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**PROCESSING OF LEACH LIQUORS  
PRODUCED BY  
NUCLEAR SOLUTION MINING**

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# PROCESSING OF LEACH LIQUORS PRODUCED BY NUCLEAR SOLUTION MINING

## Abstract

It appears that solvent extraction represents the most efficacious way to recover copper from leach liquors produced by nuclear solution mining because of the chemical properties of the system as well as the radiochemistry of contaminated solutions. A brief review of the principles of solvent extraction is given, together with a description of commercial copper chelate extractants. The specific extractant that should be used will depend on the temperature and composition of leach liquor generated and to this end guidelines for extractant selection are included.

One important consideration with regard to the chemistry of the leach liquor is that, at room temperature, the leach

liquor is supersaturated with respect to gypsum. Study of this phenomenon showed that precipitation is slow and takes on the order of several weeks. An inherent advantage of this supersaturation is that co-precipitation of radioactive strontium is normally induced and, as a result, this nuclide should be removed effectively from the aqueous phase before the liquor enters the processing plant. It is anticipated that other nuclides may behave in a similar fashion. Finally, consideration is given to the type of nuclear device that might be used and the associated processing problems with each type. Brief attention is paid to engineering aspects of the system and how the process might be implemented.

## Introduction

The successful industrial use of commercial chelation-type extractants for the solvent extraction of copper from dilute acidic leach liquors has stimulated considerable interest by the copper industry in solvent extraction (SX) technology. The success of solvent extraction has arisen from both economical considerations and environmental pressure. Prior to its introduction in 1968, the end product from the leaching of oxide copper ores and low-

grade overburden generally was limited to cement copper, an inferior product containing approximately 85% Cu; quite satisfactory, however, to be used as feed material for conventional copper smelters. The art of copper cementation, an electrochemical reaction between metallic iron and copper (II) ions, was practiced by the ancients and was reported by Basile Valentine, a medieval alchemist, in the 16th century.<sup>1</sup> The small copper producer who does

not have his own smelter is placed at a serious disadvantage, especially in recent years when trying to market cement copper, for smelter capacities have been reduced significantly because of strict air pollution standards. Likewise, large producers have felt the pinch; indeed, some have been forced to shut down intermittently.

Essentially, solvent extraction provides an alternate hydrometallurgical

route and produces a purified, concentrated aqueous copper sulfate solution, for feed to an electrolytic tank house,\* from impure dilute leach liquors produced by dump leaching operations (see Fig. 1). The organic phase is recycled in a closed

\* Alternately,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  may be recovered from the concentrated solution by crystallization, although this technique has yet to be employed industrially.

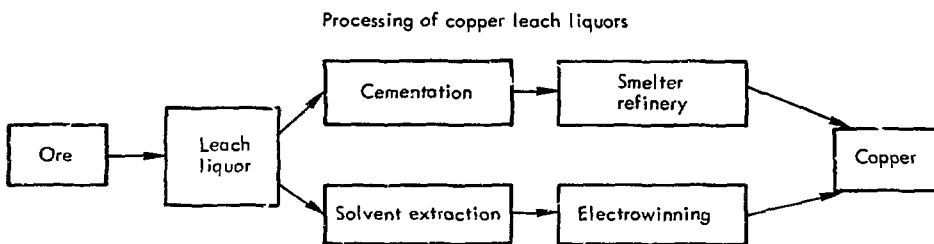


Fig. 1. Processing of copper leach liquors.

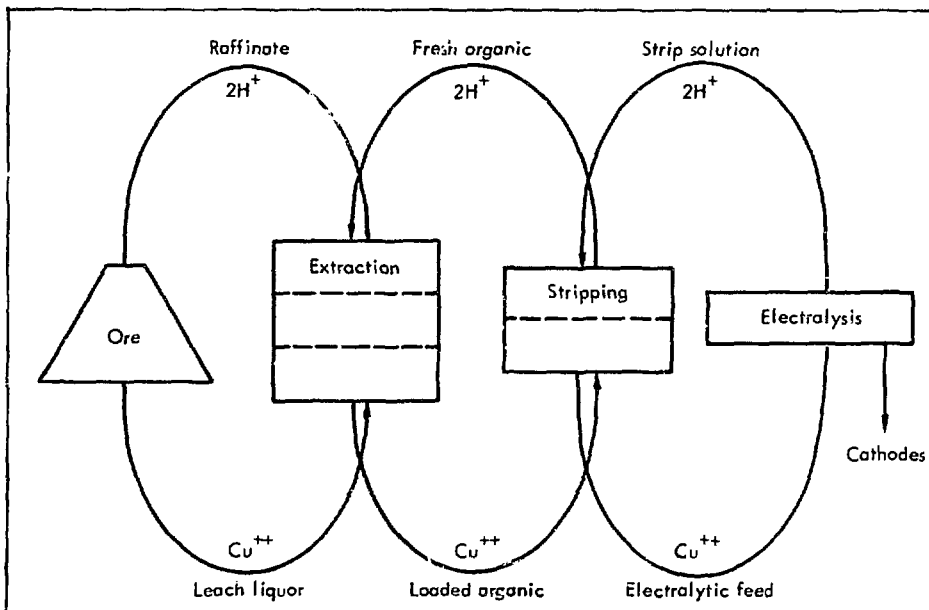


Fig. 2. Schematic representation of the solvent extraction for copper recovery.<sup>5</sup>

