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## Selective Extraction of Tungsten from Searles Lake Brines

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### ABSTRACT

Tungsten was successfully extracted from the brines of Searles Lake, Calif., in a demonstration unit based on 9 years of laboratory research conducted by the U.S. Department of the Interior, Bureau of Mines. Pilot-scale operation was initiated in July 1979 at the Westend facility of the Kerr-McGee Chemical Corp. at Trona, Calif. The extractive method, based on a novel ion exchange resin, resulted from research supporting one of the Bureau's goals: helping to insure an adequate supply of minerals to meet national economic and strategic needs. The objectives met during pilot testing included proving operational viability during seasonal changes in brine properties, concentrating the tungsten to enable concluding tungsten recovery research, supplying escalation data necessary for commercialization, and confirming earlier small-scale laboratory work. The demonstration unit typically removed 92 percent of the tungsten from alkaline brine using QRF (8-hydroxyquinaline-resorcinol-formaldehyde) resin beads produced by the Bureau. A "merry-go-round" system was employed whereby two 12-inch-diameter resin beds were loaded in series while a third bed was eluted. Testing was concluded after treating over 500,000 gallons of brine. Tungsten, isolated in the primary ion exchange system, was reconcentrated in a secondary ion exchange system. Several tungsten products were produced from tungsten-rich solutions.

### INTRODUCTION

Tungsten, a hard and heat-resistant metal, is essential to the Nation's economy and defense. Domestic reserves, however, are not sufficient to meet projected demands. Domestic production provides less than 40 percent of our demand for primary tungsten, and increasing demands far exceed our ability to produce additional metal. Unless new reserves are developed through mineral discoveries or by improved extraction techniques to economically recover tungsten from low-grade sources, our reliance on imported tungsten will increase (1).

The largest known single domestic tungsten deposit is at Searles Lake, Calif. This nearly dry brine lake contains an estimated 170 million pounds (2) of tungstic oxide representing nearly 50 percent of our known reserves (1). Although brine chemicals are extracted from the lake, an economical method for tungsten recovery has been an unsolved problem. Mindful of this opportunity, the Bureau of Mines has conducted research to recover Searles Lake tungsten as part of the Bureau's mission to help insure future supplies of critical minerals by improving domestic supply capabilities.

Tungsten recovery from the lake brines has been an elusive target during 40 years of industrial searching for economical extractive technology. Although several methods have been devised for tungsten recovery, none have proven economical. The Bureau has developed an extractive technique based on the synthesis of a novel ion exchange resin that selectively removes tungsten from lake brine without the need for altering brine characteristics specifically for tungsten removal. Advantage is taken of the availability of brine that has been made less alkaline by carbonation to produce sodium bicarbonate. This is very important from an economic standpoint.

Results of laboratory testing at the Salt Lake City Research Center were reported in 1978 (3). The purpose of this report is to acquaint you with the results of escalated testing performed at the Westend plant of the Kerr-McGee Chemical Corp. at Searles Lake.

TABLE 1. Typical Searles Lake Brine Analysis

Constituent	Analysis
NaCl.....	wt-pct.. 17.0
Na <sub>2</sub> SO <sub>4</sub> .....	wt-pct.. 7.6
KCl.....	wt-pct.. 4.3
Na <sub>2</sub> CO <sub>3</sub> .....	wt-pct.. 4.2
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .....	wt-pct.. 1.2
Na <sub>2</sub> S.....	wt-pct.. .2
NaLi <sub>2</sub> PO <sub>4</sub> .....	wt-pct.. .07
Na <sub>4</sub> PO <sub>4</sub> .....	wt-pct.. .07
WO <sub>3</sub> .....	wt-pct.. .0062
Density.....	1.305
pH.....	9.8

DESCRIPTION OF THE RESOURCE

Searles Lake is a nearly dry brine deposit in the Mojave Desert, 130 miles northeast of Los Angeles. About 50 percent of the deposit is brine encased in a lattice of salts. Mud and salt encrust almost all of the 35-square-mile surface. The saturated brine, described in table 1, is a complex mixture containing varying concentrations of tungsten ranging up to 80 milligrams of tungstic oxide per liter.

