. Spent brine and eluate were collected in receiver tanks and transferred intermittently when signaled by receiver-tank-level sensors.

Test Conditions and Results

Baseline Test Conditions

Initially, 1,007 gal, equal to 65 single-column bed volumes, of pH 8.2 brine containing an average of 0.080 g/L WO_3 were treated per cycle. Flow rate of the 90° F brine was 3.5 gpm (5 gpm/ft² of column cross-sectional area) producing a cycle time of 4.8 h. Laboratory tests had predicted that, under these conditions, resin in the lead column would be saturated with tungsten, and influent and effluent tungsten concentrations would be equal. Tungsten was eluted using 5 BV of 5 g/L Na_2CO_3 in potable water. Flow rate of the 90° F eluant was 0.5 gpm/ft². The relatively low elution flow rate was preferred because laboratory testing showed that more complete elution and higher eluate tungsten concentration were achieved at this rate than at higher flow rates. Elution was accomplished in 3.75 h, well within the 4.8-h loading time. At least six load-elution cycles were completed per test to ensure that steady-state conditions were reached.

Only 3 of the 5 BV of eluate were used for product recovery. The first bed volume was displaced brine, which was discarded. Tungsten-rich bed volumes 2, 3, and 4 were used for product recovery; the fifth bed volume, a very weak tungsten solution, was recycled. In commercial practice, the first bed volume would be added to the primary ion-exchange effluent, and the last bed volume would be recycled with fresh eluant to conserve water.

Results of Baseline Tests

The most important result achieved during the initial testing phase was that of demonstrating successful operation despite changes in brine quality caused by varying degrees of carbonation and seasonal brine changes. The more significant test results are summarized in table 16.

Overall tungsten extraction averaged 84 pct during initial pilot-scale testing at Searles Lake, with 92 pct extraction, 96 pct elution, 92 pct of the eluted tungsten saved in bed volumes 2 through 4 of the eluate, and 4 pct recycled. Extraction profiles of lead- and scavenger-loading columns (fig. 17) show that resin in the lead column was not saturated with tungsten after 65 BV of brine had passed through the column during each cycle, as predicted from laboratory results. Resin saturation in the lead column was a targeted condition because high tungsten loading maximized eluate tungsten concentration. Resin loading in the lead column averaged 4.4 g/L WO_3 at the end of each cycle; a higher loading could have been achieved by increasing brine throughput accompanied by a consequent reduction in extraction efficiency. However, better performance was achieved during field testing using fresh brine than had been predicted from results of laboratory testing, which had used brine shipped to the Salt Lake City Research Center. Laboratory results indicated a slightly lower extraction efficiency from a smaller volume of feed brine; 90-pct extraction from 56 BV of pH 8.2 brine.

The pressure drops across the lead and scavenger columns were typically 15 and 10 psi, respectively, at a flow rate of 5 gpm/ft². These drops occurred during periods when brine was not abnormally turbid with suspended soda crystals. The greater drop in the lead column resulted from the filtering action in that column. Operating pressures of nearly 60 psi were required to maintain brine flow during periods of high brine turbidity, compared with 10 psi total

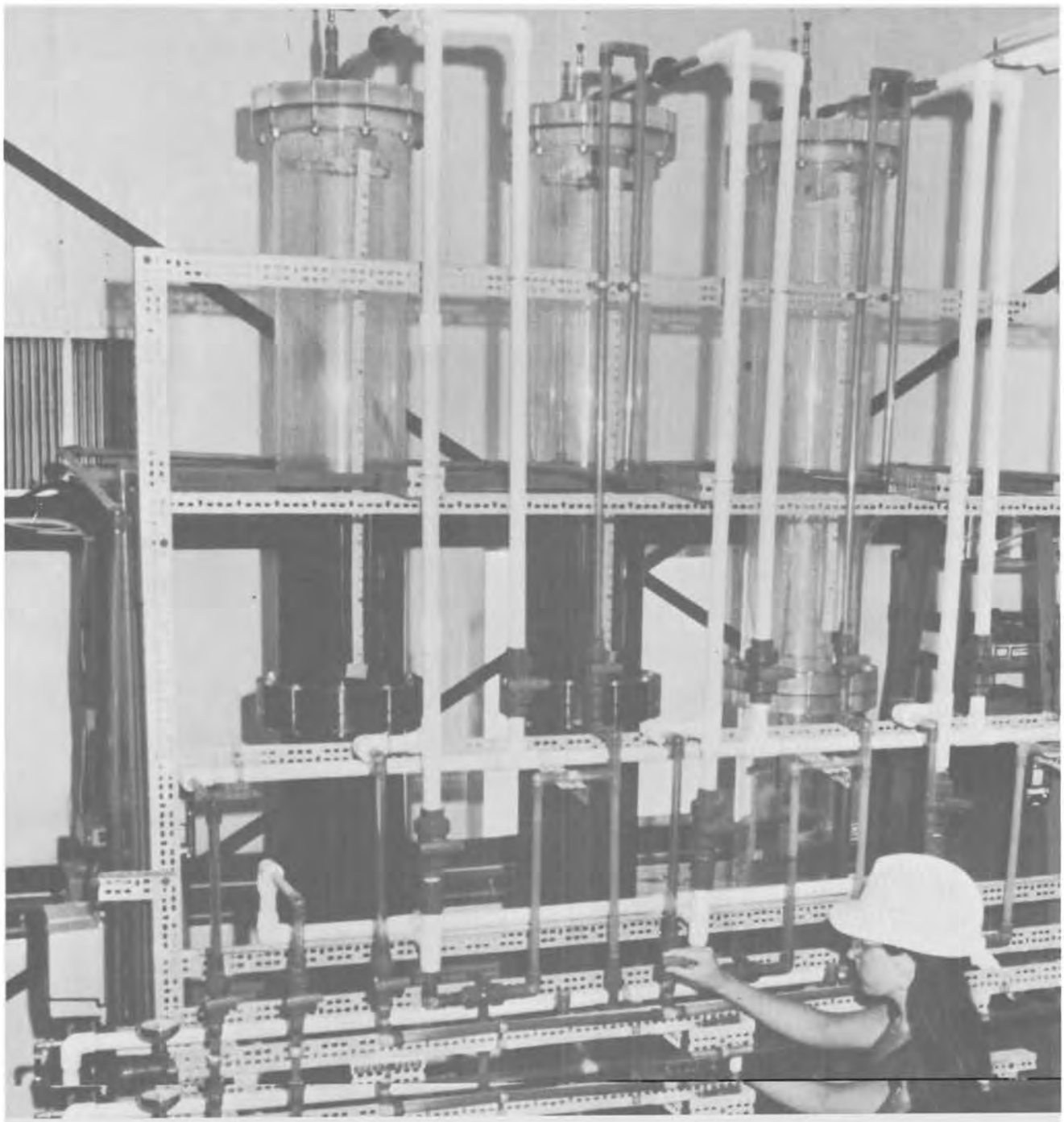

Figure 14.—Primary ion-exchange columns in pilot plant.

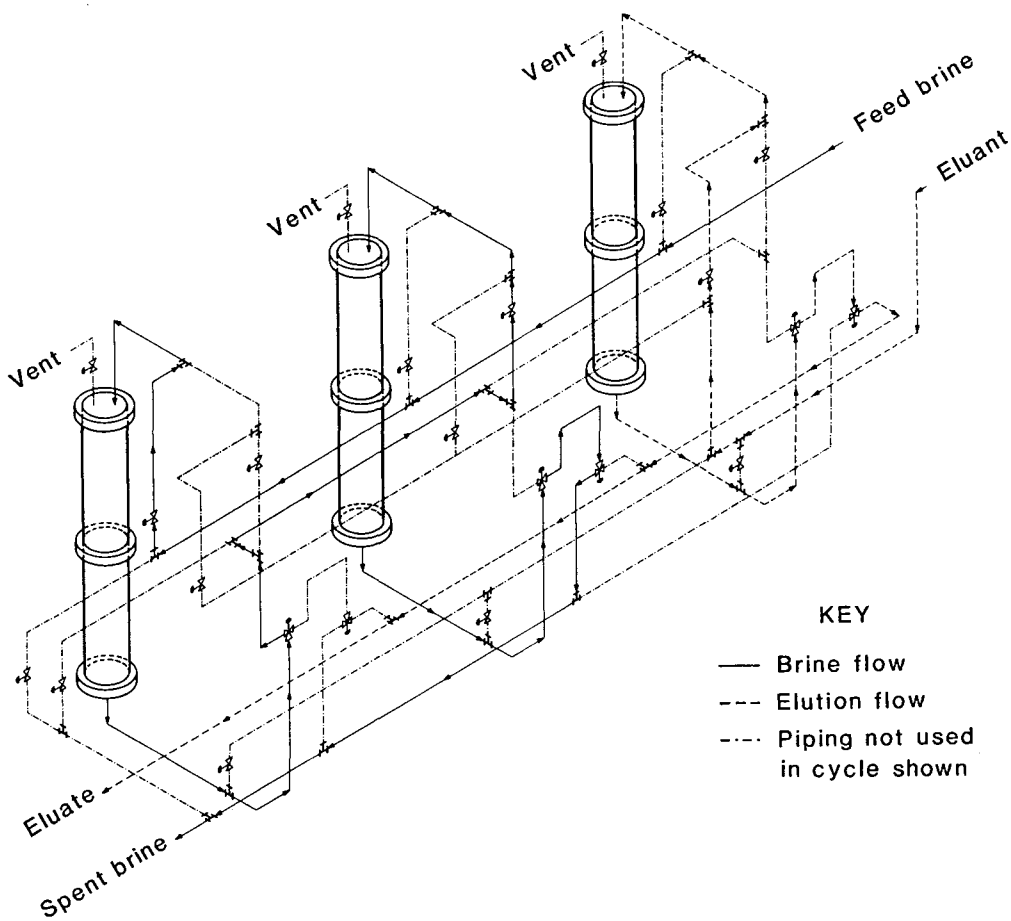

Figure 15.—Essential piping details for three-column loading and elution in pilot plant.

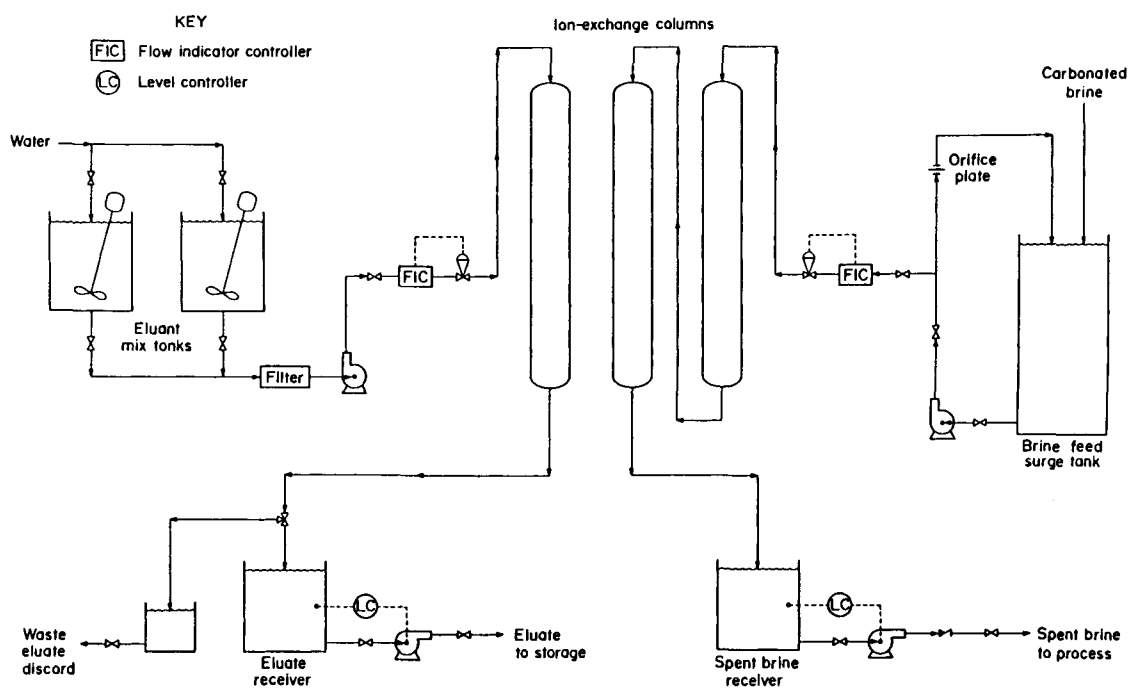

Figure 16.—Primary system support equipment at Searles Lake.

TABLE 16.—Averaged primary ion-exchange test results from pilot plant[1]

	Baseline	High feed rate	Low pH
pH	8.2	8.2	7.6
Bed volumes	65	65	110
Total flow, gal	1,007	1,007	1,704
Loading:			
Flow rate, gpm/ft²	5	10	5
Flow rate, gpm	3.5	7	3.5
Extraction, pct	92	55	90
Elution, pct	96	97	96

[1]Tests were performed in 11.25-in-ID, 36-in-deep QRF resin beds.

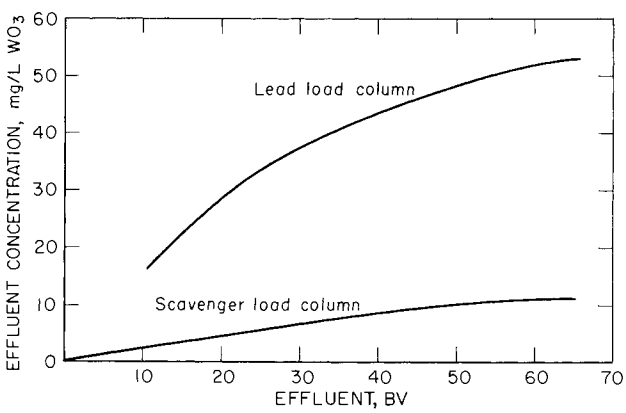

Figure 17.—Baseline two-column tungsten-extraction curves from pilot plant.

measured across both columns in the laboratory, because suspended solids reduced resin bed void volume.

More than 95 pct of the sorbed tungsten was eluted using 5 g/L Na_2CO_3 in potable water; 92 pct of the eluted tungsten was contained in eluate bed volumes 2, 3, and 4 that, when combined, contained 1.3 g/L WO_3. These results agreed well with those obtained in the laboratory. The elution profile (fig. 18) indicates a peak concentration of 2.8 g/L WO_3. The elution pressure differential was 1 psi. Eluate typically contained, in grams per liter, 16 Na, 9.8 $CO_3^=$, 3.9 Cl, 3.0 $SO_4^=$, 2.7 K, 2.1 HCO_3^-, 1.4 Br, 1.3 WO_3, 0.2 I, 0.06 SiO_2, 0.03 As, 0.02 P_2O_5, and 0.02 $S^=$. Concentrations of trace elements were, in milligrams per liter, 10 Fe, 4 Mn, 2 Zn, 0.8 Al, 0.5 Cu, 0.5 Mo, 0.1 Ni, 0.03 V, and 0.02 Sc.