circuit and the cathode copper produced by electrolysis is 99.95% Cu, almost the equivalent of electro-refined copper produced by classical pyrometallurgical operations, in most instances acceptable for wire bar. A schematic representation of the SX process, which has been recommended<sup>2</sup> for processing leach liquor generated by nuclear solution mining, is shown in Fig. 2. In principle, the system operates in a closed cycle, presenting no pollution or waste disposal problems.

The purpose of this report is to review

SX technology, especially with regard to recent developments in copper recovery; and to evaluate the possible use of this technology for processing leach liquors which might be generated by nuclear solution mining, making recommendations for implementation. Specifically, is there anything about the leach liquor, such as its solution chemistry or radiochemistry, which prohibits the use of SX processes? Furthermore, if solvent extraction can be used, which extractant should be used and what size of plant will be required to effectively process the liquor?

## Solvent Extraction Chemistry

Basically, SX systems consist of an aqueous phase and an organic phase which upon contact with each other results in redistribution of the components of each phase in an attempt to attain chemical equilibrium. The object of the exercise is to try to isolate or separate one component from the others. In the organic phase, three components can frequently be identified. They are:

**Carrier:** Inert solvent, typically kerosene.

**Extractant:** An organic molecule capable of selectively reacting with some specified component of the aqueous phase.

**Modifier:** Typically a long chain alcohol which aids in phase disengagement and can prevent formation of a third phase. Deleterious effects may be realized in some

instances, i.e., the reaction rate may be reduced due to the surface activity of the alcohol.

Also, solvent extraction systems are characterized as to their mode of extraction which can be classified as follows:

**Solvation:** Simple solubility effects.

Certain neutral complexes are more soluble in an organic solvent than they are in water, e.g.,  $\text{UO}_2(\text{NO}_3)_2$  in tributylphosphate (TBP).

**Ion Exchange:** An exchange, between phases, of either cations or anions. Frequently this exchange is a proton for a metal ion, e.g.,  $\text{UO}_2^{++}$  extraction by di-2-ethylhexylphosphoric acid.

**Chelation:** Similar to ion exchange, but distinguished by the

ring structure formed and the fact that coordination positions of the metal ion are satisfied by the extractant rather than the solvent as might be the case in an ion exchange mechanism; e.g.,  $\text{Cu}^{++}$  extraction by hydroxyoximes.

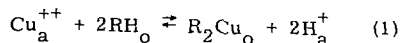
Further, common definitions, or terms, encountered in solvent extraction technology are extraction coefficient E, or distribution coefficient D, and selectivity factor. The extraction coefficient is rarely distinguished from the distribution coefficient, and the terms are used interchangeably. However, in a strict sense, the distribution coefficient only considers the partition of one species. These terms refer to the ratio of concentration of a given component in the organic phase to the concentration of the same component in the aqueous phase. The selectivity factor, as the term suggests, is a measure of the selectivity an extractant has for one component over another, and is simply the ratio of the respective extraction coefficients.

A variety of commercial chelating extractants is available for the extraction of copper under the following trade names: LIX<sup>®</sup> which is manufactured by General Mills, and Kelex<sup>®</sup> which is manufactured by Ashland Chemical Company.<sup>†</sup> In all

\*<sup>®</sup>Registered trade names of General Mills and Ashland Chemical respectively.

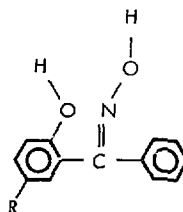
<sup>†</sup>Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

cases, the stoichiometry of the extraction and stripping reaction is as follows:



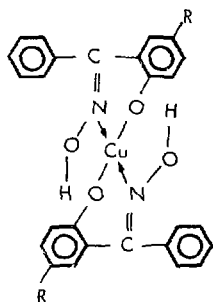
where RH represents the extractant molecule. The aqueous phase, subscript a, may contain significant quantities of iron, aluminum, calcium and magnesium, besides copper; and the composition of the organic phase, subscript o, is on the order of 10 vol% extractant in a kerosene carrier. In the case of the LIX-copper extraction system, a modifier is not used.