The Kerr-McGee Chemical Corp. operates three brine-treatment plants at Searles Lake: the Westend, Trona, and Argus facilities. These plants extract soda ash, borax, salt cake, and other brine chemicals from the lake, and depleted brine containing nearly 2 million pounds of tungstic oxide is returned to the lake every year. Recovery of this tungsten could have reduced our dependency on imported tungsten by nearly 24 percent in 1979 (1).

PROCESS DESCRIPTION

The practicality of the Bureau's tungsten recovery process is based on three key points:

- The availability of a tungsten sorbent effective for treating alkaline brine.
- Access to brine less alkaline than raw Searles Lake brine.
- Access to brine where brine wells are developed and pumping costs and process infrastructure are supported by an existing industry.

An effective tungsten sorbent was developed by the Bureau specifically for the task. The ion exchange resin, called QRF, is a translucent, amber, gel-type bead synthesized from 8-hydroxy-quinoline, resorcinol, and formaldehyde. Resin synthesis is simple, relative to the production of more conventional, styrene-divinyl-benzene resins. The Bureau's resin is unique in that tungsten is effectively sorbed at pH 8.5, although tungsten sorption improves markedly with solution acidity. Thus, tungsten extraction from raw lake brine at pH 9.8 is impractical using QRF resin. However, brines at pH 8.5 and less are available as in-process streams at Kerr-McGee's facilities at Searles Lake. Brine extraction costs are supported by this industry. Thus, the key points have been satisfied, and full-scale tungsten recovery now depends on demonstrating process profitability.

Several conceptual flowsheets for enabling tungsten recovery are being considered. The flowsheet depicted in figure 1 shows one option whereby tungsten is removed from carbonated brine and concentrated using primary and secondary ion exchange circuits followed by tungsten recovery as sodium tungstate. The ion exchange circuits operated effectively in both laboratory-and pilot-scale testing. Product recovery was tested in the laboratory.

The primary ion exchange circuit removed 92 percent of the tungsten from pH 8.2 carbonated brine. The brine, depleted of tungsten, was returned to the process for recovery of borax and other brine chemicals. Nearly all of the tungsten was eluted with a 0.5 percent solution of soda ash dissolved in potable water. Eluate from the primary circuit, containing 1 to 2 grams tungstic oxide per liter, was acidified to pH 2.8 to improve tungsten sorption, and tungsten was reconcentrated in a small secondary ion exchange unit.