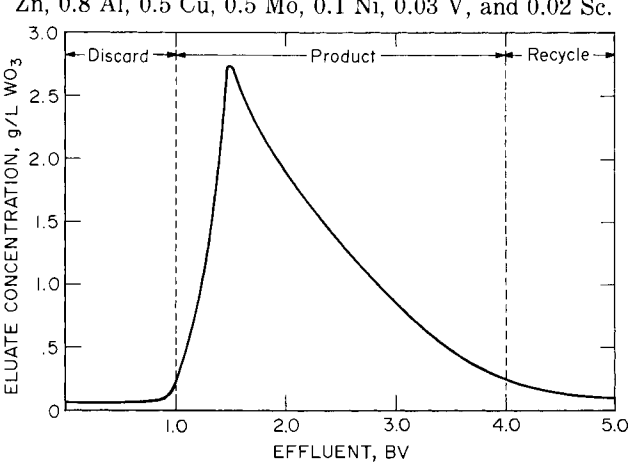

Figure 18.—Baseline tungsten-elution curve from pilot plant.

Effect of Brine Alkalinity

As expected from laboratory results, markedly improved tungsten sorption was achieved when pH 8.2 brine was acidified to pH 7.6, simulating a period of increased carbonation. Ninety percent of the tungsten was extracted from 110 BV of brine at pH 7.6, whereas 92 pct was extracted from 65 BV at pH 8.2. These results compared favorably with laboratory results in which 90 pct of the tungsten was extracted from 104 BV of pH 7.5 brine, and 90 pct was extracted from 56 BV of pH 8.2 brine. The advantage gained by effectively treating more brine per cycle was particularly evident when resin loading and elution results were compared. Resin loaded to 7.1 g/L WO_3 at pH 7.6, rather than 4.4 g/L WO_3 at pH 8.2. This enabled production of a higher grade eluate; eluate contained 2.4 g/L WO_3 after treating 110 BV of pH 7.6 brine, compared with only 1.3 g/L WO_3 after treating 65 BV of pH 8.2 brine. Thus, decreased brine alkalinity increased resin capacity, which enabled the processing of more brine per cycle, and enhanced tungsten concentration in the primary eluate, a factor of economic importance.

Effect of Brine Flow Rate

Doubling the feed rate of pH 8.2 brine from 5 to 10 gpm/ft² decreased tungsten extraction from 92 pct to an average of 55 pct per 65 BV. Lead-column loading profiles (fig. 19) show the increase in unextracted tungsten when the brine feed rate was doubled.

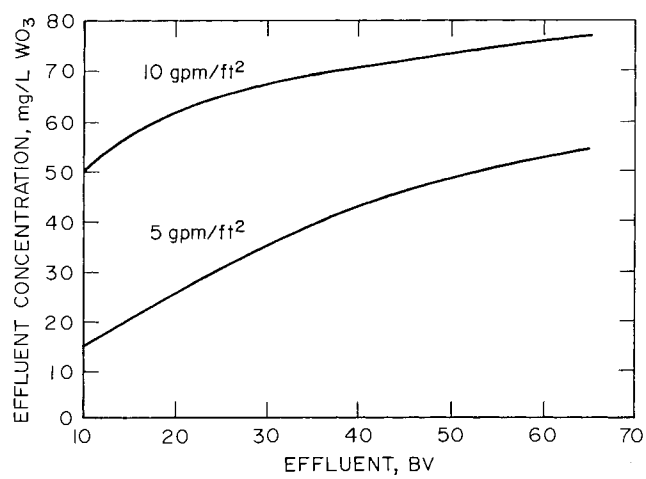

Figure 19.—Single-stage tungsten extraction versus feed rate from pilot plant.

Effect of Eluant Water Quality

Potable process water, which contains 500 ppm dissolved solids, is scarce and expensive in the Searles Lake desert area compared with brackish process water, which contains 7,000 ppm dissolved solids. Tungsten elution using brackish makeup water would be economically attractive, but proved ineffective during on-site testing. Although a 5-g/L solution of Na_2CO_3 in brackish water was an effective eluant during the first cycle, tungsten loading in the following cycle decreased by one-third. This confirmed laboratory testing using brackish water that had been shipped to the Salt Lake City Research Center for testing. The reason for this diminished subsequent loading was not determined;

however, it appeared that a brackish water constituent, possibly silica or an organic compound, blocked resin sites normally available for tungsten sorption. There was no improvement when the eluting temperature was increased from 90° to 130° F; therefore, potable water was routinely used for tungsten elution to maximize tungsten recovery.

Effect of Eluant Flow Rate

Eluting at 0.5 gpm/ft² was more effective than eluting at higher flow rates of either 1.0 or 2.0 gpm/ft², confirming laboratory results. Tungsten elution using 5 BV of a 5-g/L Na_2CO_3 solution dropped from 95 to 77 pct when the flow rate increased from 0.5 to 2 gpm/ft².

Operating Difficulties

Startup was troublesome because of two unexpected conditions: the brine was turbid with suspended soda crystals, and brine pH (8.7) was much higher than expected. Most laboratory testing had been performed with clear, pH 7.5 brine. The suspended solids blinded the resin beds, and tungsten loading at pH 8.7 was much lower than at pH 7.5. It was discovered that brine characteristics changed markedly from day to day and season to season. Startup was plagued with frequent shutdowns to backwash the resin in order to dislodge accumulated solids and prevent excessive pressure buildup within the columns. These problems were alleviated during a period of increased carbonation when brine pH dropped to 8.2 and clarity improved. Brine variability was experienced throughout the test period.

Other problems not encountered in the laboratory were caused by a variety of foreign materials in the column feed plus occasional algae growths within the columns. Inclusions of trash and oil were removed by thorough resin backwashing. Algae blooms were treated by dosing the feed with formaldehyde.

Resin Stability

The equipment was disassembled after field testing and the resin was returned to the Salt Lake City Research Center to measure degradation that occurred during pilot-scale operations at Searles Lake. Wet-screening tests showed no significant evidence of resin breakage. Some loss of sorptive capacity was detected in laboratory tests comparing equal volumes of used and fresh resin. Used resin sorbed 6 pct less tungsten from pH 7.5 brine and 10 pct less tungsten from pH 8.2 brine than did fresh resin. This apparent loss, however, is not alarming and may be related to the small progressive swelling of gel-type resin beads that frequently occurs during prolonged usage. No loss of resin capacity was noticed during field testing.

Fresh and used resins were ashed at 932° F and the solids were analyzed spectrographically to determine accumulation of elements. Analyses in table 17 show an increase in some elements.

TABLE 17.—Spectrographic analysis of pilot plant QRF resins ashed at 500° C, percent

Element	Resin sample		Element	Resin sample	
	Fresh	Cycled		Fresh	Cycled
Al	1	0.9	Mo	0.01	0.15
As	<.01	.3	Na	1	>30
B	.03	.9	Si	.03	.3
Ca	>10	.3	Ti	.01	3
Cr	<.001	.09	V	.02	.9
Fe	.03	.09	W	<.01	6
Mg	>10	2.9	Zn	.3	.9
Mn	.01	.09	Zr	<.003	.09

Results of Pilot-Scale Research

- Research showed that the basic primary ion-exchange technology established by the laboratory research performed satisfactorily under conditions encountered at Searles Lake. Over 500,000 gal of brine containing 0.080 g/L WO_3 was treated and 84 pct of the tungsten was recovered in 15,000 gal of primary eluate containing an average of 1.3 g/L WO_3.
- Primary tungsten extraction during baseline testing averaged 92 pct when 65 BV of pH 8.2 brine were treated in each cycle at a flow rate of 5 gpm/ft² of column cross-sectional area. The average resin loading was 4.4 g/L WO_3. Of the sorbed tungsten, 96 pct was eluted at 0.5 gpm/ft², using 5 BV of 5 g/L Na_2CO_3 dissolved in potable water. Ninety-two percent of the tungsten reported in bed volumes 2, 3, and 4 at an average grade of 1.3 g/L WO_3.
- Reducing brine alkalinity from pH 8.2 to 7.6, simulating a period of increased carbonation, enabled extraction of 90 pct of the tungsten from 110 BV of feed per cycle. Average resin loading increased to 7.1 g/L WO_3. Good tungsten extraction from a larger brine volume resulted in raising the eluate grade from 1.3 to 2.4 g/L WO_3.
- Potable, rather than brackish, process water was preferred for resin elution because use of brackish water interfered with tungsten extraction in subsequent loading cycles.
- No serious resin degradation was apparent.

SUMMARY OF PRIMARY ION-EXCHANGE RESEARCH

- Preferred operating conditions were established using HERF granular resin in small-scale laboratory tests; HERF resin demonstrated durability under these conditions.
- QRF bead resin demonstrated durability as well as superior exchange kinetics and tungsten capacity over HERF granular resin in small-scale laboratory tests; QRF resin was selected for use in scaled-up process research.
- Basic primary ion-exchange technology established by laboratory research performed satisfactorily in a pilot plant under conditions encountered at Searles Lake.

CHAPTER 5.—TUNGSTEN CONCENTRATION BY SECONDARY ION-EXCHANGE PROCESS

By P. B. Altringer, T. H. Jeffers, S. R. Borrowman,[1] and P. T. Brooks

Although tungsten was concentrated nearly 15-fold in the primary circuit, the primary eluate was too dilute for direct precipitation of either synthetic scheelite or tungstic acid products. Primary eluate typically analyzed, in grams per liter, 16 Na, 9.8 $CO_3^=$, 3.9 Cl, 3.0 $SO_4^=$, 2.7 K, 2.1 HCO_3^-, 1.4 B_4O_7, 1.4 Br, 1.3 WO_3, 0.2 I, 0.06 SiO_2, 0.03 As, 0.02 P_2O_5, and 0.02 $S^=$. Concentrations of trace elements were, in milligrams per liter, 10 Fe, 4 Mn, 2 Zn, 0.8 Al, 0.5 Cu, 0.5 Mo, 0.1 Ni, 0.03 V, and 0.02 Sc. Eluate also contained nearly 1 g/L of organic carbon believed to be in the form of humates. Humates are brown, poorly defined polymeric compounds found in soils and peat. They are soluble in bases but insoluble in mineral acids. Humates are natural stream pollutants that accumulated, like tungsten, in the alkaline lake over many thousands of years.

Three techniques were investigated for concentrating tungsten from acidified primary eluate: solvent extraction, coprecipitation with ferric hydroxide [$Fe(OH)_3$], and ion exchange. Only the last method was proven effective in laboratory tests and therefore was used in field testing.

BENCH-SCALE PROCESS RESEARCH

Resin Selection and Loading pH

While primary ion-exchange research was constrained by the requirement that brine characteristics remain essentially unchanged for tungsten recovery, no such constraints applied to the concentration step. The relatively small volume of primary eluate involved and its isolation from the rest of the brine-treatment process at the operating facility permitted a relatively free choice of recovery techniques.

Resin affinity for tungsten was greatly enhanced by acidifying primary eluate from pH 8.9 to 2.8. Although increased acidity improved tungsten capacity even further, excessive tungsten precipitation occurred. Several commercially available ion-exchange resins sorbed tungsten from acidic solutions; however, QRF resin proved to be the most effective in comparative batch shaker tests. Capacities were determined using pH 2.8 eluate; loading results for QRF and Rohm and Haas resins IRA-93, XE-315, IRA-911, and IRA-400 are shown in table 18. Because of its superior performance, QRF resin was selected for tungsten concentration from primary eluate.

Further batch testing with QRF resin amplified the initial findings relating resin capacity to feed pH and tungsten concentration. These relationships are shown in figure 20. For example, QRF resin loading increased from 54 to 78 g/L WO_3 as the tungsten concentration was increased from 1.0 to 9.8 g/L WO_3 in a pH 3.5 solution. When the pH was decreased from 9.8 to 7.5 to 3.5 to 2.8, resin loading increased from 5.6 to 7.0 to 54.0 to 122 g/L WO_3 from solutions containing approximately 1.0 g/L WO_3. Tests were conducted by moderately agitating 10 mL of QRF resin in 1-L sodium tungstate solutions containing approximately 0.1, 1.0, and 10.0 g/L WO_3 for 24 h. Because of the high 122-g/L WO_3 loading, pH 2.8 was selected for loading; tungstic acid precipitation became a problem at lower pH levels.

[1]Research chemist, Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT (retired).

TABLE 18.—Resin-loading capacities from pH 2.8 primary eluate

Resin	Capacity,[1] g WO_3/L
QRF	122
IRA-93	78
XE-315	53
IRA-911	37
IRA-400	0

[1]Grams WO_3 per liter of wet-settled resin.

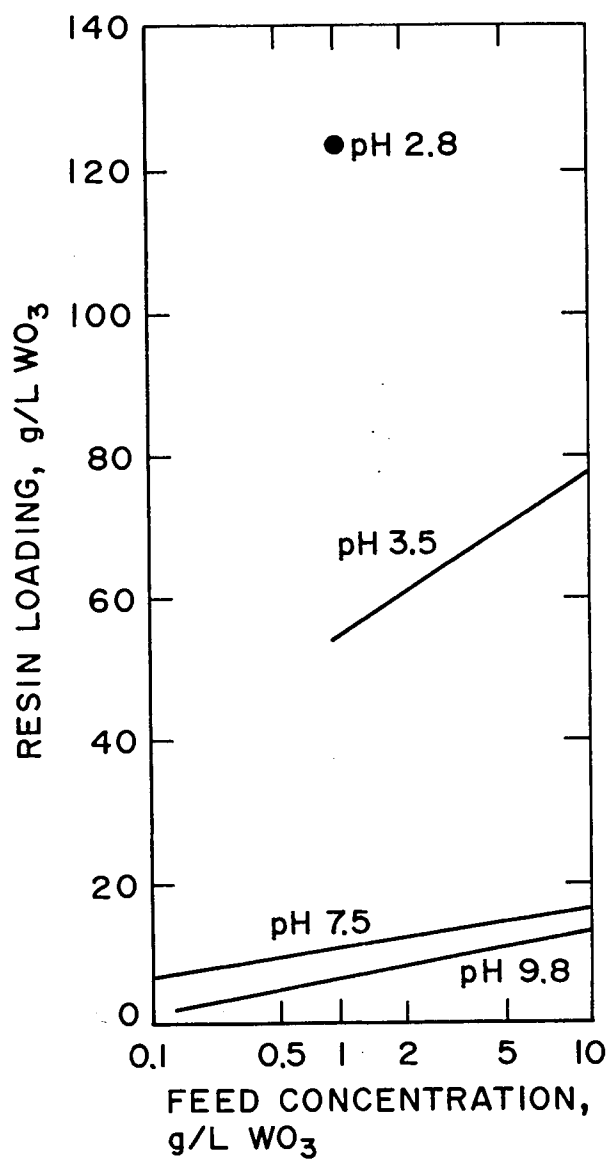

Figure 20.—QRF resin capacity as function of tungsten concentration and pH.

