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GALLIUM SOLVENT EXTRACTION FROM SULFURIC ACID SOLUTIONS USING OPAP

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ABSTRACT

The U.S. Bureau of Mines investigated solvent extraction methods for recovering gallium from sulfuric acid leach filtrates produced from hydrometallurgical zinc residues. These filtrates typically had pH values of 0 to 0.5, too low for effective gallium recovery by traditional extractants. Of the nine extractants tested, octylphenyl acid phosphate (OPAP) was the most effective. Gallium stripping was accomplished using a 1.5 $\underline{M}$-H_2SO_4 liquor. A continuous solvent extraction system was designed and operated for 32.4 hr, treating a 0.32 g/L Ga and 20 g/L Fe filtrate. Overall gallium recovery in the system was 94%.

INTRODUCTION

Gallium is an important strategic element used in solid state devices such as computer chips and light-emitting diodes. Currently, over 90% of the gallium used in the U.S. is imported, and domestic consumption is projected to increase 5 to 10% annually through the year 2000 (1). Gallium is not concentrated naturally but often occurs as a byproduct of the aluminum and zinc industries. In particular, waste residues from hydrometallurgical zinc processing operations contain a substantial amount of this metal. Due to inadequate technology for recovering gallium from low grades sources (less than 1% Ga), domestic zinc residues are not processed for gallium recovery.

In an effort to enhance domestic capabilities, the Bureau of Mines researched methods for processing zinc residue to recover gallium and its often occurring companion, germanium. Recently, details of a study optimizing gallium and germanium extraction from zinc residues using sulfuric acid leaches were published (2). In the process, filtrates containing gallium and germanium along with other impurities such as iron, copper, zinc, and cadmium were produced. The focus of this paper is the recovery of gallium from these solutions using solvent extraction.

It has been reported that in a sulfuric acid system, di(2-ethylhexyl) phosphoric acid (DEHPA) can be used to extract gallium (3,4), but commercial production has not been attained. Musto Explorations (4), in St. George, UT, tried extracting gallium from a sulfuric acid leach filtrate of Apex Mine ore with DEHPA; however, processing problems prevented the operation from becoming economically viable. A major obstacle in using DEHPA is that the pH of the leach filtrates, which range from 0 to 0.5, must be raised by neutralization to a range of 2 to 3 for high gallium extraction. Neutralization increases the cost and time required for processing. Thus, the goal of this research was to find a solvent extractant to recover gallium from low pH sulfuric acid solutions.

SOLUTION ANALYSIS

Solutions tested in this study were produced by sulfuric acid leaching of residue from a zinc processing plant located in Clarksville, TN. Solution analyses, as determined by neutron activation analysis (NAA), inductively coupled plasma spectrophotometry (ICP), atomic absorption spectrophotometry (AA), and wet chemistry techniques are shown in Table 1. The leach conditions used for filtrates B and C were previously determined to extract up to 95% of the gallium (2). Filtrate A was a preliminary test where only 60% of the gallium was extracted.

Table 1. Filtrate analyses*, (g/L)

Element	Leach filtrate A	Leach filtrate B	Leach filtrate C
Ga	0.39	0.64	0.32
Ge	.39	.55	.35
Cd	.16	.24	.17
Cu	1.5	2.1	1.06
Fe	9.9	18	11
Zn	12.9	19	12

*pH of A = 0.9, pH of B = -0.16, pH of C = 0.5

SOLVENT EXTRACTION

Nine different organic extractants were tested with leach filtrate A to determine their selectivity for extracting gallium: octylphenyl acid phosphate (OPAP) plus isodecanol (IDA), 19-hydroxyhexatriaconta-9,28 diene-18 oxime (LIX 63-70) plus IDA, tri-octylamine, di(2-ethylhexyl)phosphoric acid (DEHPA) plus IDA, tri-n-butyl phosphate (TBP), beta-dodecenyl 7-alkenyl-8-hydroxyquinoline (KELEX 100), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), bis 2,4,4,-trimethylpentyl phosphinic acid (Cyanex 272), and tri-octylphosphine oxide (TOPO) plus IDA. IDA was used as a modifier when needed to improve the aqueous-organic disengagement by preventing the formation of emulsions. Proportions of IDA lower than 10% did not prevent emulsions. Single-contact batch tests were conducted in separatory funnels on a wrist action shaker for 30 min using aqueous to organic (A:O) volume ratios of 1:1 with kerosene as the diluent.