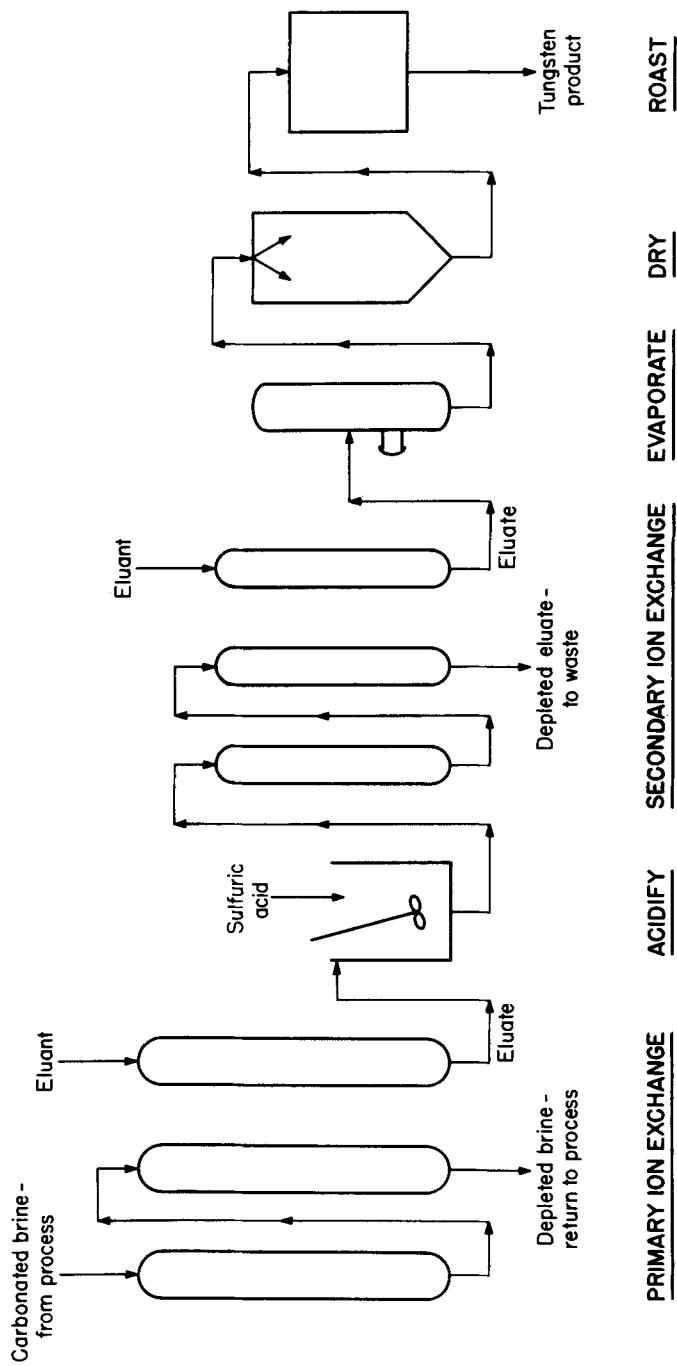


FIGURE 1. - Simplified flow diagram for recovering tungsten from Searles Lake brine.

Acidification at this point appeared economical because the volume of primary eluate was small and eluate contained little of the acid-consuming brine salts. Elution now produced a solution containing 80 to 100 grams of tungstic oxide per liter. Thus, the tungsten was concentrated a thousandfold. The eluate was evaporated, spray-dried, and calcined to produce sodium tungstate. Calcination, not ordinarily required, was necessary in this case to remove organic compounds coextracted from the brine.

DATA FOR TESTING

The specific objectives for piloting the new tungsten technology were to--

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

Although brine tested in the Salt Lake City laboratory had been carbonated in Kerr-McGee's Westend plant, changes in the brine's chemistry had taken place during transit. An increase in brine pH was corrected by recarbonation, with a consequent fallout of brine salts. This experience raised an important question: Does aged, recarbonated brine behave identically to fresh brine? Also, tungsten elution is markedly influenced by water quality. Two types of water are available at Searles Lake--brackish process water and potable water. Much of the laboratory testing was done using simulated Searles Lake waters, and this raised another important question: Would simulated and actual waters behave identically?

Laboratory testing produced insufficient tungsten-rich eluate for both tungsten recovery and use in solvent extraction and secondary ion exchange circuits. Clearly, large primary ion exchange equipment was needed to provide a good supply of eluate.

Although industrial ion exchange systems have been escalated from 3-inch-diameter column data, the use of larger columns provides much more credible escalation data.

Accelerated testing in the laboratory indicated a good life expectancy for the QRF resin; however, because resin replacement cost is an important economic factor, long-term operation under plant conditions appeared essential to substantiate the results of laboratory testing.

Finally, process demonstration at the site using plant personnel for operation and observation was essential for establishing credibility leading to successful technology transfer.

Pilot-scale research over the past 2 years included five phases:

- Resin synthesis and equipment construction.
- Startup at Searles Lake in July 1979.
- Baseline establishment from August 1979 to March 1980.
- Testing of process variations from March through June 1980.
- Secondary reconcentration from June through July 1980.

#### RESIN SYNTHESIS AND EQUIPMENT CONSTRUCTION

Nearly 20 cubic feet of QRF resin were synthesized to provide 20- to 48-mesh beads for charging the primary and secondary ion exchange columns. Resin was produced in semicommercial equipment at the Salt Lake City Research Center.

Three acrylic ion exchange columns, 11.5 inches in inner diameter and 10 feet tall, comprised the primary system shown in figure 2. Each was initially filled to a 3-foot depth with QRF resin. The columns were constructed in Salt Lake City and were moved to Searles Lake. The unit was designed to operate in a "merry-go-round" fashion. Figure 3 shows the arrangement of essential piping details for three-column loading and elution. That is, two columns were loaded in series while the third column was eluted. At the end of a cycle, the second loading column was