Feed Preparation

Primary eluate, used as feed to the secondary system, was initially adjusted with H_2SO_4 from pH 8.9 to 2.8 using 4.6 g H_2SO_4 per liter of eluate at room temperature to enable high tungsten loading. However, a significant amount of the tungsten precipitated as a mixed organic-tungsten solid. For example, when a 100-L batch of primary eluate was acidified to pH 2.8 with H_2SO_4 and settled for 2 h, 27.0 g of precipitate formed that contained 16 pct of the tungsten.

Efforts to eliminate precipitate formation by using nitric acid (HNO_3) or hydrochloric acid (HCl) failed as did raising the temperature from 20° to 60° C. Although acidification at 60° C was advantageous because the tungsten contained in the precipitate dropped to 7 pct, there was less than 10-pct variation in the amount of precipitate formed at each temperature.

Of the numerous other methods tested to eliminate the precipitate, two alternative methods proved effective: chlorination and contact with activated carbon. Chlorination destroyed the dissolved organic matter and prevented precipitation; but operational requirements precluded its use in the pilot plant at Searles Lake. Treating the primary eluate with activated carbon successfully prevented precipitate formation, but costs for the level of carbon addition necessary were prohibitive.

The precipitate problem was solved by settling, decanting, and using the clarified solution as feed to the secondary ion-exchange unit. The settled precipitate dissolved as the pH reached 4.8 during the addition of the next batch of pH 8.9 primary eluate prior to acidification. This enabled the tungsten to build up to a steady-state concentration in the feed and eliminated any tungsten loss due to precipitation.

Heating the primary eluate also had the advantage of reducing the concentration of CO_2 in solution. Without heating, sufficient CO_2 was released during the loading cycle in the secondary unit to cause displacement of solution from the column. Bubbles formed within the resin beds, causing solution channeling. Results showed that complete degassing was achieved by heating the eluate to 60° C for 5 min.

The feed preparation procedure used in subsequent testing consisted of acidifying the primary eluate to pH 2.8, heating to 60° C for 5 min, cooling to 35° C, settling for 3 h, and decanting the clarified solution. Remaining solids were dissolved in a subsequent batch of primary eluate prior to acidification.

Eluant Selection

Solutions of NH_4OH and Na_2CO_3 proved effective eluants in the secondary ion-exchange system, while Na_2SO_4, NaCl, and NaOH were ineffective. A 2*N* NH_4OH eluant recovered greater than 99 pct of the tungsten, 2*N* Na_2CO_3 97 pct, pH 11.5 2*N* Na_2SO_4 4 pct, pH 11.5 2*N* NaCl 3 pct, pH 11.5 NaOH 6 pct, and a combination of 1 BV of pH 11.5 2*N* NaCl followed by 4 BV of pH 10.9 0.1*N* NaCl only 3 pct. The added advantage of NH_4OH was that it potentially facilitated direct production of ammonium paratungstate (APT), while Na_2CO_3 had the added advantages of being immediately available at the facility and compatible with subsequent industrial tungsten recovery circuits. Multistage split-elution techniques were developed based on recycling of eluate fractions from the previous elution; these techniques maximized tungsten concentration.

Comparative elution tests were conducted using a column containing 1 L of QRF resin loaded to 120 g/L WO_3. The multistage split-elution procedure used in these tests consisted of adding the following solutions in order:

- 1 BV of distilled water acidified to pH 2.6 with H_2SO_4 to displace the remaining feed.
- 5 BV of eluant to desorb the tungsten.
- 0.5 BV of 0.3*N* H_2SO_4 to condition the resin for the next cycle.

The eluate produced was distributed as follows:

- BV 1, displaced feed, was recycled to feed.
- BV 2, containing 20 g/L WO_3, was sent to eluant makeup.
- BV 3, containing 80 g/L WO_3, was saved as product.
- BV 4 through BV 6.5, containing 20 g/L WO_3, were recycled to eluant makeup.

Although the 2*N* Na_2CO_3 eluant effectively removed tungsten from the resin, operating difficulties occurred, owing to CO_2 evolution in the column, which caused pressure buildup and solution channeling. An innovative elution system was developed that took advantage of the gas formation. The wash water was drained by forcing air into the top of the column, and 1 BV of eluant was introduced into the bottom of the column and pumped up through the resin bed. The CO_2 released during the upward elution procedure enhanced the tungsten transfer by partially fluidizing the resin bed and increasing the contact between sorbed tungstate ions and aqueous eluant. This first bed volume of eluant was retained in the column for 1 h, after which the elution proceeded downflow.

Flow Rate Determination

In order to establish the most effective flow rates for extraction and elution in the secondary ion-exchange system, a series of tests was conducted using the preferred eluants (2*N* NH_4OH or 2*N* Na_2CO_3). A sequential loading and elution procedure was used with three 3.8-cm-diam columns at 30-cm depths, each containing 350 mL of QRF resin. To determine optimum flow rate for loading, primary eluate was acidified to pH 2.8, and a 47-L volume of clarified eluate containing 1.2 g/L WO_3 was fed to the column.

The preferred loading flow rate was determined to be 84 mL/min (1.8 gpm/ft^2), which extracted 96 pct of the tungsten. Extraction did not improve when the flow rate was reduced to 60 mL/min (1.3 gpm/ft^2), and dropped to 80 pct when the flow rate was increased to 98 mL/min (2.1 gpm/ft^2). At 84 mL/min, the resin loaded to 140 g/L WO_3.

The preferred elution flow rate was determined to be 8.4 mL/min (0.18 gpm/ft^2) using the procedure previously described. Elution with NH_4OH was more effective than with Na_2CO_3, as shown by the results in table 19. Tungsten elution using NH_4OH was 95 to 99 pct complete at 5.6 to 8.4

TABLE 19.—Comparative tungsten elution as function of flow rates in secondary ion-exchange system

Eluant	Elution rate, gpm/ft$_2$	Elution, pct
NH_4OH	0.12	95
	.18	99
	.24	62
Na_2CO_3	.12	92
Do[1]	.18	90
Do[2]	.18	90

[1]Eluant retained in column 1 h prior to withdrawal.
[2]Eluant retained in column 2 h prior to withdrawal.

mL/min, while it was only 90 to 92 pct complete using Na_2CO_3. The secondary eluate product contained 90 g/L WO_3 when NH_4OH was used.

Further testing was performed in the laboratory to determine the most effective flow rates for the 91-cm (36-in) bed depth that would be used in field testing. Laboratory testing was scaled up to a single 5.1-cm-diam ion-exchange column with a 91-cm depth containing 1.8 L of QRF resin. The flow rates used were equal to the most effective volumetric flow rates used in the 3.8-cm-diam system in the previous set of tests: 433 mL/min (1.8 gpm/ft³) for loading, and 43.3 mL/min (0.18 gpm/ft³) for elution. These produced retention times of 4.2 min for loading and 41 min for elution. Greater than 90 pct of the tungsten was loaded and 92 pct eluted under these conditions. A more effective split-elution technique was also developed and used in these tests; this procedure consisted of adding the following solutions:

- 1.0 BV of pH 2.6 water to wash the feed from the resin.
- 1.0 BV of 2*N* NH_4OH to produce the tungsten product solution.
- 2.0 BV of 0.1*N* NH_4OH to produce the recycle eluate solutions for the next cycle.
- 0.5 BV of 0.6*M* H_2SO_4 to condition the resin for the next cycle.

Effect of Temperature

Tests performed to determine the effect of temperature on loading and elution were conducted in a single 3.8-cm-diam glass column containing 1 L of QRF resin. Tungsten loading varied only slightly, but elution improved as the temperature increased from 30° to 70° C. For example, QRF resin loaded to 130, 131, and 129 g/L WO_3 at 241 mL/min (1.8 gpm/ft³) from 100-L batches of pH 2.8 clarified primary eluate at 30°, 50°, and 70° C, respectively. Using an NH_4OH elution, tungsten concentration in the 1-BV product fraction of the eluate increased from 79 to 90 to 99 g/L WO_3 at 24 mL/min (0.18 gpm/ft³) at the respective temperatures. At all three temperatures, tungsten was sufficiently concentrated for further processing. In further testing, the feed temperature was reduced to 35° C after degassing at 60° C, and elution was conducted at ambient temperature to reduce the possibility of resin degradation.

Results of Bench-Scale Process Research

- A secondary ion-exchange step using QRF resin was found to be effective for concentrating tungsten from primary ion-exchange eluate.
- Required feed preparation included acidifying the primary eluate to pH 2.8, heating to 60° C for 5 min, cooling to 35° C, settling for 3 h, and decanting the clarified solution to be used as feed.
- Loading and elution efficiencies were 90 and 92 pct, respectively, for retention times of 4.5 min for loading and 41 min for elution. These volumetric flow rates were 1.8 gpm/ft³ for loading and 0.18 gpm/ft³ for elution.

PILOT-SCALE RESEARCH TO OBTAIN ENGINEERING DATA

Feed Preparation

Primary eluate, described at the beginning of this chapter, was acidified from pH 8.9 to pH 2.8 using 4.6 g H_2SO_4 per liter of eluate. The solution was freed of CO_2 by heating to 130° F for 5 min, followed by cooling to 95° F. The mixed organic-tungsten solids that precipitated were settled for 3 h, and the clarified solution was decanted to enable secondary ion-exchange without blinding the resin bed. The precipitate dissolved in the subsequent batch of primary eluate and was recovered. Feed to the secondary unit contained nearly 1.05 g/L WO_3, a decrease from the original 1.3 g/L WO_3, as the result of precipitation.

Operating Conditions

Secondary ion exchange using QRF resin was performed in a smaller replica of the extraction system. The two systems were proportional in size to the relative volumes of feed brine and primary eluate generated. Twenty secondary ion-exchange cycles were completed using three 2.9-in-diam columns at 3-ft depths, each containing 0.14 ft³ of wet-settled QRF resin. A sequential two-column loading operation using 141 BV/cycle (1.03 gal/BV) was performed at a flow rate of 5.4 gpm/ft². Nearly 2,800 gal of primary eluate was processed during the operating campaign. These tests were performed to confirm laboratory results, and no attempt was made to optimize flow conditions during field testing.

Secondary elution using 2*N* solutions of either NH_4OH or Na_2CO_3 was performed to compare the merits of each eluant. Elution flow rate was 0.65 gpm/ft². Maximum tungsten concentration was achieved using a five-stage split-elution technique with recycling of eluates from the preceding cycle. Steps in the eluting technique essentially were as follows:

1. Displace the solution in the column (acidic primary eluate from the preceding loading cycle) with 1 BV of pH 2.6 wash water. Return displaced solution to primary eluate storage.
2. Displace the wash water with 1 BV of 2*N* strong eluate recycled from step 4 of the previous elution cycle. Discard the displaced wash water.
3. Displace the strong eluate with 1 BV of a 0.1*N* weak eluate recycled from step 5 of the previous cycle. Retain the displaced eluate, containing 80 to 100 g/L WO_3, for product recovery.
4. Displace the weak eluate with 1 BV of fresh 0.1*N* eluant. The displaced weak eluate, containing from 40 to 60 g/L WO_3, was adjusted to a concentration of 2*N*; this solution became strong eluant for recycling to step 2 in the next elution cycle.
5. Displace the fresh, weak eluate with 1 BV of 0.6*M* H_2SO_4 to regenerate the resin for the next loading cycle. Recycle the weak eluate, containing from 20 to 40 g/L WO_3, to step 3 of the next elution cycle.

Ammoniacal elution was performed downflow. The first bed volume of Na_2CO_3 eluant (elution step 2), however, was pumped upflow into the acidic column to fluidize the bed and release CO_2 bubbles that blinded the bed when downflow was attempted. The remaining Na_2CO_3 elution steps were performed in the downflow manner.

Results Of Secondary Operations

Using NH_4OH elution, secondary tungsten sorption ranged from 79 to 97 pct and elution ranged from 89 to 93 pct. Recovery in secondary eluate averaged 80 pct of the influent tungsten.

Using Na_2CO_3 elution, tungsten sorption ranged from 74 to 88 pct and elution was 76 to 85 pct complete. Tungsten

recovered in the secondary eluate averaged 65 pct of the influent.

Secondary system operations demonstrated that tungsten could be concentrated to provide solutions containing greater than 80 g/L WO_3 for subsequent product recovery. Figure 21 shows a typical elution profile. Eluate analyses in table 20 show arsenic and phosphorus as major impurities in NH_4OH and Na_2CO_3 eluates. Overall recoveries were less than anticipated, and the need for further operational improvements was obvious.

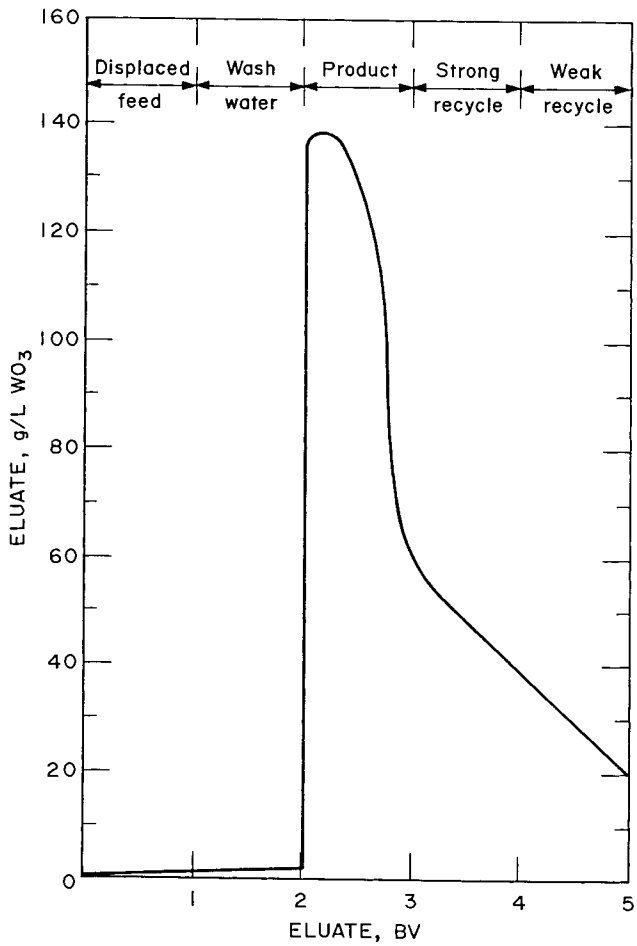

Figure 21.—Typical elution profile for secondary ion-exchange process.