Table 2 shows that of the extractants tested, 0.3 M OPAP plus 10 vol % IDA in kerosene extracted the most gallium. Although gallium extraction using DEHPA was insignificant in this test, the use of DEHPA was not eliminated at this point because other researchers had found it to be successful in recovering gallium (3,4). DEHPA and OPAP are both organophosphate extractants with similar structures (5). The commercially prepared OPAP used in this study was reportedly a 60-40 mixture of monooctylphenyl acid phosphate and dioctylphenyl acid phosphate.

Table 2. Solvent extraction results testing various extractants

Organic Extractant	Extraction, %					
	Cd	Cu	Fe	Ga	Ge	Zn
0.3 M OPAP plus IDA, 10 vol %	3.3	4	49	43	0.4	3.9
LIX 63, 10 vol % plus IDA, 10 vol %..	1.8	2	2.3	6	4	2.9
Tri-octylamine, 10 vol %	0	0	0	0	0	0
DEHPA, 10 vol % plus IDA, 10 vol %	.5	1.1	21	0	.4	.6
TBP, 10 vol %	0	0	0	0	0	0
KELEX 100, 10 vol %..	0	49	10	0	84	0
PC-88A, 10 vol %	0	0	26	0	1.6	0
Cyanex 272, 10 vol %.	1.2	.7	7	5.6	1.6	.8
0.125 M TOPO plus IDA, 10 vol %	4.9	5	10	0	8	6.2

Iron Versus Gallium Loading

Zekel (6), in studying gallium solvent extraction from hydrochoric acid solutions using TBP, found that oxidized iron (ferric) in solution loaded preferentially to gallium, which in turn loaded preferentially to reduced iron (ferrous). This relationship can be expressed in terms of the extraction coefficients as follows: $E_a^\circ(Fe^{+++}) >> E_a^\circ(Ga) >> E_a^\circ(Fe^{++})$.

The results shown in Table 2 were obtained using "as is" leach filtrate with iron in the ferric state. The extraction coefficients at this condition were calculated to be $E_a^\circ(Fe) = 0.96$ and $E_a^\circ(Ga) = 0.75$. When solvent extraction was conducted immediately after the iron in the filtrates was reduced with metallic iron, as shown in reaction A, gallium extraction increased significantly, i.e., $E_a^\circ(Ga) = 28.4$, while iron extraction decreased, i.e., $E_a^\circ(Fe) = 0.013$.

$$2Fe^{+++} + Fe^{o} = 3Fe^{++} \qquad (A)$$

Therefore, metallic iron was added to all leach filtrates prior to solvent extraction to convert the ferric to ferrous, thus ensuring high gallium loading onto OPAP. An added advantage of reducing the iron in solution with metallic iron was that copper was cemented out in the process, eliminating the need for copper removal at some later stage in the operation.

Figure 1 demonstrates the need of performing solvent extraction soon after the iron in solution is reduced. In these tests, 0.3 $\underline{M}$ OPAP plus 10 vol % IDA in kerosene (this combination will subsequently be referred to as OPAP) was repeatedly contacted with reduced solutions of filtrate B at an A:O ratio of 1:1. Following each contact, a 1.5 $\underline{M}$ H_2SO_4 liquor was used to strip the gallium. As seen, when gallium solvent extraction was performed immediately after the iron in solution was reduced, gallium extractions remained high and the amount of iron accumulating on the extractant was low as the extractant was recycled. However, when the reduced solutions were exposed to air for several weeks before solvent extraction occurred, "reoxidized," a considerable amount of iron accumulated on the extractant as it was recycled, leading to decreased gallium loading.