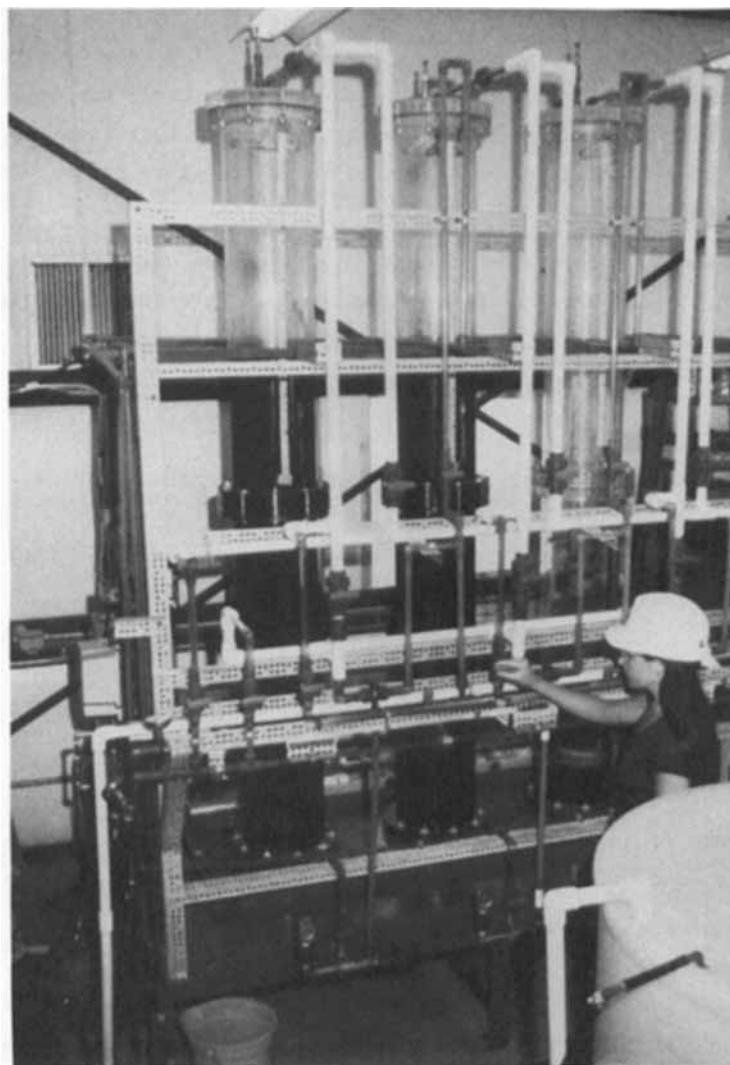


FIGURE 2. - Primary ion exchange columns.

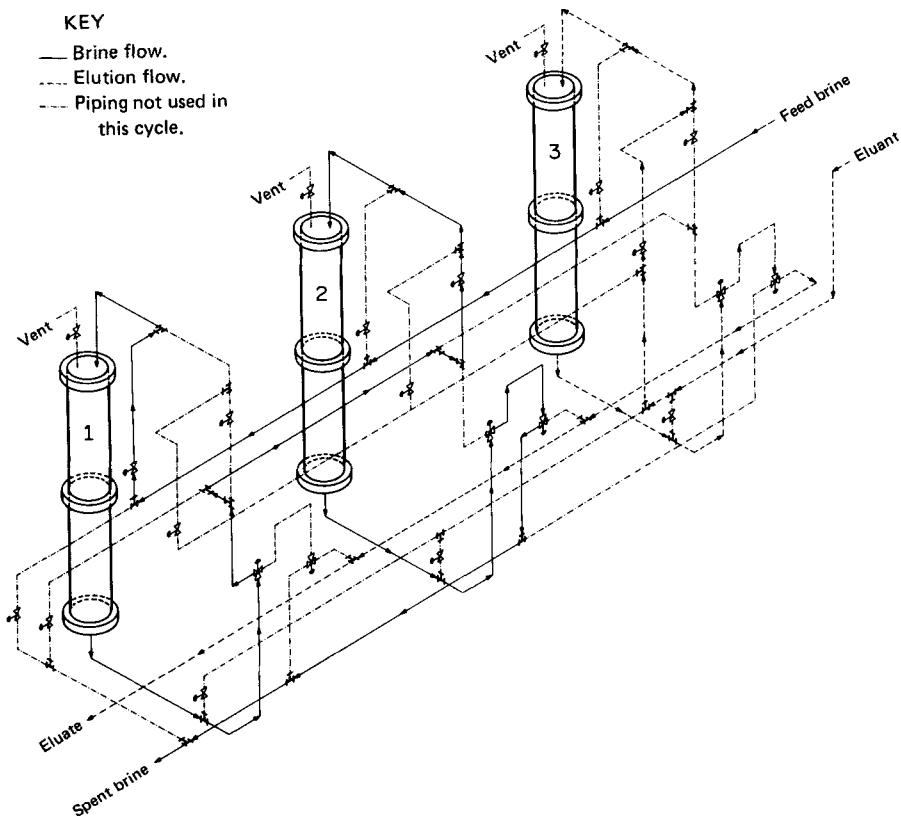


FIGURE 3. - Arrangement of essential piping details for three-column loading and elution.