TABLE 20.—Partial analysis of NH_4OH and Na_2CO_3 secondary eluates, grams per liter

Eluate analysis	NH_4OH	Na_2CO_3
WO_3	85	82
Na	0	40
NH_4	32	0
As	1.8	1.7
Cu	.001	<.001
Mg	.006	.008
Mo	.08	.08
Si	.05	.02
Ti	.009	.01
V	.006	<.001
Zn	.1	<.01
B_4O_7	.2	.2
P_2O_5	1.8	1.4

Later Laboratory Testing

Bench-scale testing of the secondary system was continued after field testing because results from testing at Searles Lake showed lower tungsten recoveries than those achieved during initial laboratory testing. Resin agglomeration in the laboratory columns, also noticed during field testing, appeared to be a probable cause for erratic results. Observation indicated resin agglomerates were caused when precipitate was carried over into the ion-exchange columns. This material apparently cemented the resin particles together. Resin agglomeration causes solution channeling, and poor loading and elution result. Thorough resin fluidization with air before elution broke resin agglomerates down to individual beads, and subsequent tungsten recoveries increased. Using NH_4OH elution, tungsten extraction was 96 pct, elution was 99 pct complete, and overall recovery was 95 pct. Using Na_2CO_3 elution, tungsten extraction was 90 pct, elution was 92 pct complete, and overall recovery was 82 pct.

Results of Pilot-Scale Research

- Research showed that basic secondary ion-exchange technology established from laboratory research needed only minor modification to operate satisfactorily under conditions encountered at Searles Lake. Almost 3,000 gal of primary eluate was treated in the field; 65 to 80 pct of the tungsten was recovered in 21 gal of secondary eluate containing 82 to 85 g/L WO_3.
- Using NH_4OH elution, secondary tungsten sorption from 141 BV of clarified pH 2.8 primary eluate at 5.4 gpm/ft^2 ranged from 79 to 97 pct. Elution was 89 to 93 pct complete at 0.65 gpm/ft^2 using a five-stage split-elution technique. Recovery in secondary eluate averaged 80 pct of the influent tungsten. Using Na_2CO_3 elution and the same operating conditions, tungsten sorption ranged from 74 to 88 pct, and elution was 76 to 85 pct complete, for an overall average recovery of 65 pct.
- Later laboratory testing indicated that the low field recoveries were due to resin agglomeration. Thorough resin fluidization with air prior to elution solved this problem, and recoveries increased. Using NH_4OH elution, tungsten extraction was 96 pct, elution was 99 pct complete, and overall recovery was 95 pct. Using Na_2CO_3 elution, tungsten extraction was 90 pct, elution was 92 pct complete, and overall recovery was 82 pct.

ALTERNATIVE METHODS TO RECOVER TUNGSTEN FROM PRIMARY ELUATE

Solvent Extraction

It has long been known that amine solvents extract tungsten from acid aqueous solutions (*33-34*) and that the extraction is pH dependent. Optimum extraction at pH O to pH 3 probably extracts the hexatungstate formed in acid solutions (*35*):

$$6WO_4^{2-} + 7H^+ = HW_6O_{21}^{5+} + 3H_2O, \qquad (1)$$

by the following reaction:

$$5R_3NH^+(org) + HW_6O_{21}^{5-}(aq) = (R_3NH)_5 \cdot HW_6O_{21}(org). \quad (2)$$

Alkaline stripping of the loaded organic would then be the reverse of reactions 1 and 2:

$$(R_3NH)_5 \cdot HW_6O_{21}(org) + 12OH^-(aq) = 5R_3N(org) + 6WO_4^{2-}(aq) + 9H_2O, \quad (3)$$

where R is an alkyl radical. Churchward and Bridges (*36*) state that tungsten is easily stripped from the primary amine, Primene JMT, by alkaline solutions and that, as long as the pH of the solution is 8 or above, stripping can be accomplished in a single stage, whereas the quaternary amine is more difficult to strip, requiring an NH_4OH-NH_4Cl strip.

In order to develop a solvent extraction technique for reconcentrating tungsten from primary eluate, basic extraction parameters were determined in batch shaker tests, and amine extractants were subsequently tested in a continuous system. Although solvent extraction is a possible method for concentration, operation was complicated and problematic.

Batch Testing

Batch shaker tests were used to determine tungsten extraction from primary eluate as a function of pH. Acidified, decarbonated primary eluate, 75 mL per batch, was adjusted to pH 2, 4, 6, and 8, and shaken for 10 min with 15 mL 0.03*M* solutions of the following:

- Primary amine: Rohm and Haas Primene JMT, a mixture of primary amines.
- Secondary amine: Sherex Adogen 283, di-tridecyl amine (DTDA).
- Tertiary amine: Henkel Alamine 336, tricaprylyl amine (TCA).
- Quaternary amine: Henkel Aliquat 336, tricaprylyl methyl ammonium chloride (TCMA).

Adogen 283 was selected for the remainder of the test series because it demonstrated good phase separation and tungsten extraction. It extracted tungsten almost as well as Primene JMT, which formed an emulsion. Extraction increased with decreased pH in all cases, with best extraction achieved at pH 2.

The remainder of the test series was run using the following standard conditions, unless otherwise noted: contacting 75 mL of conditioned primary eluate at pH 2 with 15 mL 0.03*M* Adogen 283 in kerosene (aqueous-to-organic ratio of 5:1) for 10 min at ambient temperature of 27° C. E_A^O, used as a measure of extraction efficiency, represents the extraction coefficient derived by dividing the concentration of WO_3 in the organic phase by the concentration of WO_3 in the aqueous phase.

Log E_A^O increased from 2.12 to 2.31 to 2.37 to 2.39 as contact time increased from 5 to 10 to 60 to 240 min, respectively. Interpolation of data indicated that 30 min would be the preferred contact time to yield of log E_A^O of 2.36.

Log E_A^O increased from 2.14 to 2.59 as the A-O ratio increased from 2.5 to 12.5, and dropped to 2.52 at a ratio of 15. When the pH was increased to 3, log E_A^O increased from 1.84 to 2.26 as the A-O ratio increased from 2.5 to 10.0, and decreased to 2.19 as the ratio further increased to 15.0. These data indicated that tungsten transfer to the organic phase was greatest at pH 2, but other results showed that pH 3 was advantageous in minimizing tungsten precipitation and its adverse effects of tungsten loss and third-phase formation.

At pH 3, log E_A^O increased from 2.14 to 2.24 as the temperature increased from 19° to 35° C. Although the trend showed higher temperatures were advantageous, they were not tested in the batch system because of the danger posed by the flammable nature of kerosene in an open system.

Preferred conditions in the batch system were found to be pH 3, a 30-min contact time, and an extraction temperature of 35° C or higher. These conditions were used to further evaluate the extractants.

A survey of amine extractants, summarized in figure 22, shows that the effectiveness of the amines at pH 3 was as follows, in descending order: Aliquat 336, Adogen 283, Primene JMT, Alamine 336, and Henkel Alamine 308 (triisooctyl amine, TIOA). All amines in kerosene modified with isodecyl alcohol (IDA) or tributyl phosphate (TBP) readily extracted tungsten at pH values of 3 or less. While Aliquat 336 showed the highest extraction coefficients for tungsten, this amine was not studied further because of the difficulty of stripping tungsten from the loaded solvent. Adogen 283 showed good extraction coefficients in the pH range of 0 to 5, and the amine-IDA-kerosene solvent exhibited very good phase separation from eluate at 40° C. Adogen 283 extracted tungsten well at pH 5.0; however, boron, also present in the eluate, displaced tungsten in the solvent, and only low tungsten loadings, with resultant high boron contamination, were possible. However, tungsten loaded readily at pH 3.0 with very little coextraction of boron.

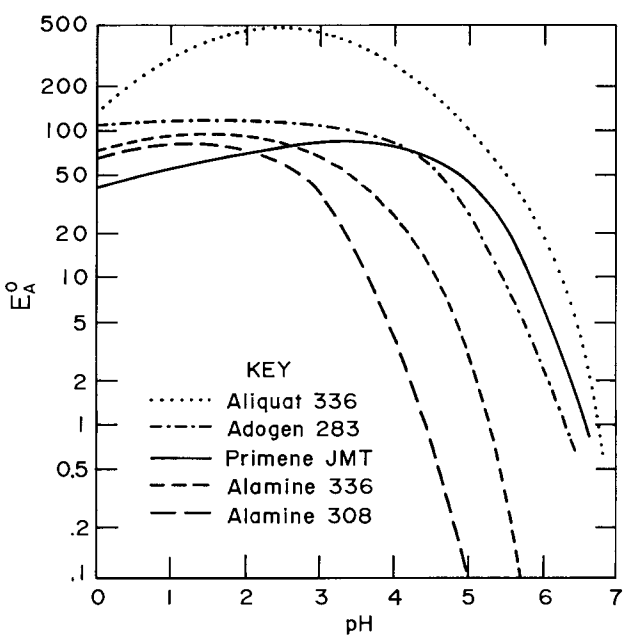

Figure 22.—Tungsten-extraction coefficients of amine extractants.

Continuous Testing

Continuous testing was conducted in the laboratory to evaluate Adogen 283. Acidification of primary eluate to pH 3 on a large scale caused precipitation of part of the contained tungsten in the form of a brown organic complex. Extraction from clarified filtrate from the acidified eluate in a continuous system was unsuccessful; the amine solvents used formed a gelatinous amine-tungsten-organic complex

that was insoluble in both alkyl and aromatic diluents. This insoluble complex caused severe phase-disengagement problems in the extraction unit, making operation of the unit extremely difficult. The problem was partly solved by chlorinating the aqueous feed to destroy the water-soluble organic material, and the resulting colorless solution, adjusted to pH 3, was treated in a multistage extraction circuit.

A five-stage solvent extraction system concentrated tungsten from chlorinated primary eluate containing 1.2 g/L WO_3 to over 100 g/L in the ammoniacal strip solution. Greater than 99 pct of the tungsten was extracted in two stages from oxidized pH 3 primary eluate by 0.03*M* Adogen 283 in a kerosene solvent containing 4 vol pct IDA that loaded to 12 to 15 g/L WO_3. The organic solvent was effectively stripped in two stages with 2*N* NH_4OH, and scrubbed in a fifth stage with acid as follows. A 285-L batch of primary eluate at an emf of 200 mV and pH 8.9 was heated to 40°C. It was then oxidized to an emf of 1,000 mV and neutralized to pH 6.5 with chlorine gas at an initial temperature of 40° C and a final temperature of 58° C. The clear solution was then acidified to pH 2.75 at 55° to 58° C with 330 mL of H_2SO_4, with no precipitate formation. The unreacted chlorine in the resultant feed was removed by aeration plus the addition of 15 g Na_2SO_3 (sodium sulfite); the resulting emf was 600 mV. This step was necessary because amines are unstable in aqueous chlorine. Tungsten was then extracted at 40° C with 0.03*M* Adogen 283 in a kerosene solvent containing 4 vol pct IDA that was subsequently stripped at 50° to 55° C with 2*N* NH_4OH. The amine was regenerated with an acid scrub using a solution of 0.1*N* HCl and 1*N* NaCl. Flow rates of 114 mL/min aqueous feed, 10 mL/min organic, 0.85 mL/min strip, and 3.3 mL/min scrub produced a concentrated tungsten solution that typically analyzed, in grams per liter, 110 WO_3, 18 NH_3, 2.1 P_2O_5, 0.6 As, 0.5 Cl, 0.47 SiO_2, and 0.2 B_4O_7.

Effective phase separation could not be achieved. The organic phase was slightly cloudy in all stages, crud formed in stage 2, APT precipitate formed in stage 3, and entrained loaded organic carried over to the stripped organic of stage 3.

While solvent extraction remains a possible alternative to ion exchange for the tungsten concentration procedure, it is more complicated to operate and phase separation difficulties remain unsolved.

Coprecipitation With Ferric Hydroxide

Another method considered for recovering tungsten from primary eluate is coprecipitation with ferric hydroxide [$Fe(OH)_3$] after addition of an iron salt. Best results were achieved using either ferric sulfate [$Fe_2(SO_4)_3$] or ferric chloride ($FeCl_3$). The chloride salt enabled minimizing the sulfur content of the tungsten precipitate. This scavenging technique, commonly used in analytical chemistry, effectively produced a low-grade concentrate suitable for further processing in tungsten refineries.

Adding a solution of 1*M* $FeCl_3$ to stirred pH 8.9 primary eluate precipitated $Fe(OH)_3$ that occluded most of the tungsten. Tungsten was loosely held by the iron precipitate; tungsten, but not iron, redissolved and was not recovered in alkaline solutions. Best tungsten removal was achieved at a final pH of 3.5. In one test series, at a W-Fe weight ratio of 2:1, tungsten precipitation at pH 3.5, 4.0, and 4.5 was 97, 93, and 90 pct, respectively. Increased acidity below pH 3.5 prevented iron precipitation. The pH was adjusted with H_2SO_4.

Test results at pH 3.5 showed that tungsten recovery decreased when precipitation was conducted at W-Fe ratios of greater than 2:1. For example, tungsten removal using W-Fe ratios of 2, 2.5, and 3.3 was 97, 90, and 78 pct, respectively.

Good results were achieved at 25°C; recoveries declined at higher temperatures. Soluble tungsten remaining in pH 3.5 solution after precipitation at a W-Fe ratio of 2 was 3 ppm WO_3 at 25° C, 10 ppm WO_3 at 45° C, and 40 ppm WO_3 at 60° C.

Using preferred operating conditions in 100-L tests, tungsten was coprecipitated from 25° C primary eluate with $FeCl_3$ at pH 3.5 using a W-Fe ratio of 2:1. The precipitate appeared too dilute for economical large-scale direct filtration, and thickening before filtration appeared advisable. The precipitate was flocculated with the cationic flocculant BETZ 1160 at 17.8 lb flocculant per ton WO_3. Flocculating the settled tungsten-iron precipitate doubled the filtration rate but failed to improve precipitate sedimentation. The precipitate settled to 20 pct of its original volume in 3 h. Analysis of batch thickening tests using the Kynch correlation (*37*) showed a need for 1,200 ft^2 of thickener area per daily ton of dry precipitate.