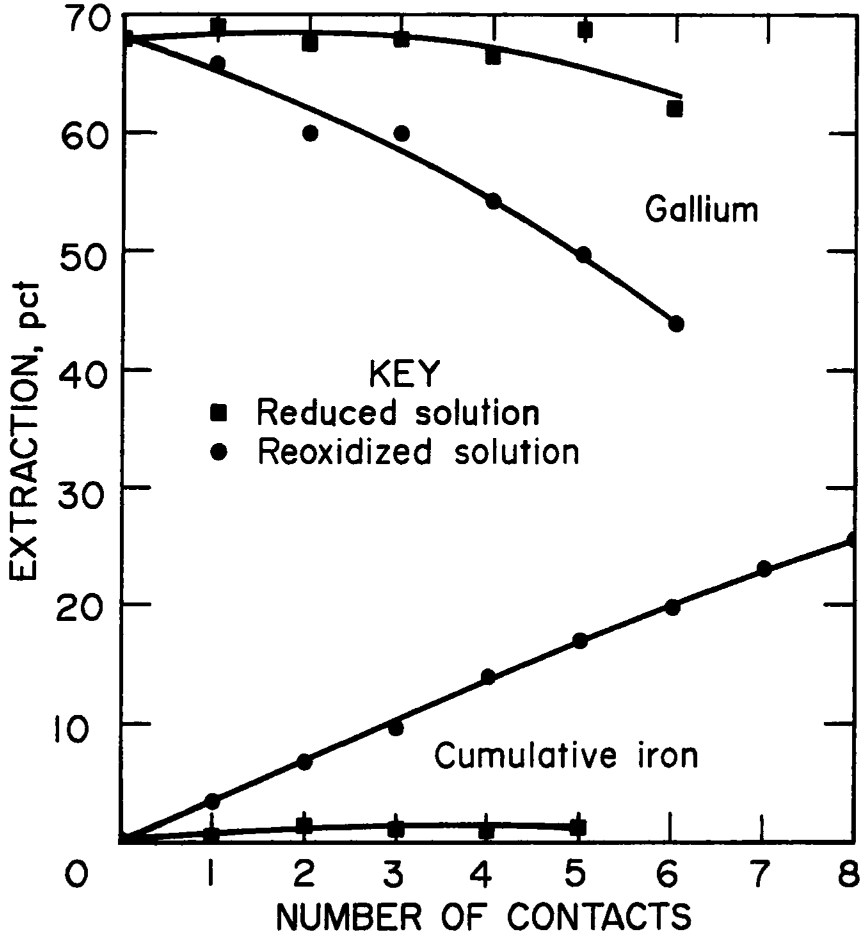

Fig. 1. Extraction from reduced and reoxidized solutions.

OPAP and DEHPA

Solvent extraction tests comparing OPAP with 10 vol % DEHPA in kerosene at various pH values were conducted using reduced leach filtrate C. The pH of the solution was varied by adding sulfuric acid or ammonium hydroxide as needed. A contact time of 30 min and an A:O ratio of 1:1 were used for each test. Results shown in Figure 2 demonstrate the superiority of OPAP for extracting gallium from solutions with low pH values. For example, at pH 0.5, 99% of the gallium was extracted using OPAP, while only 23% was extracted using DEHPA. Even when the pH of the solution was raised to 2.3, gallium extraction with DEHPA increased to only 62%. Therefore, the distinct advantage of OPAP is that the leach filtrate needs no neutralization and can be used as received.