Basically, the extractants used are oximes and mixtures of hydroxyoximes which in the case of General Mills reagents can best be represented by a major component, LIX 65N, a phenolic hydroxyoxime having the following structure:

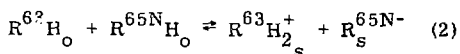


where R is an alkyl radical, most probably the nonyl group,  $-(\text{CH}_2)_8\text{CH}_3$ .<sup>3</sup> Chelation of the cupric ion occurs between the oxygen atom of the hydroxyl group, which releases its hydrogen, and the labile electron pair of the nitrogen atom, resulting in a stable, unsaturated, six-membered ring structure. Two molecules are required to satisfy the valence and coordination bonds of the cupric ion, resulting in an extracted species with a

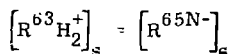
structure similar to the following:



In the case of the LIX 64N extractant (a mixture of LIX 65N and LIX 63, an aliphatic hydroxyoxime), the rate of extraction appears to be limited by the reaction of cupric ion at the interface with the phenolic hydroxyoxime. The reaction is first-order with respect to the cupric ion concentration, and half-order with respect to each of the extractant molecules. For details, the reader is directed to the work of Atwood.<sup>4</sup> The following reaction mechanism has been proposed for extraction with LIX 64N:

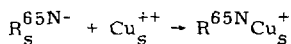


where

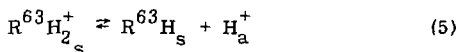
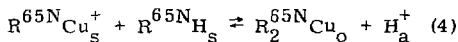


## Copper Solvent Extraction Practice

Because of the high specificity these extractants have for copper, the number of theoretical extraction stages are minimal (3 or 4), and coupled with the large volume flow rates, the mixer-settler reactor, shown in Fig. 3, is favored



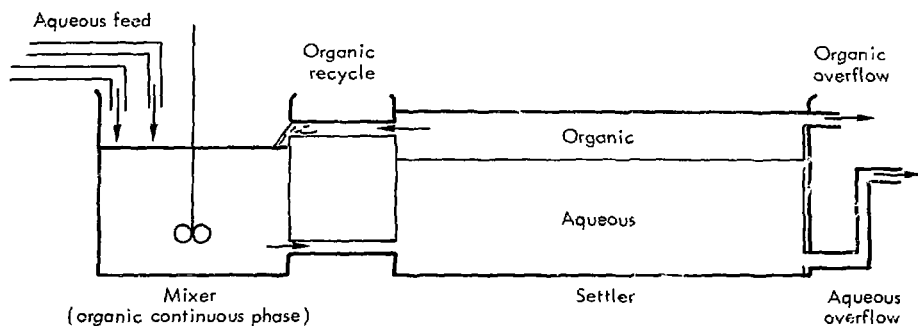
(rate-controlling step) (3)



The suite of chelating extractants available are such that any leach liquor containing from 1 to 60 gpl of Cu can be processed. Such flexibility is achieved by structural modifications of the hydroxyoximes which in effect changes the pK of the exchangeable hydrogen atom and consequently alters the extraction response.<sup>3</sup> It is recommended, as a rule of thumb, that for leach liquors containing >6-8 gpl Cu and in excess of 15 gpl acid that the LIX 70 series of extractants be used, which cost about \$3.00/lb. For more dilute solutions, the LIX 60 series of extractants should be used—the most popular being LIX 64N. This series of reagents costs approximately \$2.50/lb. The structural difference between the two series of extractants appears to be chlorination of the aromatic ring of the LIX 70 series which delocalizes the electrons on the hydroxyl oxygen and lowers the pK value of the extractant.

above other liquid-liquid extraction reactors.

At the present time, two plants are successfully using this new technology. They are Ranchers Exploration's Bluebird operation at Miami, Arizona which



Single stage mixer-settler

Fig. 3. Single-stage mixer settler with provision for recycle.

Table 1. Comparison of the leaching-solvent extraction circuit at Bluebird<sup>5</sup> and Bagdad.<sup>6</sup>

	Bluebird	Bagdad
<u>Leach liquor</u>		
Flowrate (gpm)	1000	3000
Copper (gpl)	3.0	1.3
Number of extraction stages	3.0	4.0
Acid (gpl)	3.8	--
<u>Raffinate (recycled for leaching)</u>		
Copper (gpl)	0.3	0.13
Acid (gpl)	2.8	--
Solvent loss	--	--
<u>Loaded organic</u>		
Flowrate (gpm)	2000	--
Copper (gpl)	1.37	--
Extractant (vol %)	7% LIX 64N (kerosene)	--
<u>Strip solution (spent electrolyte)</u>		
Acid (gpl)	100	--
Copper (gpl)	30	25
Number of stripping stages	2.0	3.0
<u>Electrolyte feed</u>		
Copper (gpl)	34	50

processes 1000 gpm and produces 16 tpd of copper; and Bagdad Copper's facility at Bagdad, Arizona which processes 3000 gpm and produces 23 tpd of copper. Another plant, the largest yet (14,000 gpm), is being constructed for N'Changa Consoli-

dated in Chingola, Zambia. The two operating plants process a leach liquor generated by dump leaching techniques. Characteristics of their leaching-solvent extraction circuits are compared in Table 1.<sup>5,6</sup>



Table 2. Operating cost data for a SX-electrowinning plant which produces 30,000 tons of Cu per annum from a leach solution containing 2 gpl Cu.<sup>8</sup>