The filtration rate of the flocculated, settled, and decanted precipitate in a plate and frame press was 0.06 gpm/ft^2. Dried at 110° C, the precipitate typically assayed, in percent, 44 WO_3, 1.8 B_4O_7, 1.2 S, 0.5 As, 0.12 Mo, 0.12 Sb, 0.11 Pb, 0.1 Bi, and 0.02 P. The high arsenic content would incur a price penalty at a tungsten refinery (*38*). Most of the other impurities appeared acceptable for refining. The borate content, however, is questionable because no tolerance level for borate currently exists.

While this method is another possible alternative, its effectiveness compared with that of ion exchange remains to be proven.

SUMMARY

- Secondary ion exchange using QRF bead resin was effective in the laboratory for concentrating tungsten from pretreated primary ion-exchange eluate.
- Basic secondary ion-exchange technology established from laboratory research needed only minor modification to perform satisfactorily in a pilot plant under conditions encountered at Searles Lake.
- Solvent extraction is a possible alternative to ion exchange for tungsten concentration from the primary eluate; however, solvent extraction is more complicated to operate and phase separation is difficult.
- Coprecipitation with ferric hydroxide is another alternative to ion exchange for tungsten concentration from the primary eluate, but the effectiveness of coprecipitation compared with that of ion exchange has not been proven.

CHAPTER 6.—RECOVERY OF TUNGSTEN PRODUCTS FROM SECONDARY ELUATES

By P. B. Altringer, T. H. Jeffers, P. J. McDonough,[1] and P. T. Brooks

The QRF two-stage ion-exchange process concentrates the tungsten nearly 1,000-fold, producing secondary eluates containing more than 80 g/L WO_3. Secondary elution techniques using Na_2CO_3 and NH_4OH (described in chapter 5) produced eluates with compositions listed in table 20. Both eluates contained nearly 20 g/L organic carbon, believed to be present as humates, that adversely affects tungsten recovery as an intermediate product suitable for treatment in existing refineries.

Tungsten refineries treat a variety of intermediate chemical forms from which final products are made. The most important forms are concentrates of synthetic scheelite, sodium tungstate, and high-purity APT. Synthetic scheelite may be added directly to the steel bath in the production of steel, it may be used to produce ferrotungsten, which in turn is used as part of the charge in steelmaking, or it may be used to produce APT. Sodium tungstate is consumed in various chemical uses and is frequently processed into synthetic scheelite for charging to the steel bath. APT, the most widely traded intermediate product, is used to make metallic tungsten powder by hydrogen or carbon reduction (*39*, pp. 130–142).

Acceptable impurity levels for intermediate chemical forms are determined by the targeted end use and the technology involved in processing. Maximum impurity levels for commercial-grade APT are very stringent. One prominent tungsten producer, GTE Sylvania, cites the following maximum impurity contents for APT, in weight percent: 0.002 As, 0.0003 Cu, 0.003 Fe, 0.002 Mo, 0.004 Si, 0.002 Na, and 0.005 nonvolatile matter (summation of sodium, silicon, potassium, and calcium) (*40*). There is no single specification for tungsten concentrates. Because of their varied usage, other types of concentrates usually have a higher tolerance for impurities. There has evolved in the marketplace, however, an informal consensus specification on which market prices for concentrates are based. This specification for tungsten concentrates containing at least 65 pct WO_3 is presented in table 21 (*38*). The only impurity levels that proved difficult to achieve in laboratory research were those for arsenic and phosphorus.

TABLE 21.—Consensus specification for tungsten concentrates containing at least 65 pct WO_3

Constituent	*Wt pct*
As	0.20
B	NL
Cu	.40
Mo	.40
P	.08
S	.75
Sn	1.0

NL No limit.

[1]Metallurgist, Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

Five different solid tungsten concentrates were produced in laboratory testing to demonstrate methods for recovering intermediate chemical forms for final refining. These concentrates were sodium tungstate, tungstic oxide, synthetic scheelite, tungstic acid, and semipure APT. In addition, the LIX-APT solvent extraction technique (*39*, pp. 119–124) was tested to determine the merit of producing high-purity APT. The process was not applicable because the organics present in secondary eluates caused stable emulsions that made phase separations impractical. Even if the LIX-APT process could be modified to handle the QRF eluates, the process may not be economical because the relatively small (0.5 MMlb WO_3) annual production (*2*, *13*) that could be derived from the Westend feed brine stream would not justify the large initial capital expense necessary for APT production.

The interrelationships between solution composition and both product purity and recovery are complicated. Organic impurities pose the primary problem, followed by the inorganic impurities arsenic and phosphorus. The following sections described the experimental techniques, test results, and limitations of the procedures used to produce the five tungsten products mentioned.

PRODUCT RECOVERY FROM UNTREATED ELUATES

Eluate Evaporation

The simplest method for recovering solid tungsten products from secondary eluates is to evaporate the water and dry the evaporite at 200° C. This technique produced either sodium tungstate or tungstic oxide. Neither of the products prepared by evaporation, however, was sufficiently pure for ready marketability. Ammoniacal evaporite, chiefly tungstic oxide, contained, in weight percent, 77 WO_3, 19 organic C, 2 P_2O_5, 1.4 As, and 0.1 B_4O_7. Sodium carbonate evaporite, chiefly sodium tungstate, contained, in weight percent, 50 WO_3, 14 organic C, 1.2 P_2O_5, 0.9 As, and 0.2 B_4O_7. Both arsenic and phosphorus, particularly objectionable to refiners at levels exceeding 0.2 pct As and 0.18 pct P_2O_5, were significant contaminants. Also, organic carbon discolored the products and diluted the tungsten.

Precipitation

Tungstic acid and synthetic scheelite were prepared from secondary eluates using appropriate precipitation techniques. The presence of organics caused poor product grade and poor recovery. Neither of these products was sufficiently pure for marketing as an intermediate product without upgrading (*38*).

Tungstic Acid

Directly acidifying NH_4OH eluate at 80° C to pH 1 using 4*M* HCl recovered 38 pct of the tungsten as a brown

tungstic acid precipitate containing 63 pct WO_3 after drying. Recovery from Na_2CO_3 eluate was 95 pct under similar test conditions using concentrated HCl, but product grade remained low (63 pct WO_3). Again, poor product grade and color were apparently caused by organics.

Synethetic Scheelite

Scheelite was prepared directly from NH_4OH eluate by adding a stoichiometric amount of $CaCl_2$ at 70°C and agitating for 1 h. The brown precipitate assayed, in weight percent, 58 WO_3, 13 Ca, 0.7 P_2O_5, and 0.4 As. The remainder of the precipitate was chiefly composed of organic compounds containing carbon, oxygen, and hydrogen. Recovery was only 64 pct, and additional $CaCl_2$ did not improve recovery or product grade.

Scheelite was also precipitated from Na_2CO_3 eluate by acidification to pH 3.4 followed by pH adjustment to 9.2 with NaOH. Acidification decarbonated the eluate and prevented calcium carbonate ($CaCO_3$) precipitation that otherwise would decrease product grade. The decarbonated solution was then treated in the same manner as NH_4OH eluate. This scheelite assayed, in weight percent, 55 WO_3, 11 Ca, 0.7 As, and 0.5 P_2O_5. The remainder of the precipitate was again chiefly organic compounds. Tungsten recovery was only 56 pct.

PRODUCT PURIFICATION TECHNIQUES

Product purification investigations took several routes. Roasting was potentially the simplest method for destroying organic impurities in eluate evaporites. However, the expense of roasting and organic interference with product precipitation prompted testing of techniques to directly oxidize and destroy the organic material contained in the secondary eluate. Inorganic impurities were reduced most successfully by magnesia precipitation from the secondary eluate.

Destruction of Organic Impurities

Roasting

Roasting solid evaporites at 600° C for 4 h improved product grade and recovery during subsequent precipitation procedures. Roasting eliminated nearly 99 pct of the carbon and more than two-thirds of the arsenic.

Oxidation

Electrochemical oxidation and oxygenation at elevated temperature and pressure were shown to effectively eliminate organic carbon; aqueous chlorination and ozonation were not as effective. The amount of organic matter remaining in the eluate following oxidation was determined by measuring the COD. The method of COD determination used provides a measure of the oxygen equivalent needed to oxidize organic matter that is susceptible to oxidation by hot dichromic acid (*32*). The degree of organic destruction was determined by comparing initial and final COD's.

Chlorination

Chlorination partially destroyed organics. Chlorinating alkaline Na_2CO_3 eluate by sparging with chlorine through fritted glass at a rate of 1 L/min per liter of solution destroyed organic material as measured by COD. Chlorination also increased eluate acidity, as shown by equation 1.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-. \quad (1)$$

Thus, pH provided a general measure of chlorine consumption. In one test, organic destruction was 78 pct complete after 30 min of chlorination from an initial pH of 9.4 to a final pH of 1.8. Eluate acidification to pH 3.3 using H_2SO_4 before chlorination enhanced the reaction; 78-pct organic destruction was achieved in only 5 min at a final pH of 1.7. This trend follows the general rule that chlorine reacts more rapidly with materials as the pH decreases (*41*).

Electrochemical Oxidation

Electrochemical oxidation effectively destroyed organics in both eluates. This technique was tested in a laboratory electrolytic cell using lead and lead oxide electrodes at a current density of 108 A/ft^2 and cell voltage of 1.8. Organic destruction of 90 pct was achieved in 15 min at 25° C.

Pressurized Oxidation

Organics were also destroyed by hot, pressurized oxygenation of secondary Na_2CO_3 eluate, a technique used industrially for treating waste streams containing organic materials. Most laboratory testing was performed in a 22-mL electrically heated pressure reactor to conserve scarce eluate. A 16-mL sample was pressurized with oxygen, heated to the target temperature, agitated for 10 min using a wrist-action shaker, and cooled. Once pressurized, the reaction vessel was not repressurized to replace oxygen consumed in the reaction. Results in table 22 show a maximum of 48 pct organic destruction at 180° C and a total pressure of 950 psi. Increasing the oxygen partial pressure to 1,200 psi was not advantageous. A temperature of 180° C was more effective than 160° C.

TABLE 22.—Organic destruction by hot-pressurized oxygenation

Temp, °C	Total pressure, psi,	Organics destroyed, pct
180	600	30
	950	48
	1,200	48
160	600	18
	950	38
	1,200	38

Organics were more effectively destroyed using a larger, better agitated system and adding oxygen periodically to maintain pressure. Results in table 23 show

TABLE 23.—Scheelite recovery from secondary Na_2CO_3 eluate

Oxidation technique	Organics destroyed, pct	Product grade, pct WO_3	Tungsten recovery, pct
None	0	56	59
Chlorination	78	74	92
Ozonation	22	66	67
Pressurized oxidation	85	77	99
Electrochemical oxidation	90	73	90
Drying and roasting	>90	78	98

that 85 pct of the organics were destroyed in a pressurized oxidation test conducted using a 1-L autoclave containing 300 mL of secondary eluate agitated by an impeller at 180° C and maintained at 500 psi with an excess of oxygen. The 85-pct organic destruction is appreciably higher than the maximum 48 pct attained using the smaller system with limited oxygen.

Ozonation

Treatment with ozone partially destroyed the organics. Air containing 4 pct ozone was sparged through Na_2CO_3 eluate samples for 60 min at a flow rate of 1 L/min of air per liter of solution. Unlike chlorination, little change in solution pH occurred after ozonation. Organic destruction at pH 9 was only 22 pct effective; whereas, 45-pct destruction occurred after acidifying eluate with H_2SO_4 to pH 4 before ozonation.

Removal of Inorganic Impurities

Arsenic and phosphorus are contaminants that are particularly objectionable to refiners at levels exceeding 0.2 pct As and 0.18 pct P_2O_5. Treating secondary eluates with MgO or $MgCl_2$ (magnesium chloride) precipitated arsenic and phosphorus as mixed magnesium arsenates and phosphates (*42*). Test results in table 24 show precipitations after 1 h of stirring at 50° C and a Mg-As weight ratio of 3:1. Organic carbon was not precipitated. For purifying Na_2CO_3 eluate, $MgCl_2$ precipitated phosphorus more effectively than did MgO, but MgO precipitated both phosphorus and arsenic more effectively than did $MgCl_2$ from NH_4OH eluate. As shown by the results in table 25, further testing indicated no marked differences in impurity levels when precipitation temperatures ranged from 25° to 75° C. Arsenic and phosphorus removal was more favorable at pH 10 than at pH 7. A reaction time of 30 min or more enabled good arsenic removal, whereas 15 min was inadequate. Maximum arsenic precipitation was achieved at Mg-As weight ratios exceeding 1.5:1, but no advantage was gained at ratios exceeding 3:1.

PURIFIED PRODUCT RECOVERY

Marked improvements in recovery and product grade were achieved after organics were destroyed using oxidative techniques on the secondary eluate or using a roast and leach technique on the evaporites prior to product precipitation, and after inorganic impurity levels in the products were reduced by a magnesia precipitation treatment. The following paragraphs discuss recovery procedures and product characteristics.

Tungstic Acid

Poor product grade, recovery, and color resulted when tungstic acid was precipitated directly from secondary eluate. Better results were achieved after roasting NH_4OH evaporite at 600° C to remove both organic carbon and arsenic. When the roasted material was treated with concentrated HCl at 80° C, 99 pct of the tungsten precipitated from the resulting solution as yellow tungstic acid dihydrate. Roasting eliminated carbon interference and markedly improved both recovery (from 38 to 99 pct) and product grade (from 63 to 93 pct). The dried precipitate contained, in weight percent, 93 WO_3, 1.5 P_2O_5, and 0.1 As. Acid usage was 1.7 g of HCl per gram of roasted evaporite.

TABLE 24.—Secondary eluate purification using magnesium compounds[1]

Eluate and precipitant	Precipitation, pct		
	WO_3	As	P_2O_5
NH_4OH, pH 9.8:			
MgO	3	74	44
$MgCl_2$	6	30	13
Na_2CO_3, pH 9.4:			
MgO	4	61	35
$MgCl_2$	4	62	70

[1]Mg-As weight ratio of 3, mixing time of 1 h, temperature of 50° C.