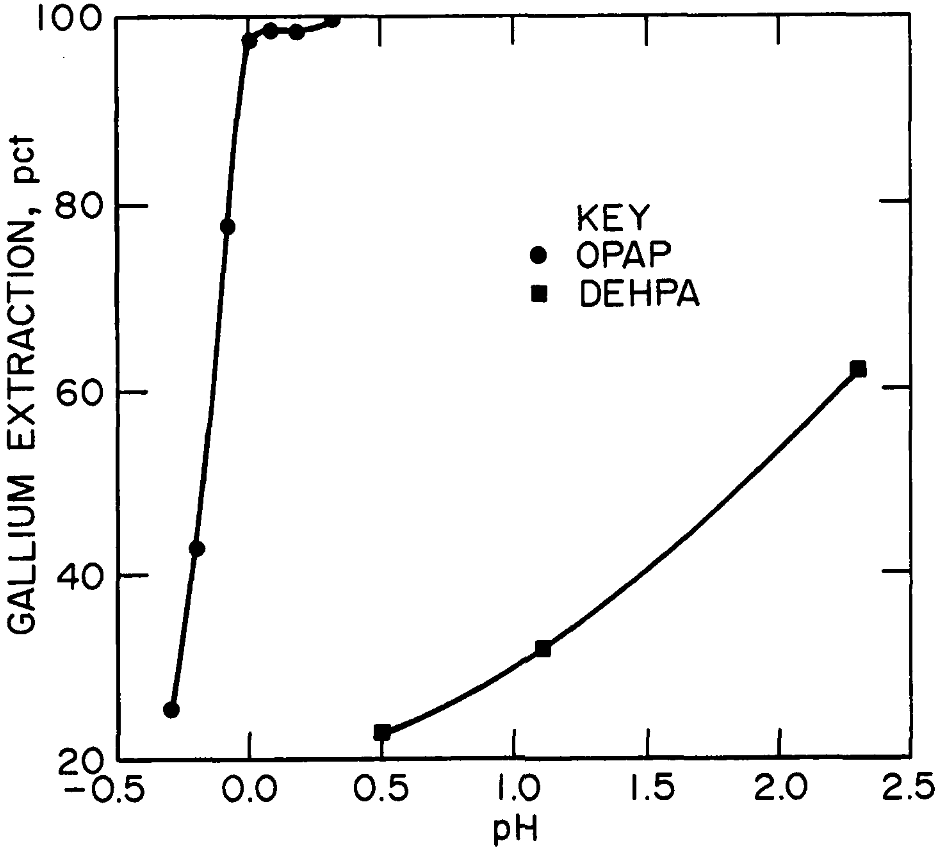

Fig. 2. Effect of pH on gallium extraction.

Rate and Equilibrium Analysis

Rate and equilibrium analyses were conducted using OPAP to better understand its gallium loading and stripping properties. In all further work, reduced leach filtrate C was used.

Gallium loading. Figure 3 shows that a contact time of 10 min on a wrist-action shaker was sufficient for gallium equilibrium loading onto OPAP. A McCabe-Thiele analysis of the gallium loading isotherm for a 0.3 M-OPAP organic and a 0.32 g/L-Ga filtrate, showed that a loaded solvent containing 0.32 g/L Ga could be produced at an A:O ratio of 1:1 using four mixer-settlers (Figure 4).

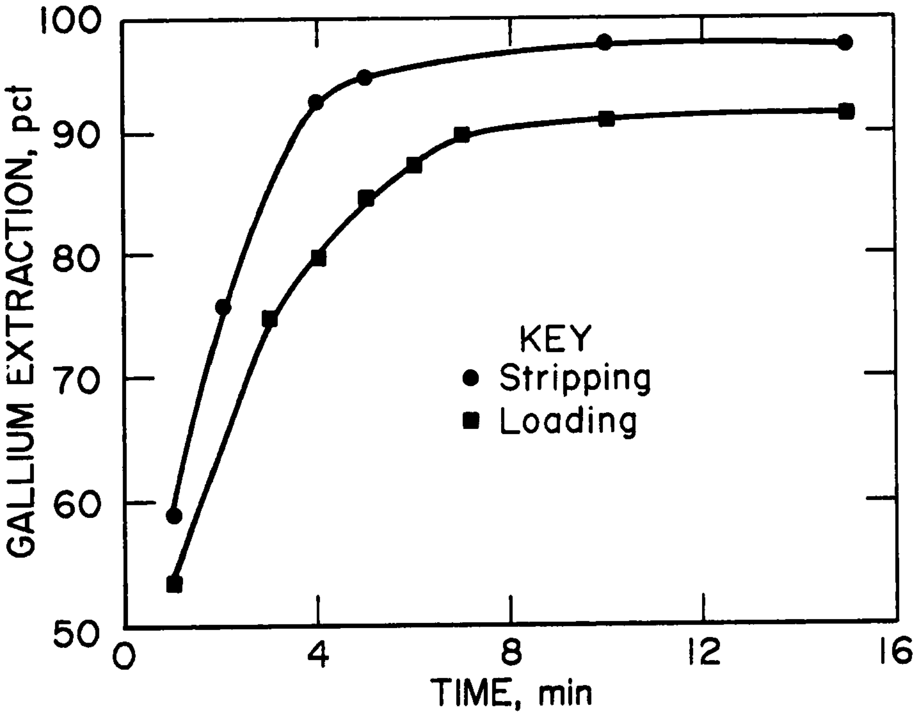

Fig. 3. Gallium equilibrium loading and stripping on 0.3 M OPAP.