Item	Cost (dollars per ton of Cu)
Power (1¢/kWh)	29.00
Organic solvent (assuming flotation unit)	6.00
Sulfuric acid	9.50 to 29.00, depending on leach operation
Utilities (steam, H <sub>2</sub> O, etc.)	2.00 to 5.00
Maintenance	2.00 to 5.00
Labor	24.00
<b>Total</b>	<b>\$72.50 to \$98.00</b>

As would be expected, the capital cost of a SX plant depends both on the copper production rate and on the flowrate of leach liquor. The variation in capital cost of a typical solvent extraction plant containing three extraction stages and two stripping stages as a function of leach liquor flowrate for a phase ratio of unity can be approximated by the following formula:<sup>7</sup>

$$\text{Investment cost} = \left(\frac{\text{FR}}{6}\right)^{0.73} \times 3.65 \times 10^6 \text{ dollars} \quad (6)$$

where FR is the flowrate of the leach liquor in units of 1000 gpm.

With regard to operating costs, Table 2 presents anticipated costs for both solvent extraction and electrowinning facilities for a plant producing 30,000 tons of copper annually from a leach liquor containing 2 gpl of copper.<sup>8</sup> These operating costs are estimated to be from 27% to 51% below those of the leaching-cementation approach. A major concern of most companies is solvent loss which, without a flotation unit, can vary between 0.2 gal solvent per 1000 gal of aqueous treated to 0.1 gal per 1000 gal, and corresponds to a cost of from 1 to 2 cents per pound of copper processed. In this regard, the projected organic solvent cost in Table 2 may be quite optimistic.

### Leach Liquor from a Nuclear Chimney

From both theoretical predictions and experimental observation, the leach liquor generated at the pilot plant is in equilibrium with hematite, Fe<sub>2</sub>O<sub>3</sub>, and anhydrite, CaSO<sub>4</sub>. The hematite forms as a result of pyrite and chalcopyrite oxidation and subsequent hydrolysis of

ferric iron. The anhydrite forms due to the reaction of sulfate ions, also a product of the sulfide oxidation, with calcium ions, which are released in acid solution from the decomposition of calcium minerals present in the rock.

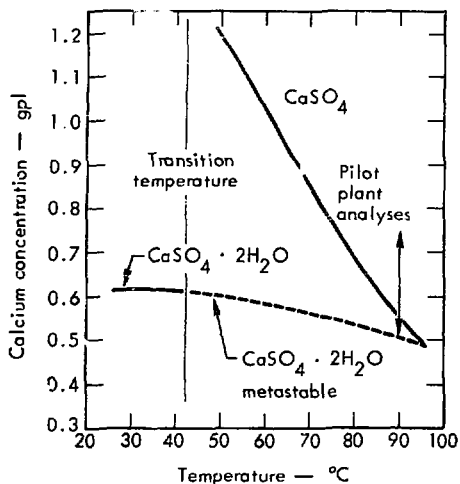


Fig. 4. Solubility of calcium sulfate in water as a function of temperature.<sup>9</sup>

In saturated, aqueous systems, calcium sulfate precipitates as anhydrite ( $\text{CaSO}_4$ ) at temperatures exceeding  $42^\circ\text{C}$ . However, below this temperature the dihydrate, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), is the stable form. The transition is accompanied by a significant change of solubility in water, as shown in Fig. 4. As is commonly reported, the solubility increases as the temperature is lowered. In this regard, it was, at first glance, surprising to find that analytical samples, taken from the pilot plant leach liquor ( $90^\circ\text{C}$ ), precipitated gypsum on aging for extended periods of time at ambient temperature. A closer look at the system, however, reveals that at the high ionic strengths ( $\approx 1.0\text{ M}$ ) and the high sulfate ion concentrations approaching 25 gpl encountered in the leach liquor, the temperature coefficient of solubility is inverted, i.e., the solubility of calcium sulfate decreases with a decrease in tem-

perature. Figure 5 shows calcium sulfate solubility data taken from the literature<sup>9</sup> in the presence of various soluble sulfates at a sulfate concentration of 25 gpl. Also included are the analyses of pilot plant liquor, sample 1-1-32, when sampled at  $90^\circ\text{C}$  (11/8/71) and after storage at room temperature (6/23/72). Notice that the solubility of calcium sulfate in the leach liquor samples conforms quite well with data from the literature, and accounts for the observed phenomenon.