TABLE 25.—Impurity removal from secondary NH_4OH eluate using MgO precipitant[1]

Eluate pH	Weight ratio, Mg-As	Reaction time, min	Impurity removal, pct	
			As	P_2O_5
7	3	60	41	24
8	3	60	62	56
9	3	60	62	79
10	1.5	60	84	92
	3	15	65	91
	3	30	90	94
	3	[2]30	92	91
	3	[3]30	91	85
	3	60	89	89
	3	240	93	91
	4.5	60	91	93
	6	60	91	91

[1]At 25° C, except as noted.
[2]At 50° C.
[3]At 75° C.

Tungstic Oxide

Roasting the NH_4OH evaporite at 600°C for 4 h improved tungstic oxide product grade from 77 to 86 pct WO_3 and eliminated nearly 99 pct of the carbon. The roasted product assayed, in weight percent, 86 WO_3, 1.8 P_2O_5, 0.28 As, and 0.2 organic C.

Tungstic oxide prepared by evaporating and roasting NH_4OH secondary eluate after MgO treatment was of higher grade and contained much less arsenic and phosphorus than did tungstic oxide prepared from untreated eluate. Magnesia treatment reduced the arsenic level by over one-half and the phosphate level by almost 90 pct. The product assayed, in weight percent, 99 WO_3, 0.12 As, 0.22 P_2O_5, and less than 0.4 B_4O_7. The arsenic level met the guideline specifications presented in table 21, but the phosphate level still exceeded 0.18 pct P_2O_5.

Sodium Tungstate

Roasting the Na_2CO_3 evaporite had a similar advantageous effect: Sodium tungstate grade was increased from 50 to 58 pct WO_3. The roasted product assayed, in weight percent, 58 WO_3, 0.3 As, 0.9 P_2O_5, and 0.2 organic C. Once again, MgO treatment reduced the arsenic to an acceptable level. Sodium tungstate prepared from MgO-treated Na_2CO_3 eluate assayed, in weight percent, 58 WO_3, 0.11 As, 0.42 P_2O_5, and 0.18 B_4O_7.

Ammonium Paratungstate (APT)

After purifying NH_4OH eluate with MgO, the solution was evaporated to half the original volume, cooled at 4° C for 16 h, and the precipitated APT crystals were collected,

washed, and dried. The APT assayed, in weight percent, 81 WO_3, 0.2 As, and 0.2 P_2O_5. Tungsten recovery was only 64 pct.

Although the 80 g/L WO_3 secondary eluate solutions have similar tungsten content to that of the 80- to 100-g/L WO_3 solution obtained by pressure digesting tungsten mineral concentrates, they are markedly dissimilar with respect to organic carbon. The commercial LIX-APT process (*39*, pp. 119-124) was not effective in recovering tungsten from ion-exchange secondary eluates because the high organic content of the eluates produced stable emulsions.

Because of the stringent purity requirements for APT, the preferred route for APT production appeared to be through production of an intermediate product, such as scheelite, followed by treatment in an existing refinery where impurity-removal techniques are well established.

Synthetic Scheelite

Synthetic scheelite was prepared from pH 9 secondary Na_2CO_3 eluates after partial organic destruction by oxidation. As shown in table 23, organic destruction improved both recovery and product grade. Similar results were achieved after roasting Na_2CO_3 evaporite at 600° C followed by water dissolution and tungsten precipitation with stoichiometric $CaCl_2$; test results in table 26 show recoveries and scheelite quality from solution containing 95 g/L WO_3. The magnesium treatment decreased the arsenic and phosphorus contents in the scheelite product to acceptable levels. Synthetic scheelite produced from MgO-treated, roasted Na_2CO_3 evaporite assayed, in weight percent, 79 WO_3 g 13 Ca, 0.12 As, 0.33 P_2O_5, and 0.008 B_4O_7.

TABLE 26.—Scheelite precipitated following dissolution of roasted Na_2CO_3 eluate, percent

	Solution treatment[1]		
	None	MgO	$MgCl_2$
WO_3 precipitation	98	99	99
Scheelite assay:			
WO_3	78	79	80
Ca	14	13	14
As	.6	.1	.1
P_2O_5	.6	.3	.1

[1]Mg-As weight ratio of 3:1 used for precipitation.

The leaching portion of the technique was not applicable for NH_4OH eluates. Tungstic oxide, prepared by roasting NH_4OH eluate evaporite, was soluble in concentrated HCl, but high reagent requirements made scheelite precipitation impractical. The roasted evaporite was not soluble in water, in caustic or in dilute acid solutions.

SUMMARY

- Impure tungstic oxide containing 77 pct WO_3 was recovered by evaporating NH_4OH secondary ion-exchange eluate to dryness; major impurities were, in weight percent, 19 organic C, 2 P_2O_5, and 1.4 As.
- Impure sodium tungstate was recovered by evaporating Na_2CO_3 secondary eluate to dryness; solids assayed, in weight percent, 50 WO_3, 14 organic C, 1.2 P_2O_5, and 0.9 As.
- Synthetic scheelite containing 55 to 58 pct WO_3 was precipitated from untreated secondary eluates using $CaCl_2$; recoveries ranged from 56 to 64 pct.
- Low-grade, impure tungstic acid containing 63 pct WO_3 was recovered from untreated secondary eluates; recoveries ranged from 38 to 95 pct.
- Both arsenic and phosphorus concentrations in secondary eluates were decreased by precipitation using either MgO or $MgCl_2$.
- Impure APT containing 81 pct WO_3 was precipitated from MgO-treated NH_4OH secondary eluate at a recovery of 64 pct; major impurities were, in weight percent, 0.2 As and 0.2 P_2O_5.
- Organic carbon impurities, apparently brine humates, interfered with product recovery from eluate.
- Organics were effectively destroyed by roasting eluate evaporites at 600° C or by electrochemical oxidation or pressurized oxygenation of the secondary eluate. Chlorination or ozonation only partially destroyed the organics.
- Higher grade tungstic oxide was recovered by roasting MgO-treated NH_4OH evaporite, producing solids that assayed, in weight percent, 99 WO_3, 0.12 As, 0.22 P_2O_5, less than 0.4 B_4O_7, and 0.2 organic C.
- Higher grade sodium tungstate was recovered by roasting MgO-treated Na_2CO_3 evaporite, producing solids that assayed, in weight percent, 58 WO_3, 0.11 As, 0.42 P_2O_5, 0.18 B_4O_7, and 0.2 organic C.
- Tungstic acid dihydrate containing 93 pct WO_3 was precipitated from roasted NH_4OH eluate that had been redissolved in HCl; the recovery was 99 pct.
- Synthetic scheelite was produced from roasted Na_2CO_3 evaporite from MgO-treated eluate at recoveries of 90 pct or better; this produced solids that assayed, in weight percent, 79 WO_3, 13 Ca, 0.12 As, 0.33 P_2O_5, and 0.008 B_4O_7.

CHAPTER 7.—RECOMMENDATIONS FOR APPLICATION OF BASIC TECHNOLOGY

By P. B. Altringer

The information presented in this bulletin is intended to serve as a basis for tungsten recovery from Searles Lake brines. These research results provide basic technology for producing three tungsten products. The alternative processing routes are all based on a two-stage ion-exchange process for tungsten extraction and concentration. The three flowsheets discussed are workable alternatives that most likely would be modified to suit current circumstances when implemented. The research has also identified a number of process steps or unit operations where additional improvements may be possible. The potential for significant cost reductions appears promising. A discussion of the recommended additional research and development follows.

Additional carbonation of the lake brine as it enters the plant would decrease brine alkalinity and enhance tungsten recovery because tungsten capacity of QRF resin increases as the pH decreases. Significant reductions in resin inventory may result from use of increased carbonation. This would seem to be advantageous for the entire existing salt recovery process since soda ash recovery would also increase. Basic process research and an economic evaluation of this option should be conducted.

Development of the ion-exchange resin was an evolutionary process. The bead used in the pilot plant research was a third-generation form, the most highly developed at that time. Additional research to optimize bead synthesis conditions, to increase selectivity for tungsten over other impurities, and to decrease pH sensitivity could produce an improved bead. Pioneering research indicated that the porosity of the bead can be increased dramatically while maintaining bead integrity and strength. This would enhance the resin capacity for tungsten and thereby decrease the size of the ion-exchange operation and improve economics.

Results from testing variations in the primary ion-exchange elution operation showed promise for concentrating the tungsten to higher levels in less solution. Further testing is needed to determine the long-term effect of moderately increased temperature on resin stability. In addition, a technique for selectively eluting impurities was devised that may eliminate the need for the subsequent magnesia precipitation step. Long-term testing of this technique is needed to determine its effectiveness after many cycles of resin use. An economic evaluation would determine whether the advantages gained by the use of these techniques would outweigh any disavantages such as the possibility of shortened resin life.

Brackish water from the Trona, CA, area was tested and found unusable as eluant makeup water because less tungsten loaded in the next extraction cycle. Further research is needed to identify the interfering constituent(s), which block one-third of the sites normally available for subsequent tungsten sorption. If silica causes the problem, seeding and filtration would help; if organics cause the problem, oxidation would help. A solution to this problem would enable use of local brackish water and enhance process economics.

Although flowsheets were developed for producing three other tungsten products, development of a technique for producing purified APT would increase the attractiveness of the process. Pure APT is the most marketable tungsten product, but the most expensive to produce. With the relatively small (0.5 MMlb WO_3) potential annual production from the Westend feed brine stream, it is doubtful that the commercial liquid ion-exchange (LIX–APT) process could be economically modified to produce purified APT from this brine.

Additional research on tungsten recovery from Searles Lake brines processed at the Argus facility could improve process economics for that brine type. Larger scale testing is needed to obtain engineering data and also to provide sufficient amounts of primary eluate for a more extensive secondary ion-exchange investigation. Larger scale secondary testing would, in turn, produce sufficient amounts of secondary eluate to study a wide variety of promising product-recovery techniques.

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APPENDIX A.—PLANT COST ESTIMATE

By T. A. Phillips[1]

PLANT DESCRIPTION

A cost estimate of a tungsten recovery plant based on the Bureau's ion-exchange technology is presented. The plant location is assumed to be adjacent to Kerr-McGee's Westend chemical production facility at Searles Lake, CA. Feed to the plant is overflow from sodium bicarbonate thickeners referred to as soda grainers at the Westend facility. The design feed rate is 1,800 gpm with a pH of 8.2.

Flowsheets for the recovery of tungstic oxide, sodium tungstate, and synthetic scheelite were evaluated. All three utilize the same primary and secondary ion-exchange system to recover the tungsten from the brine feed and to concentrate it. If tungstic oxide is to be recovered, NH_4OH elution is used in the secondary ion-exchange step. Tungstic oxide is recovered by spray drying the eluate and calcining the product. To recover sodium tungstate, a Na_2CO_3 eluant is used. As before, the sodium tungstate product is recovered by spray drying the eluate and calcining the dryer product. Synthetic scheelite is recovered by redissolving the calcined sodium tungstate in water and precipitating synthetic scheelite by adding $CaCl_2$.

Primary Ion Exchange

Brine from the soda grainers is pumped through two columns in series to extract 90 pct of the tungsten. The first column becomes fully loaded with tungsten while the second acts as a scavenger. A third column is used to allow continuous extraction. When the first column is fully loaded, brine is fed through the second and third columns; the third becomes the scavenger column. After tungsten in the loaded column is eluted, this column becomes the replacement column for the next cycle.

Five series of three fixed-bed ion-exchange columns are used in parallel. Each is a 9.6-ft-diam, 9-ft-tall column made of fiberglass. The bed of resin is 3 ft deep. About 65 BV of brine are fed through the columns each cycle at a flow rate of 5 gpm/ft^2 of cross-sectional area. A cycle lasts about 4.8 h.

At the completion of a cycle, tungsten in the loaded column is eluted with 5 BV of Na_2CO_3 solution at a flow rate of 0.5 gpm/ft^2. The first bed volume of eluate is primarily brine flushed from the resin bed, which is returned to the main plant. The next 3 BV of eluate are saved as the primary eluate and are pumped to the acidification section. The remaining eluate, containing lower levels of tungsten, is recycled to make up fresh eluant.

Acidification

Tungsten-rich eluate from primary ion exchange is fed to a mixing tank and acidified with H_2SO_4 to reduce the pH to 2.8. The acidified solution is pumped through a heat exchanger to raise the temperature to about 55° C, then fed to one of two tanks and allowed to cool. Two tanks are required to allow one to be filled while the other is cooling. The heating and slow cooling decarbonates the solution. All vapors are vented to the atmosphere. Solids that precipitate during the cooling period settle to the bottom of the tank. These remain in the tank when it is empty but are redissolved when fresh hot eluate is fed to the tank. At the end of a 3-h cooling period, the decarbonated and acidified eluate is pumped to secondary ion exchange for tungsten concentration.

Secondary Ion Exchange

Acidified and decarbonated primary eluate is fed to a surge tank, then pumped through a series of two ion-exchange columns. A three-column cyclic procedure is used as in primary ion exchange. Only one series of three 4.3-ft-diam columns is required. Each column contains a 3-ft bed of ion-exchange resin. Then 100 BV of feed is pumped down through the column pair, each cycle at a flow rate of 5.7 gpm/ft^2 of cross-sectional area. Each cycle lasts 6.6 h.

At the end of a loading cycle, the tungsten is recovered by different elution techniques, depending on the desired product. If tungstic oxide is to be recovered, an NH_4OH solution is used; to produce either sodium tungstate or synthetic scheelite, a Na_2CO_3 solution is used.

Ammonium Hydroxide Elution

The loaded ion-exchange resin is first washed with 1 BV of pH 2.6 water. Next, it is eluted with 1 BV each of a strong recycle eluate, a weak recycle eluate, and a fresh NH_4OH solution at a flow rate of 0.18 gpm/ft^3. Finally, the resin bed is conditioned by pumping 1 BV of a weak H_2SO_4 solution through the column. Each solution displaces the preceding solution from the column. The first solution to leave the column is primary eluate leftover from the loading cycle. It is discarded along with the next solution, the wash water. Strong recycle eluate becomes the product eluate upon being displaced from the column and is pumped to the purification system. Weak recycle eluate becomes the strong recycle eluate in the next cycle, and the fresh NH_4OH solution becomes the weak recycle eluate in the next cycle. Both are pumped to holding tanks. The H_2SO_4 solution remains in the column until it is displaced at the start of the next loading cycle. All eluants are pumped down through the resin bed. The holding tank for the strong recycle eluate is equipped with an agitator to mix the small quantity of NH_4OH that is added to this solution.