advanced to the lead load position, the eluted column became the scavenger column, and the loaded column was eluted. The secondary ion exchange system was operated identically, using 2.9-inch-inner-diameter columns with 3-foot resin beds.

Equipment arrangement for supporting the primary ion exchange system is shown in figure 4. The supporting equipment for the primary system was comprised of a feed tank, eluant mix tanks, and eluate and spent brine receivers. Both brine and eluant were con-

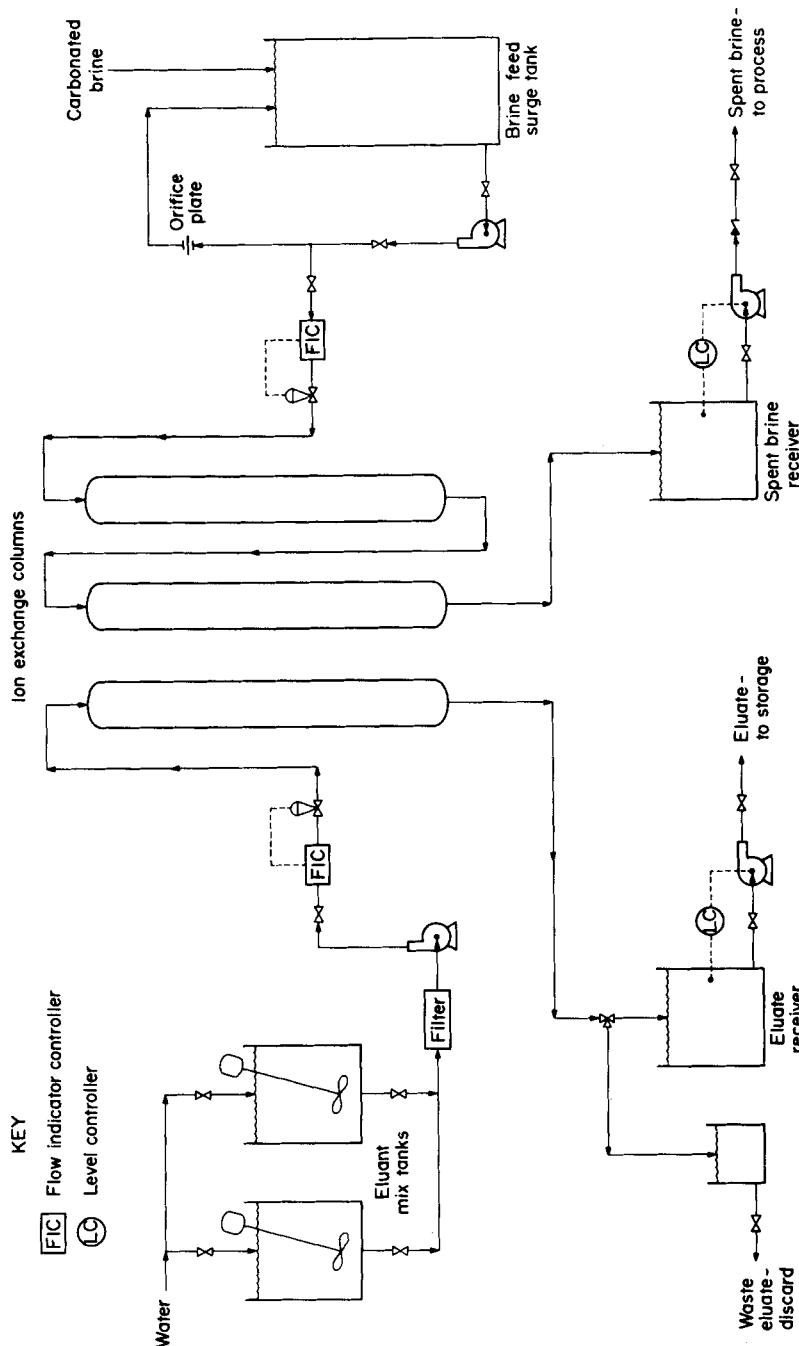


FIGURE 4. - Equipment arrangement for supporting the primary ion exchange system.

trolled by electronic flow indicator controllers. Spent brine and eluate were pumped intermittently when signaled by level sensors.