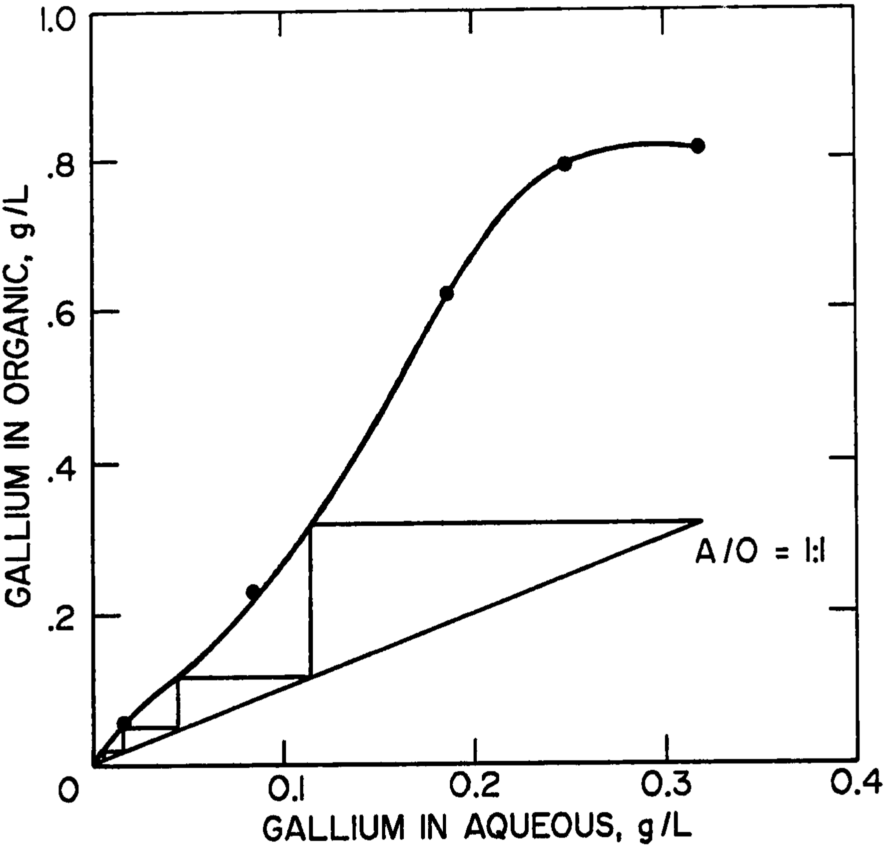

Fig. 4. McCabe-Thiele analysis loading 0.32 g/L Ga aqeuous on 0.3 M OPAP.

Gallium stripping. Batch solvent extraction tests conducted on a wrist-action shaker showed that gallium could be stripped from OPAP using 1 to 3 M-H_2SO_4 solutions. Figure 3 reveals that stripping with a 1.5 M-H_2SO_4 solution removed 98% of the gallium in 10 min. A McCabe-Thiele analysis of the equilibrium stripping isotherm for a 1.5 M-H_2SO_4 strip solution and a 0.3 M-OPAP organic phase containing 0.32 g/L Ga indicated that a strip liquor containing 1.3 g/L Ga could be produced at an A:O ratio of 1:4 with four stages (Figure 5).

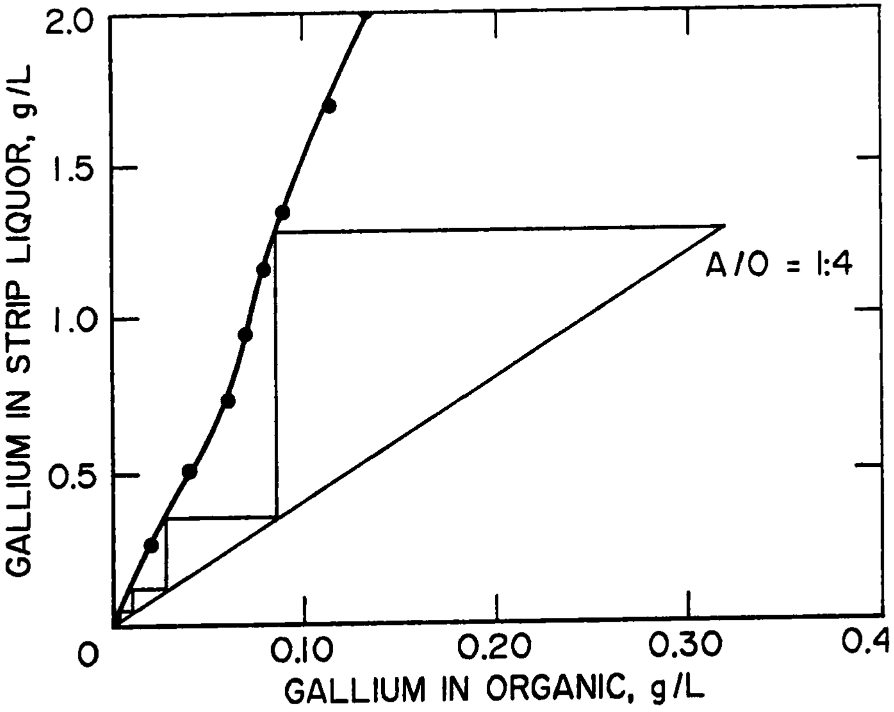

Fig. 5. McCabe-Thiele analysis stripping 0.32 g/L Ga loaded organic using 1.5 M H_2SO_4.