Sodium Carbonate Elution

When Na_2CO_3 solution is used for elution, the technique is almost the same as for the NH_4OH elution. First, the resin is washed with acidic water, then a strong recycle eluate, a weak recycle eluate, and a fresh eluant are pumped through the resin bed. Finally, the resin is conditioned with H_2SO_4. There are two differences, however. First, the strong recycle eluate is pumped up through the resin bed instead of down, allowing removal of CO_2 gas formed during this procedure. Second, 2 BV of weak recycle eluate, instead of one, are pumped through the column. When displaced from the column, the first bed volume becomes the strong recycle eluate and the second is returned to the weak recycle eluate holding tank. To make the eluant, Na_2CO_3 is fed

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from a storage bin to a mixing tank and dissolved in water. Sodium carbonate is also fed to the strong recycle eluate holding tank, where it is dissolved.

Impurity Removal

Impurity removal is the same for the product eluate from either NH_4OH or Na_2CO_3 elution. Each secondary elution cycle produces 240 gal of eluate, which is fed to a mixing tank. To this, 18 lb of MgO is added, and the slurry is stirred for 1 h at ambient temperature, then pumped through a pressure filter to remove the resulting arsenic-containing MgO precipitate. The purified filtrate is pumped to drying and calcination. The precipitate is loaded into drums and discarded as waste. No equipment is included for special handling of these solids.

Drying and Calcination

Tungstic Oxide Recovery Using Ammonium Hydroxide Elution

Filtrate from impurity removal is collected in a single tank then pumped to a spray dryer. Solids collected in the dryer are fed directly to a rotary calciner where they are calcined at 600° C, producing an anhydrous tungstic oxide analyzing 99 pct WO_3. Vapors from the spray dryer and calciner contain ammonia, which is condensed in a direct-contact condenser. The condensate is cooled in a heat exchanger and recycled to the condenser. Excess condensate is bled from the circuit and returned to secondary ion exchange as fresh eluant.

Solids leaving the calciner are cooled in a rotary cooler. The product is then loaded into drums for storage and shipment. About 478,000 lb of tungstic oxide can be produced annually based on 330 d/yr of operation.

Sodium Tungstate Recovery Using Sodium Carbonate Elution

Filtrate from impurity removal is also spray dried and then calcined at 600° C in the above manner. Vapors from the dryer and calciner, pass through a dust collector then are vented directly to the atmosphere. The cooled calcine is loaded in drums as before, if sodium tungstate is the final product. If synthetic scheelite is to be recovered, the calcine is conveyed to the scheelite recovery system. The sodium tungstate product contains about 58 pct WO_3, and about 833,000 lb can be recovered annually based on 330 d/yr of operation.

Scheelite Recovery From Sodium Tungstate Calcine

To recover synthetic scheelite, the sodium tungstate calcine is fed to a tank and dissolved in water. A 40-pct-$CaCl_2$ solution in water is then added and agitated for 1 h at 70° C. Synthetic scheelite precipitates and is recovered by filtration. The filter cake is dried in a tray dryer and loaded into drums for storage and shipment. About 590,000 lb of scheelite averaging 79 pct WO_3 can be produced annually assuming 330 d/yr of operation.

COST ESTIMATE

The cost estimate presented in this report is based on laboratory data from the Bureau of Mines Salt Lake City Research Center and from pilot plant data from investigations at Kerr-McGee Chemical Corp.'s Westend plant.

Capital Costs

The capital cost estimates are of the general type called a study estimate (*43*)[2]. This type of estimate, prepared from a flowsheet and a minimum of equipment data, can be expected to be within 30 pct of the actual cost for the plant described. The estimated fixed capital cost on a third-quarter 1984 basis (Marshall and Swift, M and S, index of 783.9) for the two plants to produce either tungstic oxide or sodium tungstate is $6.7 million. When scheelite is recovered, the fixed capital cost is $7.1 million. All three plants process 1,800 gpm of carbonated Searles Lake brine and recover 1,448 lb/d WO_3 as either tungstic oxide or sodium tungstate, or 1,433 lb/d WO_3 as scheelite. The plants are designed to operate three shifts per day, 7 days per week, 330 d/yr through secondary ion exchange. All remaining operations run one shift per day. A breakdown of the capital costs for the three plants is shown in table A-1.

TABLE A-1.—Estimated capital cost[1]

	Tungstic oxide process	Sodium tungstate process	Scheelite process
Fixed capital:			
Primary ion exchange	$3,928,900	$3,928,900	$3,928,900
Acidification	367,400	367,400	367,400
Secondary ion exchange	272,600	313,100	313,100
Impurity removal	100,000	100,000	100,000
Drying and calcination	1,355,900	1,326,000	1,274,600
Scheelite recovery	NAp	NAp	405,100
Subtotal	6,024,800	6,035,400	6,389,100
Plant facilities, 2 pct of above subtotal	120,500	120,700	127,800
Plant utilities, 4 pct of above subtotal	241,000	241,400	255,600
Basic plant cost	6,386,300	6,397,500	6,772,500
Escalation costs during construction	71,100	71,200	75,400
Total plant cost	6,457,400	6,468,700	6,847,900
Land cost	0	0	0
Subtotal	6,457,400	6,468,700	6,847,900
Interest during construction period	218,100	218,500	231,200
Fixed capital cost	6,675,500	6,687,200	7,079,100
Working capital:			
Raw material and supplies	21,900	23,800	25,000
Product and in-process inventory	196,100	196,800	206,600
Accounts receivable	196,100	196,800	206,600
Available cash	112,500	113,000	117,600
Working capital cost	526,600	530,400	555,800
Total capital cost	7,202,100	7,217,600	7,634,900

NAp Not applicable.
[1] Basis: M and S equipment cost index of 783.9.

[2]Italic numbers in parentheses refer to items in the list of references preceding the appendixes.

Equipment costs for the proposed process are based on cost-capacity data and manufacturers' cost quotations. Cost data are brought up to date by the use of inflation indices. In developing the plant capital costs, corrosion-resistant construction materials were used where appropriate. For example, the ion-exchange columns are constructed of fiberglass to withstand the salt brine.

Factors for piping, etc., except for the foundation and electrical systems, are assigned to each section, using as a basis the effect fluids, solids, or a combination of fluids and solids may have on the process equipment. The foundation cost is estimated for each piece of equipment individually, and a factor for the entire section is calculated from the totals. The electrical factor is based on the motor horsepower requirements for each section. A factor of 10 pct, referred to as miscellaneous, is added to each section to cover minor equipment and construction costs that are not shown with the equipment listed.

For each section, the field indirect cost, which covers field supervision, inspection, temporary construction, equipment rental, and payroll overhead, is estimated at 10 pct of the direct cost. Engineering cost is estimated at 10 pct, and administration and overhead cost is estimated at 5 pct of the construction cost. A contingency allowance of 10 pct and a contractor's fee of 5 pct are included in the section costs.

The costs of facilities and plant utilities are estimated as 2 and 4 pct, respectively, of the total process section costs. Both are lower than would be expected for a new plant because this is to be an addition to the existing Westend plant. Facilities include only site preparation such as clearing and grading. Existing roads and fences are assumed to be adequate as are auxiliary buildings such as offices, shops, laboratories, and other plant facilities. Plant utilities, including water, power, and steam distribution systems are assumed to be adequate to carry the addition. The utility factor covers only the hookup to the existing systems.

The cost for interest on the capital borrowed for construction is included as interest during construction, assuming an interest rate of 12 pct. To determine the interest cost during construction, the total plant cost is factored by an adjusted interest rate, which depends upon the length of the construction period and the interest rate at which the money is borrowed. Cost for the plant owner's supervision is not included in the capital cost of the proposed plant.

Working capital is defined as "the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant." Working capital, also shown in table A-1, is estimated from the following items: (1) raw material and supplies inventory (cost of raw material and operating supplies for 30 days), (2) product and in-process inventory (total operating cost for 30 days), (3) accounts receivable (total operating cost for 30 days), and (4) available cash (direct expenses for 30 days).

Operating Costs

The estimated operating costs are based on the average of 330 d/yr of operating over the life of the plant. This allows 35 d/yr downtime for inspection, maintenance, and unscheduled interruptions. The operating costs are divided into direct, indirect, and fixed costs.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. The raw material costs do not include transportation costs because the plant is assumed to be located adjacent to the Westend plant. Electricity, water, natural gas, and steam are purchased utilities. The temperature of the water from the local wells is assumed to be 32° C.

The direct labor cost is estimated on the basis of assigning 4.2 employees to each position that operates 24 h/d, 7 days per week, and 1.4 employees to each position that operates 8 h/d, 7 days per week. The cost of labor supervision is estimated at 15 pct of the labor cost. Plant maintenance is separately estimated for each piece of equipment and for the buildings, electrical system, piping, plant utility distribution systems, and plant facilities.

Payroll overhead, estimated as 35 pct of direct labor and maintenance labor, includes vacation, sick leave, social security, and fringe benefits. The cost of operating supplies is estimated as 20 pct of the cost of plant maintenance.

Indirect costs are estimated as 40 pct of the direct labor and maintenance costs. The indirect costs include the expenses of control laboratories, accounting, plant protection and safety, plant administration, marketing, and company overhead. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. The annual costs of taxes and insurance are each estimated as 2 pct of the plant construction cost. Depreciation is based on a straight-line, 10-yr period.

Tables A-2, A-3, and A-4 present the estimated operating cost for recovering tungstic oxide, sodium tungstate, and synthetic scheelite, respectively, from Searles Lake brine. Recovering tungstic oxide or sodium tungstate is estimated to cost \$5.03/lb WO_3. Producing scheelite from the sodium tungstate is estimated to cost an additional \$0.26/lb WO_3, for a total operating cost of \$5.29/lb WO_3. For each process the individual unit operation costs and the total are presented. Royalty payments of \$0.26, \$0.22, and \$0.18/lb WO_3 are included in the operating cost estimates for the respective products. The royalty payment is computed as 5 pct of the gross product value for each process and assumes that 100 pct of the Searles Lake brine is from wells on government leases.

The estimated values of tungstic oxide, sodium tungstate, and synthetic scheelite are \$5.14, \$4.32, and \$3.61/lb WO_3, respectively, as of October 1984. Only the tungstic oxide process is profitable. Using the interest rate-of-return method, the rate of return on investment after taxes for this process is only about 1 pct. Fifteen percent is generally considered to be the minimum acceptable rate of return on investment for a new venture. For the tungstic oxide recovery process, the product value must be \$8.10/lb WO_3 to yield a 15-pct return on investment.

In recent years, the published price for tungsten concentrate has fluctuated significantly, dropping from a high of \$6.59/lb WO_3 in July 1981 to a low of \$3.77/lb WO_3, rising to \$5.50/lb WO_3 in July 1984, then falling to its October 1984 value of \$3.61/lb WO_3. Figure A-1 is provided to show how the interest rate of return on investment after taxes for producing tungstic oxide varies with the value of tungstic oxide. The tungstic oxide recovery process was chosen because this process has the highest valued product and thus the highest rate of return on investment. Although the tungstic oxide value is not published regularly, it is estimated to be about \$1.53/lb WO_3 over the published value of tungsten concentrate. For a 15-pct rate of return on investment after taxes, a concentrate value of \$6.71/lb WO_3 is required, which is roughly equivalent to its value in 1981.

The cost of the QRF ion-exchange resin is not well known since it is not commercially available today. For this report, its cost has been estimated to be \$200/ft^3. The initial

investment of $728,500 to fill the columns is about 11 pct of the fixed capital cost. The estimated $200/ft³ resin cost is based on the large initial resin purchase to fill the columns. Makeup resin will be purchased in much smaller lots and may cost more. Raising the makeup resin cost 50 pct to $300/ft³ will increase operating cost about $0.03/lb WO_3 or about 0.5 pct of the cost to recover tungstic oxide.

TABLE. A-2.—Estimated operating cost for recovering tungstic oxide from Searles Lake brine, dollars per pound WO_3 recovered

	Primary ion exchange	Acidification	Secondary ion exchange	Impurity removal	Drying and calcination	Total
Direct cost:						
Raw materials:						
Sodium carbonate at $0.06/lb	$0.28	$0.00	$0.00	$0.00	$0.00	$0.28
Sulfuric acid at $35/ton	.00	.08	.00	.00	.00	.08
Ammonium hydroxide at $0.11/lb	.00	.00	.01	.00	.00	.01
Magnesium oxide at $0.20/lb	.00	.00	.00	.01	.00	.01
Makeup resin at $200/ft³	.07	.00	.00	.00	.00	.07
Total	.35	.08	.01	.01	.00	.45
Utilities:						
Electric power at $0.065/kW·h	.13	.05	.01	.00	.03	.22
Process water at $0.50/Mgal	.06	.00	.00	.00	.00	.06
Raw water at $0.05/Mgal	.00	.00	.00	.00	.01	.01
Natural gas at $5.70/MMBtu	.00	.00	.00	.00	.05	.05
Steam, 15 psig at $8/Mlb	.00	.25	.00	.00	.00	.25
Total	.19	.30	.01	.01	.09	.59
Direct labor	.18	.00	.18	.09	.09	.54
Plant maintenance	.33	.04	.03	.01	.21	.62
Payroll overhead	.13	.01	.07	.03	.07	.31
Operating supplies	.07	.01	.00	[1].00	.04	.12
Royalty payment	NAp	NAp	NAp	NAp	NAp	.26
Total direct cost	1.25	.44	.30	.14	.50	2.89
Indirect cost	.20	.01	.09	.04	.12	.46
Fixed cost:						
Taxes and insurance	.18	.02	.01	.01	.06	.28
Depreciation	.90	.09	.07	.02	.32	1.40
Total operating cost	2.53	.56	.47	.21	1.00	5.03

NAp Not applicable.

[1]Rounded down to $0.00.

TABLE. A-3.—Estimated operating cost for recovering sodium tungstate from Searles Lake brine, dollars per pound WO_3 recovered

	Primary ion exchange	Acidification	Secondary ion exchange	Impurity removal	Drying and calcination	Total
Direct cost:						
Raw materials:						
Sodium carbonate at $0.06/lb	$0.28	$0.00	$0.05	$0.00	$0.00	$0.33
Sulfuric acid at $35/ton	.00	.08	.00	.00	.00	.08
Magnesium oxide at $0.20/lb	.00	.00	.00	.01	.00	.01
Makeup resin at $200/ft³	.07	.00	[1].00	.00	.00	.07
Total	.35	.08	.05	.01	.00	.49
Utilities:						
Electric power at $0.065/kW·h	.13	.05	.01	[1].00	.03	.22
Process water at $0.50/Mgal	.06	.00	[1].00	.00	.00	.06
Natural gas at $5.70/MMBtu	.00	.00	.00	.00	.06	.06
Steam, 15 psig at $8/Mlb	.00	.25	.00	.00	.00	.25
Total	.19	.30	.01	.00	.09	.59
Direct labor	.18	.00	.18	.09	.09	.54
Plant maintenance	.33	.04	.03	.01	.21	.62
Payroll overhead	.13	.01	.07	.03	.07	.31
Operating supplies	.07	.01	[1].00	[1].00	.04	.12
Royalty payment	NAp	NAp	NAp	NAp	NAp	.22
Total direct cost	1.25	.44	.34	.14	.50	2.89
Indirect cost	.20	.01	.09	.04	.12	.46
Fixed cost:						
Taxes and insurance	.18	.02	.01	.01	.06	.28
Depreciation	.90	.09	.08	.02	.31	1.40
Total operating cost	2.53	.56	.52	.21	.99	5.03

NAp Not applicable.