A more important pragmatic consideration is: does this phenomenon present engineering problems in subsequent unit operations such as in a heat exchanger, filter press, or extraction circuit? The precipitation reaction is slow. Laboratory studies showed that precipitation occurs in about 2 weeks at  $50^\circ\text{C}$ , whereas at  $25^\circ\text{C}$  precipitation was not observed in

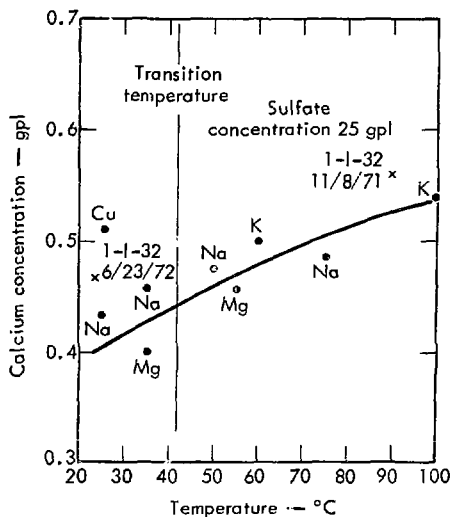


Fig. 5. Solubility of calcium sulfate in aqueous solutions containing 25 gpl sulfate as a function of temperature.<sup>9</sup>

the same time interval. Inferences from these results suggest that the reaction may be slow enough to present minimal problems in subsequent operations. However, it is recognized that precipitation from supersaturated solutions is strongly dependent on nucleation phenomena, and it may be that problems could arise.

For example, the vigorous contact with the organic phase in a mixer may provide the necessary nucleation sites to enhance the rate of precipitation. Initial laboratory shake-out tests with pilot plant leach liquor samples and LIX 64N indicated that although a small amount of precipitation had occurred at the interface, there was no problem with phase disengagement.

It is encouraging to note that strong evidence exists which indicates that formation of these salts, anhydrite in particular, may provide an effective mechanism (co-precipitation) for removal of radionuclides present in the leach liquor. A case in point is the behavior of strontium. In preliminary experiments by Sisson,<sup>10</sup> precipitation of anhydrite from a synthetic leach solution, spiked with radioactive strontium and in the presence of San Manuel ore fragments, results in a strontium removal which reduces the activity two to three orders of magnitude below the original activity. Such results are not unexpected in that co-precipitation is enhanced when the carrier, or substrate, contains a like cation and when the surface is of opposite charge to that of the tracer. Precipitation of anhydrite from high sulfate solution meets both these requirements. Further, it is anticipated that other radionuclides may be effectively gathered in this fashion. For example, it would not be unreasonable to expect

hematite to act as an effective carrier for ruthenium.

As mentioned previously, one matter of concern in processing the leach liquor produced by nuclear solution mining is the possible radioactivity resulting from the dissolution of radionuclides in the leach liquor. At ORNL, in 1971, the distribution and activity of radionuclides were estimated for a 50-kt device (90% fission).<sup>2</sup> After 300 days, tritium was predicted to be most abundant in the leach liquor, with significant amounts of <sup>106</sup>Ru. Estimates from this study, presented in Table 3, were based on rather cursory study of the rate of dissolution of radionuclides from chimney rubble and glass and do not accurately represent anticipated leaching conditions now being considered.<sup>11</sup> In particular, reaction times were relatively short—on the order of 16 hr—and the dissolution reaction was studied at 1 atm. Presently, the anticipated leaching process will take several years at high oxygen pressures and temperatures of approximately 100°C. To what extent these new leaching conditions will alter the estimated radionuclide concentrations in the leach liquor are unknown at the present time. However, experiments are in progress to this end.<sup>12</sup>

Extraction of copper from synthetic leach liquors has been studied both in batch tests and in a continuous experiment in which the copper was stripped and electrolyzed in a small electrolytic cell.<sup>2</sup> Extraction coefficients for radionuclides that might be present in the leach liquor were determined with two different extractants, LIX 64 and Kelex 100. The results obtained with LIX 64 are shown as a function of pH in Fig. 6. Notice that

Table 3. Estimated concentrations of radionuclides in circulating leach liquor for a 50-kt device (10% fission, 90% fusion).<sup>2</sup>

- Assumptions: (1) No migration of radionuclides from the chimney.  
 (2) Leaching at 300 days after the shot.  
 (3) Uniform distribution of the dissolved radionuclides in 45 million gallons of circulating leach liquor.

Isotope	Estimated percent dissolution	Concentration in leach liquor ( $\mu\text{Ci/ml}$ )
$^{96}\text{Zr}-^{95}\text{Nb}$	0.01 - 1	$6 \times 10^{-6} - 6 \times 10^{-4}$
$^{144}\text{Ce}$	0.01 - 1	$5 \times 10^{-6} - 5 \times 10^{-4}$
$^{141}\text{Ce}$	0.1 - 2	$2 \times 10^{-6} - 5 \times 10^{-5}$
$^{106}\text{Ru}$	0.1 - 2	$6 \times 10^{-5} - 9 \times 10^{-4}$
$^{103}\text{Ru}$	0.1 - 2	$4 \times 10^{-6} - 7 \times 10^{-5}$
$^{137}\text{Cs}$	0.1 - 2	$7 \times 10^{-6} - 1 \times 10^{-4}$
$^{125}\text{Sb}$	0.1 - 2	$3 \times 10^{-6} - 5 \times 10^{-5}$
$^{90}\text{Sr}$	0.5 - 5	$1 \times 10^{-5} - 1 \times 10^{-4}$
$^{89}\text{Sr}$	0.5 - 5	$3 \times 10^{-5} - 3 \times 10^{-4}$
$^{91}\text{Y}$	0.5 - 5	$5 \times 10^{-5} - 5 \times 10^{-4}$
$^{147}\text{Pm}$	0.001 - 0.1	$1 \times 10^{-7} - 1 \times 10^{-5}$
$^3\text{H}$	100	6