Ferric Stripping. Even when extracting freshly reduced solution, a small equilibrium amount of ferric iron was present and loaded onto the OPAP. A sulfuric acid strip alone did not satisfactorily remove this extracted iron. Tests showed that a 50%-H_3PO_4, 50%-H_2O solution stripped 92% of the ferric iron from OPAP within 5 min. When the OPAP was reused, it extracted gallium as well as fresh extractant. A McCabe-Thiele analysis (Figure 6) of the iron stripping isotherm for a 50%-H_3PO_4 solution and a 0.3 M-OPAP organic containing 0.53 g/L Fe showed that the amount of iron on the OPAP could be reduced to 0.02 g/L in three stages at an A:O ratio of 1:4.

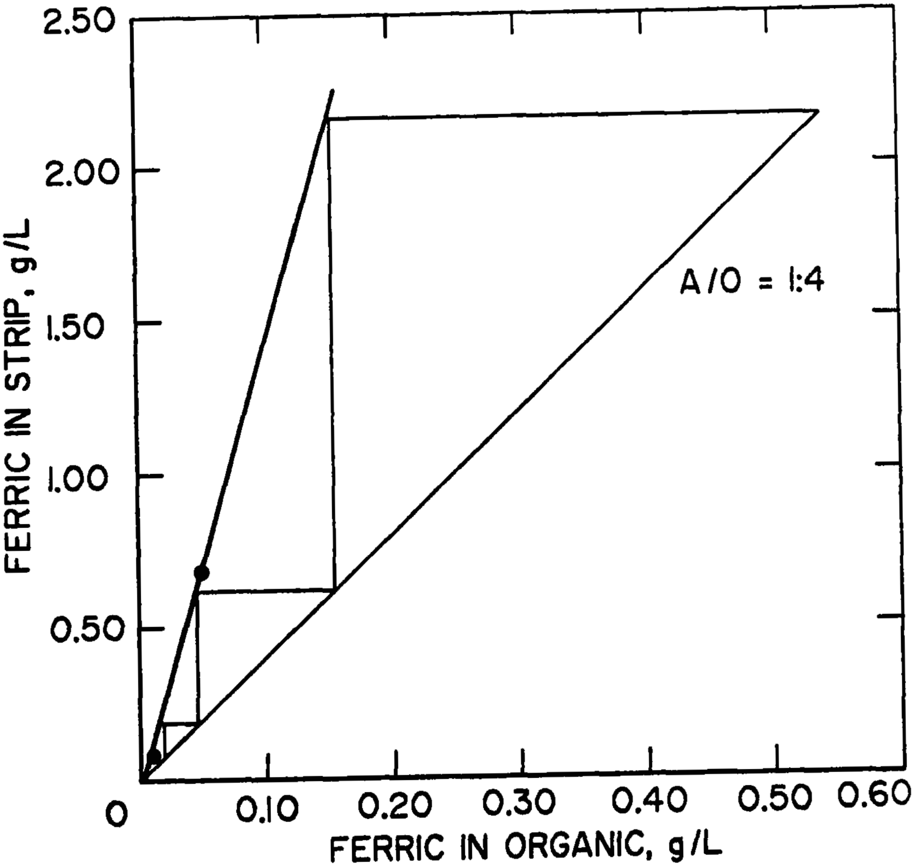

Fig. 6. McCabe-Thiele analysis stripping iron with 50% H_3PO_4. (Additional data point x=0.68, y=7.09)

CONTINUOUS SOLVENT EXTRACTION OF GALLIUM

With this background information, it was possible to operate a continuous gallium solvent extraction circuit using OPAP for gallium loading and sulfuric acid and phosphoric acid for gallium and iron stripping.