[1]Rounded down to $0.00.

TABLE. A-4.—Estimated operating cost for recovering scheelite from Searles Lake brine, dollars per pound WO_3 recovered

	Primary ion exchange	Acidification	Secondary ion exchange	Impurity removal	Drying and calcination	Scheelite recovery	Total
Direct cost:							
Raw materials:							
Sodium carbonate at $0.06/lb	$0.28	$0.00	$0.05	$0.00	$0.00	$0.00	$0.33
Sulfuric acid at $35/ton	.00	.08	.00	.00	.00	.00	.08
Magnesium oxide at $0.20/lb	.00	.00	.00	.01	.00	.00	.01
Calcium chloride at $0.05/lb	.00	.00	.00	.00	.00	.02	.02
Makeup resin at $200/ft³	.07	.00	[1].00	.00	.00	.00	.07
Total	.35	.08	.05	.01	.00	.02	.51
Utilities:							
Electric power at $0.065/kW·h	.13	.05	.01	.00	.03	.01	.23
Process water at $0.50/Mgal	.06	.00	[1].00	.00	.00	.00	.06
Natural gas at $5.70/MMBtu	.00	.00	.00	.00	.06	.01	.07
Steam, 15 psig at $8/Mlb	.00	.26	.00	.00	.00	[1].00	.26
Total	.19	.31	.01	.00	.09	.02	.62
Direct labor	.19	.00	.19	.07	.07	.07	.59
Plant maintenance	.33	.04	.03	.01	.21	.04	.66
Payroll overhead	.13	.01	.07	.03	.06	.03	.33
Operating supplies	.06	.01	[1].00	.01	.04	.01	.13
Royalty payment	NAp	NAp	NAp	NAp	NAp	NAp	.18
Total direct cost	1.25	.45	.35	.13	.47	.19	3.02
Indirect cost	.20	.02	.09	.04	.10	.04	.49
Fixed cost:							
Taxes and insurance	.18	.02	.01	.01	.06	.02	.30
Depreciation	.90	.09	.08	.02	.31	.10	1.50
Total operating cost	2.53	.58	.53	.20	.94	.35	5.31

NAp Not applicable.

[1]Rounded down to $0.00.

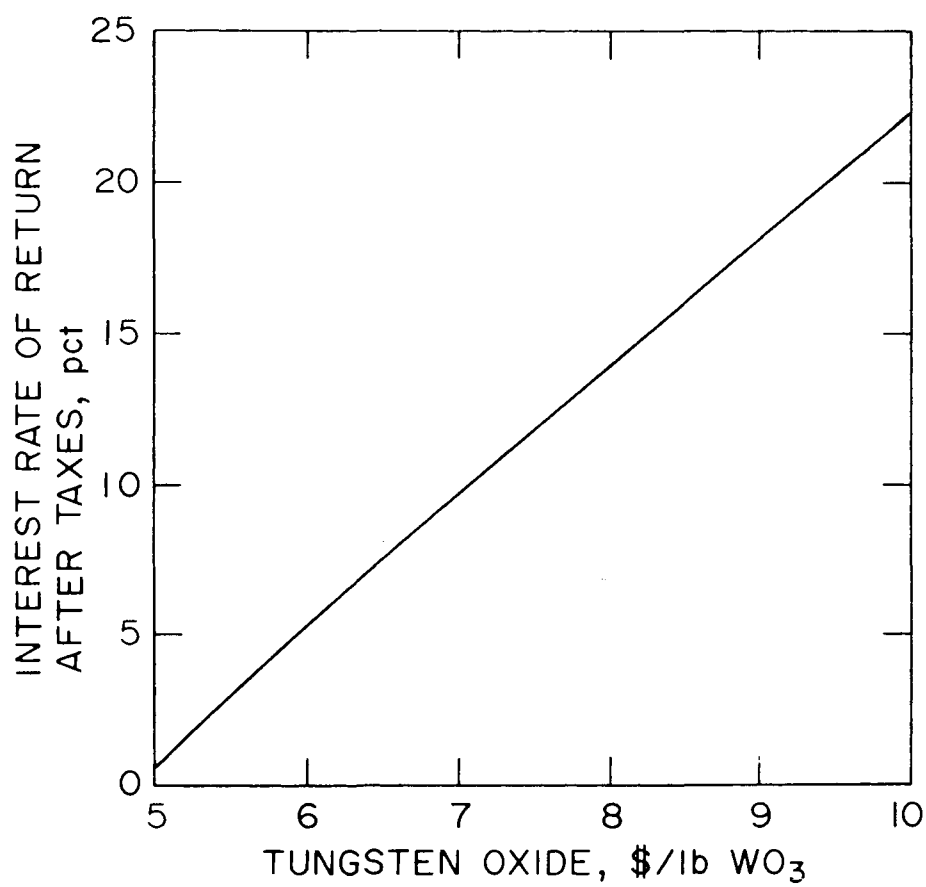

Figure A-1.—Interest rate of return on investment as function of tungstic oxide value.

APPENDIX B.—TUNGSTEN RECOVERY FROM SEARLES LAKE ARGUS BRINE

By R. O. Dannenberg,[1] P. L. Placek,[1] and D. C. Seidel[2]

DESCRIPTION OF FEED

An analysis of the Searles Lake brine from the Argus facility used in this investigation is shown in table B-1, together with an analysis of typical Searles Lake brine from the Westend facility. The raw Argus brine is less alkaline than the raw Westend brine, and the tungsten concentration in the Argus brine (0.040 g/L WO_3) is one-half the concentration in the Westend brine (0.080 g/L WO_3). A full description of the brines from Searles Lake is presented in chapter 1.

Test work on Westend brine showed that carbonation to reduce the brine pH to about 7.5 was essential for effective tungsten extraction (*5–6*).[3] Carbonation is an already existing step in the Searles Lake brine processing operations, reducing brine alkalinity to pH 7.5 to 8.5 at the Westend facility and to pH 7.5 at the Argus facility. Argus brine was transported to the Salt Lake City Research Center for testing. The brine was recarbonated to pH 7.5 to compensate for the increase in alkalinity during shipment, and the sodium bicarbonate crystals that resulted from the carbonation were settled out prior to feeding the solution to the ion-exchange system.

TABLE B-1.—Analysis of raw Searles Lake brines

	Argus facility	Westend facility
Analysis, wt pct:		
WO_3	0.0033	0.0062
NaCl	16.0	17.0
Na_2SO_4	6.7	7.6
KCl	1.3	4.3
Na_2CO_3	6.5	4.2
$Na_2B_4O_7$	0.5	1.2
Na_2S	0.06	0.2
$NaLi_2PO_4$	ND	0.07
Na_3PO_4	0.06	0.07
WO_3, g/L	0.040	0.080
Density, g/cm³	1.220	1.305
pH	8.5	9.8

ND No data.

EXPERIMENTAL PROCEDURE AND RESULTS

The scope of the Argus brine evaluation was determined by limitations imposed by the volume of feed solution available and other constraints. Only conditions found to produce the best results in earlier tests on Westend brine were tested on Argus brine. The same basic three-column system described in chapter 4 was used in both extracting and concentrating ion-exchange operations in this investigation.

Tungsten Extraction

Ion-exchange tests for tungsten extraction were conducted in three, 3-in-diam, transparent plastic columns with 36-in-deep beds of QRF resin. The resin bed volume was 4.2 L. Carbonated pH 7.5 brine was fed to the two columns in series at a flow rate of 5 gpm/ft² of column area, the rate found to give the best results in earlier tests on Westend brine. Tests were made using 110, 95, and 80 BV of brine per cycle. Multiple-cycle tests were made at each set of conditions to assure steady-state conditions. Table B-2 shows the test results together with the results of a test using a Westend brine for comparison. The resin capacity for tungsten from Westend brine was 2.4 to 2.7 times greater than that from the Argus brine. This result is reasonable because early test results demonstrated that QRF resin loading increases with increased tungsten concentration in the feed. Thus, treatment of Argus brine would require a larger capital investment in equipment and resin inventory to recover tungsten at the same rate.

Sorbed tungsten was eluted with a 5-g/L Na_2CO_3 solution at 0.5 gpm/ft² of column surface area. The primary eluate contained 0.7 g/L WO_3 compared with an average concentration of 1.3 g/L WO_3 in primary eluate from Westend brine. Thus, compared with elution of resin from Westend brine, elution of resin loaded from Argus brine would require approximately double the amount of sodium carbonate per pound of tungstic oxide.

TABLE B-2.—Primary ion-exchange test results

	Argus brine			Westend brine, 110 BV/cycle
	110 BV/cycle	95 BV/cycle	80 BV/cycle	
Brine pH	7.5	7.5	7.5	7.6
WO_3, pct:				
Extracted	68	89	93	90
Eluted	99	94	93	96
Resin loading, g/L WO_3	3.0	3.4	3.0	8.0
Resin requirements, ft³/lb WO_3	5.3	4.7	5.4	2.0

Secondary Ion Exchange

Primary eluate containing 0.7 g/L WO_3 was concentrated to 83 g/L WO_3 using a secondary ion-exchange system similar to that described in chapter 5. The primary eluate, after acidification to pH 2.8 with H_2SO_4, was passed through a series of two 0.75-in-diam columns containing 36-in beds of resin at a flow rate of 5 gpm/ft² of cross-sectional area. Of the tungsten, 95 pct was extracted from 178 BV of primary eluate; this percentage is approximately equivalent to that of the secondary ion-exchange recovery achieved from the Westend brine.

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[2]Research supervisor.
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[3]Italic numbers in parentheses refer to items in the list of references preceding the appendixes.

Secondary elution was accomplished with 2*N* NH_4OH solution at a flow rate of 0.65 gpm/ft² using a five-stage split-elution technique as follows:

1. Displace remaining primary eluate with 1 BV of water. Recycle effluent to feed for the next cycle.
2. Displace wash water with 1 BV of strong 2*N* NH_4OH solution recycled from step 4 of previous cycle; discard effluent.
3. Displace strong recycle with 1 BV of weak 0.1*N* NH_4OH solution recycled from step 5 of the previous cycle. Save effluent for product recovery.
4. Displace weak recycle with 1 BV of fresh 0.1*N* NH_4OH. Add fresh NH_4OH to effluent to increase strength to 2*N* and recycle to step 2 of next cycle.
5. Displace weak recycle with 1 BV of 0.6*M* H_2SO_4. This conditions the resin for the next extraction cycle. Recycle effluent to step 3 of the next cycle.

Over 99 pct of the sorbed tungsten was recovered in a concentrated NH_4OH eluate containing 83 g/L WO_3. The secondary eluates produced from the Argus brine were approximately the same grade as those obtained from the Westend brine. Based on test work on Westend brine presented in chapter 5, a 2*N* Na_2CO_3 solution would be expected to work as well as the NH_4OH solution for secondary elution.

Product Recovery

Two methods were used to recover a tungsten product from secondary NH_4OH eluate containing, in grams per liter, 83 WO_3, 1.5 As, 0.2 B_4O_7, and 1.5 P_2O_5. In both methods, arsenic and phosphorus impurities, which are particularly objectionable to refiners at levels exceeding 0.2 and 0.08 pct (*38*), respectively, were precipitated by adding MgO (*42*).

The first product-recovery method, which produced tungstic oxide, was the same as the method used on Westend NH_4OH secondary eluate and comprised the following steps:

1. Add enough MgO to produce a Mg-As weight ratio of 3:1.
2. Filter the MgO precipitate containing the inorganic impurities.
3. Evaporate the filtrate to dryness.
4. Roast the evaporite for 4 h at 600° C to destroy the organic impurities.

Table B-3 shows the analysis of the tungstic oxide together with the analysis of tungstic oxide from Westend NH_4OH secondary eluate.

The second product-recovery method, which produced synthetic scheelite, was different from that used on Westend eluate and comprised the following steps:

1. Add the stoichiometric amount of $CaCl_2$ to convert the tungsten to calcium tungstate.

TABLE B-3.—Analysis of tungsten products, weight percent

	Scheelite		Tungstic oxide	
Component	Argus	Westend	Argus	Westend
WO_3	79.0	79.0	87.3	86.0
Ca	12.	13.2	ND	ND
As	1.2	.1	.9	.1
P_2O_5	1.	.3	2.	.2
B_4O_7	.07	.01	.8	ND

ND No data.

2. Add MgO at a Mg-As weight ratio of 3:1.
3. Filter the MgO precipitate containing the inorganic impurities.
4. Evaporate the filtrate to dryness.
5. Roast the synthetic scheelite evaporite for 4 h at 600° C to destroy the organic impurities.

Addition of the $CaCl_2$ in step 1 did not precipitate any calcium tungstate from Argus NH_4OH secondary eluate, whereas similar treatment of NH_4OH secondary eluate from Westend brine precipitated 64 pct of the tungsten. This difference is attributed to the higher concentration of organic material in the Argus eluate, which appears to form an organotungsten complex. Table B-3 shows the analysis of the scheelite product from NH_4OH Argus secondary eluate together with the analysis of a scheelite product precipitated from Westend NH_4OH secondary eluate. Arsenic and phosphorus rejection by precipitation with MgO was not as complete as that achieved in the treatment of Westend ammoniacal eluate.

The tungsten concentration in the scheelite and the tungstic oxide prepared from the Argus brine was comparable to that in the products from Westend brine. Impurity levels, however, were higher in both Argus products. The MgO purification step was less effective in the Argus product recovery system.

CONCLUSIONS

Tungsten can be effectively recovered from carbonated Argus brine using an ion-exchange system similar to that proven effective for treating Westend brine; however, the resin capacity for tungsten is approximately 2.5 times greater when treating Westend brine than when treating Argus brine. Consequently, compared with treatment of Westend brine, treatment of Argus brine would require nearly 2.5 times as much resin to recover tungsten at the same rate. Equipment and reagent requirements would be similarly increased. The purity of the tungsten product from the Argus brine was slightly lower than the purity of the product from the Westend brine.