most of the radionuclides have rather low extraction coefficients compared to that of Cu. Ruthenium-106, a significant contaminant of Cu in the cementation process, as well as tritium have extraction coefficients of  $<0.005$ . Fortunately, the three radionuclides with significant extraction coefficients  $^{95}\text{Zr}-^{95}\text{Nb}$ ,  $^{110}\text{Ag}$ , and  $^{59}\text{Fe}$ —are expected to be present at rather low concentrations in the leach liquor, thus minimizing potential radiation hazards. The extraction coefficients were determined for a 5-min reaction time. Noticeably absent in these experiments were uranium and plutonium of which the latter may be worthy of consideration, especially if a fission nuclear explosive containing plutonium were used to create the chimney.

Results from the continuous SX-electrowinning circuit were encouraging in that the electrolytic Cu produced had a very low-level radioactivity ( $1 \times 10^{-5} \mu\text{Ci/g}$ ) which was due to  $^{106}\text{Ru}$  and could only be detected on a special high-sensitivity, low-counting instrument. By way of comparison, in the cementation system  $^{106}\text{Ru}$  contamination of cement Cu reached a level of  $0.1 \mu\text{Ci/g}$ . The final electrolyte contained  $0.005 \mu\text{Ci/l}$  of  $^{95}\text{Zr}-^{95}\text{Nb}$  and  $0.01 \mu\text{Ci/l}$  of  $^{106}\text{Ru}$ . In view of the low extraction coefficient of Ru, it appears that the transfer mechanism is probably aqueous phase entrainment, rather than an exchange reaction. If Ru is transferred (which is unlikely), centrifugation of the loaded organic phase might be necessary.

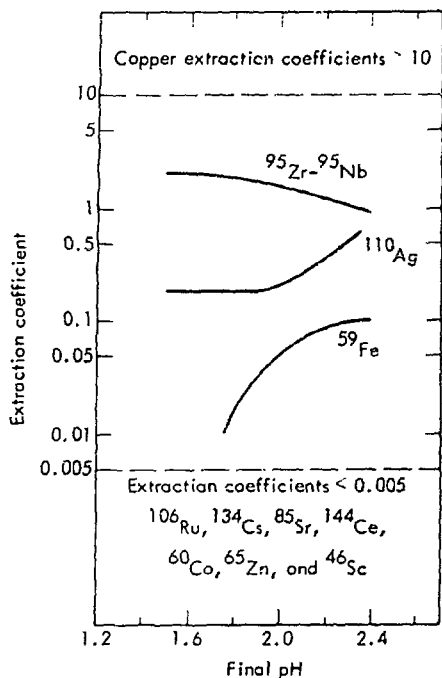


Fig. 6. Extraction coefficients of selected radionuclides as a function of pH with LIX 64.<sup>2</sup>

To adequately assess the concentration of radionuclides which might be expected in leach liquor generated by nuclear solution mining, the extraction of Zr and Ru should be studied in further detail. It may be that their extraction coefficients can be lowered by a sulfate complexation reaction in the stripping section or in the electrolytic cell. Further advantage can be realized by operating the SX system close to maximum loading with respect to Cu which should minimize the extraction of unwanted radionuclides.

If a fusion explosive were used, personnel exposure to tritium should be considered. The major concern would arise

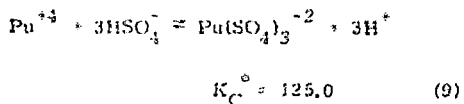
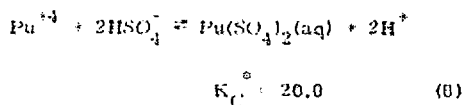
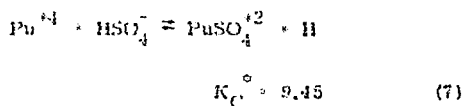
from ingestion and inhalation of tritium from either the gaseous or aqueous phase. The extraction plant can be adequately vented and controlled. However, the tank house presents problems in that a mist or spray is generated due to the anodic reaction and the temperature of the electrolyte. Furthermore, the finished cathodes must be removed periodically which presents some problems if one were to try to enclose the system. In this regard, it is rather apparent that more information on the rate of tritium exchange is required. Transfer of tritium to the electrolyte can be achieved by three transfer mechanisms:

1. Mechanical entrainment in the solvent.
2. Solubility of aqueous phase in the solvent.
3. Exchange reaction with hydrogen atoms of the organic phase.