#### STARTUP

Primary system startup was complicated by two unexpected conditions. The brine was turbid with suspended soda crystals, and the pH was 8.7. Laboratory testing had been conducted with clear, pH 7.5 brine. This experience was our introduction to nonuniformity in brine quality, which changed seasonally and with variations in brine carbonation. Tungsten sorption at pH 8.7 was much less than that at pH 7.5, and the suspended solids blinded the resin beds. Startup was plagued with frequent shutdowns to backwash the columns, dislodge the accumulated crusts, and prevent a disastrous pressure buildup. These problems were alleviated when plant feed composition was changed, causing carbonated brine pH to drop to 8.2 and suspended solids to decrease.

Over the years of testing, brine composition varied from day to day and season to season. All results reported herein were obtained during the experimental campaign of March through June 1980.

#### BASELINE TESTING

##### Baseline Operating Conditions for Extraction

One thousand and seven gallons of pH 8.2 brine, or 65 bed volumes, were treated in each cycle of the primary system at a flow rate of 3.6 gallons per minute, or 5 gallons per minute per square foot of cross-sectional area. Brine temperature was 90° F. The 4.9-hour cycle time was determined by the amount of feed necessary to saturate the lead load column with tungsten. Pressure drops across the lead column and scavenger column were 15 and 10 pounds per square inch, respectively. See figure 5 for a typical two-column tungsten extraction history. The loading profiles show tungsten concentrations in column effluents as a function of brine throughput.

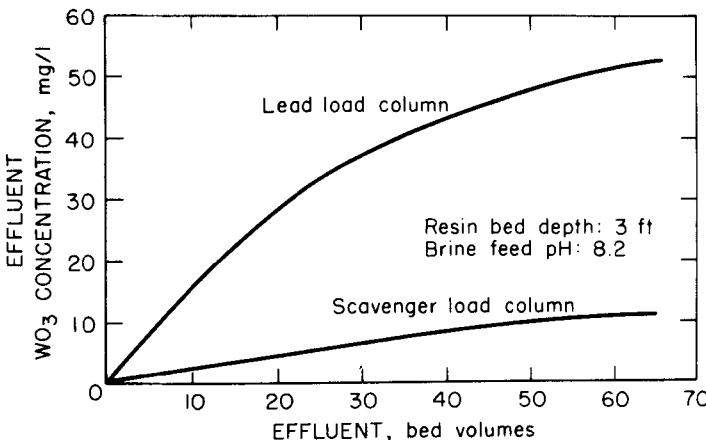


FIGURE 5. - Typical two-column tungsten extraction history.

#### Baseline Operating Conditions for Elution

Tungsten was eluted using 81 gallons, or 5 bed volumes, of 0.5 percent soda ash dissolved in potable water. Solution flow rate was 0.5 gallon per minute per square foot of cross-sectional area, and elution temperature was 90° F. Pressure drop across the column during elution was about 1 pound per square inch. A typical tungsten elution history is shown in figure 6. Essentially all of the tungsten was eluted by five bed volumes of eluant. The first bed volume of column effluent was displaced brine, which was returned to the lake. Bed volumes 2, 3, and 4 contained 90 percent of the eluted tungsten at an average concentration of 1.4 grams WO<sub>3</sub> per liter. The fifth bed volume was returned to the lake, but in a full-scale facility it would be recycled with fresh eluant to recover contained tungsten and to conserve scarce water.