System Design

A continuous system was constructed consisting of mixer-settlers arranged so that the organic was fed at the top of the operation and cascaded down through the set-up. The mixer-settlers were divided into three sections. Gallium was loaded in the highest section and stripped in the middle section. The lowest section was for ferric iron stripping. Mixer-settlers could be added or removed from each section as needed. Pumps and flowmeters made it possible to adjust the flows so proper A:O ratios and retention times could be maintained. To ensure that the iron in solution remained in the reduced state, an up-flow column containing metallic iron was inserted before the first mixer settler. All solution entering the system passed through this column.

System Operation

The continuous system was operated for maximum gallium recovery using conditions determined by McCabe-Thiele analyses for a leach solution containing 0.32 g/L Ga and for an organic containing 0.3 M OPAP, (Figures 4-6). The gallium loading section contained four mixer-settlers and was operated at an A:O ratio of 1:1. Gallium stripping with a 1.5 M-H_2SO_4 liquor was conducted in four mixer-settlers at an A:O ratio of 1:4. A two-stage iron scrub with 50% H_3PO_4, A:O ratio 1:4, was used to keep ferric iron concentration on the OPAP below 0.05 g/L, thus allowing OPAP to function efficiently as it was recycled. Twelve liters of reduced leach filtrate containing 0.32 g/L Ga and 20 g/L Fe were pumped through the system in 32.4 hr. Organic and aqueous flow rates were set to maintain a retention time of at least 10 min in each mixer.

Operation of the system at these conditions resulted in a raffinate containing 0.02 g/L Ga and 20 g/L Fe. Organic loadings averaged 0.31 g/L Ga and 0.36 g/L Fe. The sulfuric acid strip liquor averaged 1.07 g/L Ga and 0.74 g/L Fe. Gallium extraction from the leach filtrate averaged 95%; gallium recovery from the organic averaged 99%, producing an overall recovery of 94%. Operating the continuous system at these conditions concentrated the gallium by a factor of 3.3 (.32 g/L to 1.07 g/L). Organic solvent was lost at a rate of 13.3 mL per liter of leach filtrate processed.

Testing was continued for an additional 20 hr (treating 7.9 L) with the phosphoric acid strip removed. This was done to see how necessary iron stripping was to the success of the operation. The gallium extraction subsequently dropped from 94% to 84%, while the iron concentration on the organic steadily increased from 0.36 g/L to 0.79 g/L. This indicates that a phosphoric acid strip was needed to maintain high gallium recovery. The results of the continuous solvent extraction system clearly showed that OPAP is an effective extractant for gallium recovery.

Strip Liquor Purification

Although gallium recovery was high in the continuous system, the strip liquor contained too much iron to effectively precipitate a high purity gallium product. Batch tests showed that by repeating the OPAP loading and stripping three times, 99.9% of the remaining iron was removed. When the liquor from the final strip was neutralized with ammonium hydroxide, a 99% pure gallium-sulfur-oxygen product was precipitated. Although X-ray diffraction analysis could not identify the exact compound, such a product is considered suitable for feed to traditional gallium electrolysis and purification systems (7).

CONCLUSIONS

Solvent extraction was tested for recovering gallium from sulfuric acid filtrates produced from leaching zinc processing residue. The following conclusions were made:

1. Solvent extraction with the organophosphate, OPAP, successfully extracted over 98% of the gallium from solutions with pH values as low as 0.

2. Gallium extraction using OPAP was hindered when ferric iron was present in solution. Reducing the ferric to ferrous by contacting the solution with metallic iron helped ensure high gallium extraction.

3. By analyzing the results of rate and equilibrium tests for a leach solution containing 0.32 g/L Ga and an organic containing 0.3 $\underline{M}$ OPAP plus 10 vol % IDA in kerosene, the following conditions for a continuous gallium solvent extraction system were determined: 10 min contact times for loading and stripping, four gallium loading stages, four gallium stripping stages, and two iron stripping stages.

4. The continuous circuit effectively extracted 95% of the gallium onto the organic phase. Stripping the organic phase with a 1.5 $\underline{M}$-H_2SO_4 solution recovered 99% of the gallium, leading to an overall gallium recovery of 94%.

5. A 50%-H_3PO_4 strip effectively reduced the amount of ferric iron remaining on the OPAP to below 0.05 g/L, enabling the continuous system to maintain high gallium recoveries.

6. A 99% pure gallium-sulfur-oxygen precipitate was obtained by neutralizing the final strip liquor of a batch, three-cycle, load-strip solvent extraction process.

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