Mechanisms 1 and 2 would be rather rapid, but can be minimized and may be of little consequence. For example, the Oak Ridge report indicated the distribution coefficient of tritium was  $<0.005$  for a 5-min reaction time. Knowledge of the rate at which mechanism 3 occurs is important to determine to what extent the tank house electrolyte will be contaminated with tritium.

On the other hand, if a fission explosive containing plutonium were used to create the chimney, the extraction response of this radionuclide should be examined besides those already mentioned. The Oak Ridge study did not address itself to this radionuclide nor to its extraction response with commercial Cu chelate extractants. Its extraction response might be anticipated based on solution chemistry

considerations and its behavior in other SX systems. Assuming that Pu is released to solution and is not removed from the leach liquor by adsorption or co-precipitation, it should be present in the  $+4$  state complexed to a large extent by the sulfate ligand,<sup>14</sup> as shown by Eqs. (7), (8) and (9). If (VI) were stable, which seems to be of low probability, sulfate complexation tendency would be approximately equivalent.



<sup>c</sup> 0.5M acid and 0 to 0.2M sulfate. Solutions were  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  containing a varying amount of sulfate.

In essence,  $\text{PuSO}_4^{+2}$  is the principal species below 0.03M sulfate.  $\text{Pu}(\text{SO}_4)_2(\text{aq})$  is predominant at sulfate concentrations of 0.2M, above which the anionic species becomes significant. In terms of the leach liquor generated from pilot plant studies of Lewis and Braun,<sup>11</sup> it would be anticipated that the initial sulfate concentration at the time processing begins would be at least 0.1M where the first sulfate complex would predominate, and would increase with time to, perhaps, 0.3M where the concentration of the anionic complex would be significant.

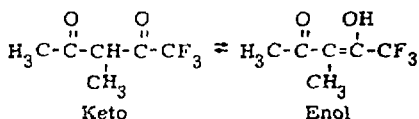
The oxidation state as well as the presence or absence of a complexing ligand are important in predicting the extraction behavior of Pu. As would be expected, for most cationic and neutral extractants, Pu extraction decreases with increases in sulfate ion concentration, as shown in Table 4. Although exceptions can be found, as a rule of thumb, Pu (VI) does not extract as well as Pu (IV).

It is difficult to speculate on the Pu extraction behavior for hydroxyoximes, because even with a given group of extractants structural variation can change the

Table 4. Selected plutonium extraction systems.<sup>13</sup>

Extractant	Aqueous phase	Observation.
TBP (neutral)	0.5M $\text{H}_2\text{SO}_4$	Extraction coefficient decreased by a factor of 10 or more when compared to results in the absence of sulfuric acid.
D2EHPA (cationic)		Much less complete in the presence of sulfuric acid.
TOPO (neutral)	3.0M $\text{H}_2\text{SO}_4$ 0.5M $\text{H}_2\text{SO}_4$ + 2.5M $(\text{NH}_4)_2\text{SO}_4$	D = 30 D = 0.1
TFA (cationic-chelation)	0.75M $\text{HNO}_3$ 0.638M $\text{HNO}_3$ + 0.5M $\text{Na}_2\text{SO}_4$	D = 0.51 D = 0.018

extraction response by orders of magnitude. In the case of chelation exchange with the enol form of 1,3-diketones, branching between the carbonyl groups, e.g., methylacetyltrifluoroacetone,<sup>9</sup> completely inhibits Pu extraction; whereas in the absence of branching, large extraction coefficients can be realized. In this regard, it is possible that Pu (IV) may be



extracted to a significant extent, and experiments to determine the extraction response have been designed.<sup>14</sup>

In a manner similar to that used in the Oak Ridge report, Cohen<sup>15</sup> has estimated the distribution of radionuclides in a leach liquor which might result if an all-fission nuclear explosive were used to create the chimney. For this case, the hazard estimates were presented in terms of time and the volume (demand volume) necessary to dilute to drinking water standards. Tritium does not exist in significant amounts, but significant amounts of <sup>90</sup>Sr, <sup>137</sup>Cs, and <sup>106</sup>Ru might be anticipated,

## Engineering Considerations

On the basis of the anticipated leaching conditions in a nuclear chimney and the leach liquor derived therefrom, recovery of Cu by a SX-electrowinning circuit seems to be a viable process. Specific areas of concern but not necessarily bonafide problems are:

1. Precipitation of gypsum in the extraction circuit.
2. Radionuclides that might be present in the leach liquor.
3. Type of extractant and extraction conditions.
4. Integration of the leaching-extraction circuits.

The first two matters have been discussed extensively in the previous section. Essentially, precipitation problems should be minimal in that the reaction appears to be rather slow. The leach liquor will be filtered to remove fine particulates before entering the SX circuit. Furthermore, the extraction circuit should be equipped

with a flotation unit which will not only curtail solvent losses but also keep the system free of particulate material.

The second area of concern, radionuclides, may only be imaginary in the case of heavy metal radionuclides, in that they may never reach the processing plant due to:

- (1) solubility limitations,
- (2) adsorption on chimney rubble, and
- (3) co-precipitation.