#### Results of Baseline Testing

The most important accomplishment during operation of the primary ion exchange system was the successful operation of the unit in spite of occasional plant upsets and changes in brine quality. The unit operated in spite of occasional inclusions of

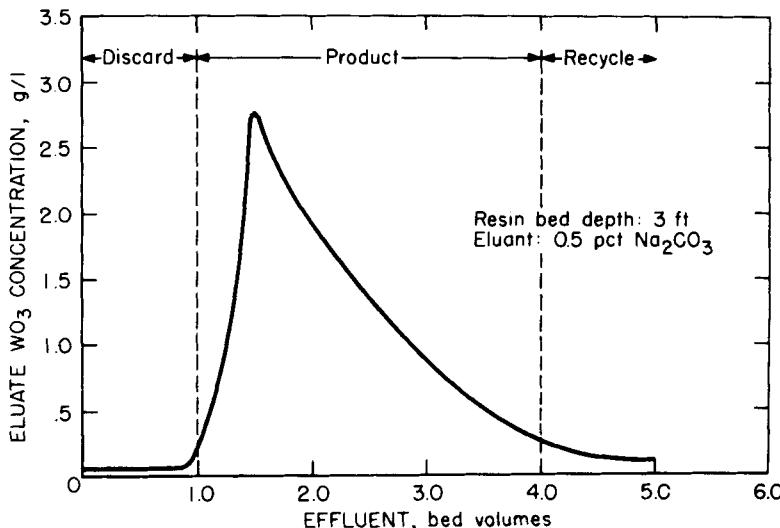


FIGURE 6. - Typical tungsten elution history.

foreign materials, lubricating oil, and algae growths. Furthermore, field test results were as good as or better than laboratory results that were obtained using aged brine. For example, using pH 8.2 brine, resin loadings of 4.6 and 3.9 grams  $\text{WO}_3$  per liter of resin were achieved at Searles Lake and in the laboratory, respectively. Thus, credibility was established between the two testing regimes.

The need to use potable water rather than brackish process water for tungsten elution was demonstrated. Solutions of either potable water or simulated brackish water containing 0.5 percent sodium carbonate were effective tungsten eluants in the laboratory. However, there were problems when actual brackish water was used for elution. Although soda ash in actual brackish water eluted the tungsten, only two-thirds the normal amount of tungsten was sorbed in the next cycle. Something in the brackish water blocked resin sites normally available to tungsten in subsequent loading cycles. Although potable water is scarce and expensive, potable water appeared necessary for successful operation.

The resin's sorptive stability showed no degradation during 12 months of intermittent operation, and no significant resin attrition was apparent based on resin screening tests. Thus, no evidence appeared that would indicate a short resin life.

Pressure drop across the loading columns proved to be much higher than observed during laboratory testing. Column pressures of 25 pounds per square inch and more were necessary to maintain target flows because suspended solids reduced resin bed void volume. The columns were visibly strained at 30 pounds per square inch. In March of 1980, the Bureau installed new acrylic ion exchange columns with a wall thickness sufficient to enable operation at 60 pounds per square inch.

Five hundred thousand gallons of brine were treated, and 15,000 gallons of primary eluate were produced during the first testing phase. Tungsten was concentrated from 0.08 gram WO<sub>3</sub> per liter in the brine to an average of 1.2 grams WO<sub>3</sub> per liter in the eluate. Other brine chemicals were not concentrated. For example, borate concentration in the brine was 10 grams per liter and only 1.4 grams per liter in the eluate. Arsenic concentration in the brine was 0.19 gram per liter and only 0.03 gram per liter in the eluate.

#### TESTING PROCESS VARIATIONS

Installation of the new ion exchange columns enabled doubling the feed rate of pH 8.2 brine without dangerously stressing the equipment. In addition, brine was acidified with sulfuric acid to pH 7.6 to simulate operations with less alkaline, highly carbonated brine.

#### Results of Testing Process Variations

Doubling the feed rate of pH 8.2 brine was not advantageous because tungsten extraction markedly diminished at the high flow rate. In one comparative test, for example, tungsten removal at 10 gallons per minute per square foot of cross-sectional area was only