Even if they were to have significant solubility in the leach liquor, the extraction response of the radionuclides in a hydroxyoxime extraction circuit is poor and they should be rejected from further process streams. In the event a fusion explosive were used, adequate ventilation and safety precautions must be maintained to prevent inhalation and ingestion of tritium.

With regard to the type of extractant and extraction conditions, on the basis of

pilot plant analyses, previous experience, and General Mills data, it would be most advantageous to operate the extraction circuit between 40° and 50°C using the LIX 65N extractant. At these temperatures, the kinetics of extraction with the phenolic oxime become fast enough that the aliphatic component need not be added. Also, the rate of phase disengagement is enhanced and this is an important consideration when determining the settler size. However, above 50°C the rate of degradation of extractant becomes significant, and it is doubtful that solvent losses could be tolerated. If for some reason the circuit were to be operated at ambient temperatures, LIX 64N would be used. In either case, the extraction-stripping circuit would be similar to those at Bluebird and Bagdad. If the acidity of the leach liquor were to exceed 15 gpl, the LIX 70 series of extractants should be considered.

With regard to item 4 above, integration of the leaching system with the recovery plant, it is difficult to design the system without accurate knowledge of the rate at which Cu will be released from a given chimney, or set of chimneys. Many models have been suggested, based on the experimental data collected at LLL.<sup>11,16,17</sup> One convenient functional form (strictly empirical) of the rate expression which seems to fit many ore-leaching reactions, both oxide and sulfide, is a pseudo, first-order rate law which was first used by Taylor and Whelan<sup>18</sup> to describe ore leaching.

The expression is as follows:

$$\ln(1 - \alpha) = -kt \quad (10)$$

where

$\alpha$  is the fraction reacted,  
 $k$  is the rate constant ( $t^{-1}$  units), and  
 $t$  is time ( $t^1$  units).

A plot of the pilot plant data, for pressure leaching of San Manuel ore, Run 1, is shown in Fig. 7. After the initial deviation, the data fit the above relation well, as do data from other bench scale experiments. The rate constant is  $6.7 \times 10^{-4}$ , which of course will be dependent to a greater or lesser extent on pH, temperature, oxygen pressure, particle size, and ore type.

As an example of how a set of chimneys would be interfaced to processing facilities, consider a mass balance on the system in terms of  $mt^{-1}$ . The change in Cu concentration with time, assuming complete removal of Cu by the SX system, would be

$$\frac{dc}{dt} V_{ch} = \text{rate of dissolution of Cu from the ore.} \quad (11)$$

If, for mathematical convenience, we assume the validity of the empirical relation mentioned previously, and neglect the initial deviation which is to say at

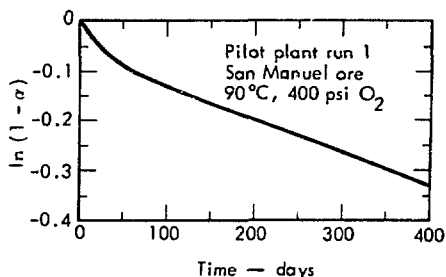


Fig. 7. Pseudo, first-order rate plot of the dissolution of copper from San Manuel ore. Pilot Plant Run 1, 90°C, 400 psi O<sub>2</sub>.



$t = 0$ , approximately 5% of the ore has reacted, the mass balance on the system would be:

$$\frac{dc}{dt} V_{ch} = M_{Cu} k e^{-kt} - c Q_{SX} \quad (12)$$

where

- $V_{ch}$  - volume of liquor in the chimneys,  $\ell^3$
- $c$  - concentration of Cu in the chimney,  $m\ell^{-3}$
- $M_{Cu}$  - mass of Cu initially in the rubblized ore, m
- $k$  - rate constant,  $t^{-1}$
- $Q_{SX}$  - volume flow rate of liquor to the SX plant,  $\ell^3 t^{-1}$

Assuming perfect mixing, the solution to the differential equation is:

$$c_t = \frac{\left[ c_i \left( k - \frac{Q_{SX}}{V_{ch}} \right) + \frac{M_{Cu} k}{V_{ch}} \right] \exp\left(-\frac{Q_{SX}}{V_{ch}} t\right) - \frac{M_{Cu} k}{V_{ch}} \exp(-kt)}{\left( k - \frac{Q_{SX}}{V_{ch}} \right)} \quad (13)$$

where

- $C_t$  - Cu concentration at time,  $t(m\ell^{-3})$
- $C_i$  - initial Cu concentration when the liquor is first processed  $(m\ell^{-3})$

and

$$\frac{Q_{SX}}{V_{ch}} = \frac{1}{\tau}, \text{ or the reciprocal of the effective residence time } \tau \text{ in the set of chimneys.}$$

As one method of interfacing the leach liquor from a set of chimneys with the surface plant, the leach liquor could be processed until the requirements of the processing plant were no longer met. At this time another set would be processed, returning to the original chimney set at some later time, depending upon the rate of production, leaching rate constant and the number of chimneys per set.

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