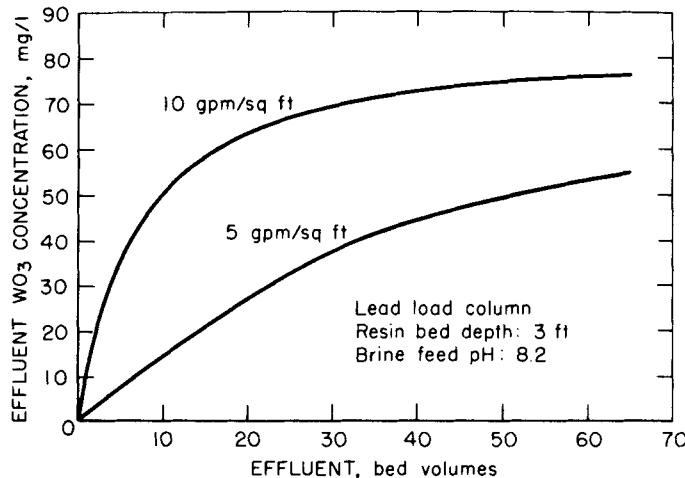


FIGURE 7. - Single-stage tungsten extraction versus feed rate.

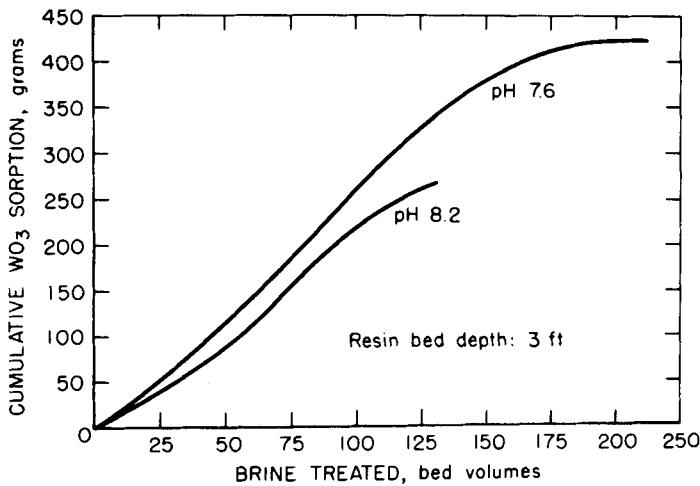


FIGURE 8. - Tungsten sorption versus feed pH during two loading cycles.

60 percent of the extraction achieved at 5 gallons per minute per square foot. See figure 7 for single-stage tungsten extraction versus feed rate. An advantage gained by reducing feed alkalinity was shown in comparative tests at pH 7.6 and pH 8.2 where the lead load column was in equilibrium with the feed. That is to say, effluent tungsten concentration from the lead load column equaled tungsten concentration in the feed. At pH 7.6, 1,780 gallons, or 110 bed volumes, of feed were treated in each cycle before resin in the lead column was saturated. At pH 8.2, however, only 65 bed volumes of feed were treated before resin in the lead column was saturated because of the lesser resin capacity for tungsten at pH 8.2. Figure 8 shows tungsten sorption versus feed pH during two loading cycles. It indicates treatment of 220 bed volumes at pH 7.6 and 130 bed volumes at pH 8.2 because these quantities of brine were treated in the two loading cycles that preceded elution. High resin loading enabled producing a more concentrated eluate. In comparable tests, eluates produced from resin loaded at pH 7.6 and pH 8.2 contained 2.5 and 1.4 grams  $WO_3$  per liter, respectively.

#### TUNGSTEN RECONCENTRATION

Tungsten was recovered directly from primary eluate in laboratory testing by coprecipitation with ferric hydroxide. The iron-tungsten precipitate is an intermediate product and must be treated further to recover tungsten for most uses. Primary eluate is too dilute to enable efficient recovery of marketable products such as ammonium paratungstate or tungstic acid. Reconcentration by solvent extraction proved troublesome, but a secondary ion exchange system proved effective. A three-column array was successfully operated in the laboratory and at Searles Lake. Composited primary eluate containing 1.2 grams  $WO_3$  per liter was acidified to pH 2.8, loaded in two 2.9-inch-diameter columns, and eluted in the third column using either 2 N ammonium hydroxide or 2 N sodium carbonate in potable water, which resulted in eluates containing 80 grams  $WO_3$  per liter. A variety of tungsten chemicals, including sodium tungstate, calcium tungstate, tungstic oxide, and ammonium paratungstate, was subsequently produced in the laboratory using secondary eluate.

CONCLUSIONS

The major conclusions resulting from pilot testing include--

- Bureau-devised technology successfully extracted tungsten from Searles Lake brines under a variety of conditions.
- Results of field testing and laboratory testing are in good agreement.
- Bureau-developed resin showed little, if any, physical or chemical degradation during field testing.

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