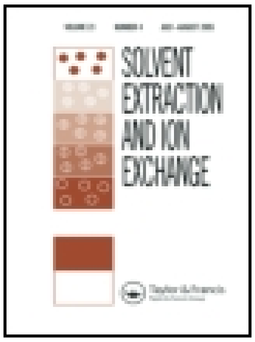

SOLVENT EXTRACTION AND ION EXCHANGE

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GERMANIUM SOLVENT EXTRACTION FROM SULFURIC ACID SOLUTIONS (AND CO-EXTRACTION OF GERMANIUM AND GALLIUM)

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ABSTRACT

The U.S. Bureau of Mines investigated solvent extraction methods for recovering germanium from sulfuric acid leach filtrates. A new organic extractant system was developed which synergistically and selectively recovered germanium from these solutions. A continuous solvent extraction circuit was operated for over 150 hr, extracting over 90% of the germanium from 0.30 g/L Ge filtrates containing 40 to 60 g/L free acid. Over 90% of the loaded germanium was stripped from the organic phase with water at 75 °C. A section on germanium and gallium co-extraction is also presented.

INTRODUCTION

Germanium is a strategic metal which is finding an increasingly important role in U.S. industry in infrared and fiber optics, catalysts, and semiconductor devices including transistors, diodes, and rectifiers (1). Germanium is generally not concentrated naturally; currently only one ore body in the world has been identified as having any appreciable amount of germanium (Apex Mine near St. George, UT) (2). Germanium can also occur as a byproduct of hydrometallurgical zinc processing operations.

Although the U.S. has an abundant supply of zinc residue, there is a void in domestic process technology for recovering germanium from this type of material. Consequently, select domestic zinc residues are processed in foreign countries by proprietary techniques to recover the germanium (1). To enhance domestic capabilities, the Bureau of Mines previously investigated various sulfuric acid leaching techniques for extracting germanium from zinc residues (3) and domestic ores (4). The focus of this paper is the recovery of germanium from these leach solutions.

Although several techniques are known for recovering germanium from acid solutions, each has a drawback. Hydrogen sulfide selectively precipitates germanium (5); however, its use is hazardous and has adverse environmental implications. Tannin can selectively precipitate germanium, but the process requires many complicated and time-consuming steps (6). Resins have been experimented with, but low loading capacity, as well as high cost and strict separation conditions have limited their usefulness(7).

Solvent extractants such as KELEX 100 (8) (beta-dodecenyl 7-alkenyl-8-hydroxyquinoline) and LIX 63 (9) (19-hydroxyhexatriaconta-9,28 diene-18 oxime) have been mildly successful in extracting germanium from sulfuric acid solutions. KELEX 100 effectively loads germanium from acidic solutions; however, the rate of disengagement of the aqueous and organic phases is slow, and a harsh caustic, 3-5$\underline{M}$ NaOH, is needed to strip germanium from the organic. LIX 63 is only effective with solutions containing high amounts of acid, over 100 g/L, and 4.4$\underline{M}$ NaOH, is needed to strip germanium from the organic phase. More importantly, patents for germanium solvent extraction technology are owned by foreign companies which have been reluctant to lease the know-how to U.S. firms. Although solvent extraction appears most promising for germanium recovery, it is clear that other extractants need to be found. It was the goal of this research to identify an effective solvent extractant for recovering germanium from acidic leach solutions and to test such an extractant in a continuous solvent extraction circuit.

TABLE 1. CONCENTRATION OF METALS IN LEACH FILTRATES, g/L

Element	Synthetic solution A	Zinc residue filtrate B	Germanium ore filtrate, C
Ge	0.24	0.64	0.30
Ga	0	.55	.12
Cd	0	.24	<.1
Cu	0	2.10	3.5
Fe	0	18	81
Zn	0	19	1.8
As	0	<.1	2.3

SOLUTION PREPARATION AND ANALYSIS

Three germanium solutions were tested in this work: 1) synthetic solution A, produced by dissolving 99.99% pure GeO_2 (obtained from Johnson Matthey Chem. Ltd.) in water and then adding sulfuric acid; 2) filtrate B, obtained by sulfuric acid leaching of zinc residue; and 3) filtrate C, produced by leaching a germanium ore. Table 1 shows the concentration of metals in each solution as determined by inductively coupled plasma spectrophotometry (ICP) and atomic absorption spectrophotometry (AA). Radioisotope tracers were used in this research for determining germanium extraction from these solutions.

RESULTS AND DISCUSSION

Identifying a Solvent Extractant

In preliminary tests, thirty-seven different organic extractants were tested for germanium selectivity using solution A spiked with 100 g/L or 10 g/L H_2SO_4. In each test, 10 vol % (v/v) of liquid extractant was mixed with 90 vol % kerosene. Where the extractant was a solid, the final concentration of the extractant in kerosene was 0.3$\underline{M}$. Single contact batch tests were conducted in separatory funnels on a wrist action shaker for 30 min using

TABLE 2. TESTING VARIOUS ORGANICS FOR GERMANIUM SELECTIVELY

Organic extractant	Ge ext., % H_2SO_4, g/L		Organic extractant	Ge ext., % H_2SO_4, g/L	
	100	10		100	10
Adogen 283	1	0	LIX 64N	2	2
Adogen 364	2	5	LIX 622	1	2
Adogen 381	0	2	LIX 860	1	1
Adogen 464	9	11	LIX 84	1	1
Alamine 304	1	2	Lix 984	0	3
Alamine 308	0	2	M-5640	0	0
Alamine 310	1	2	MEHPA	0	0
Alamine 336	0	2	NeodecanoicPrine	0	0
Aliquat 336	0	0	Octyl-oxime	1	0
Amberlite LA2	1	2	OPAP	0	0
BC-150	0	0	PC88A	0	0
Cyanex 272	0	0	P-5050	0	0
Cyanex 301	89	65	P-5100	1	0
Cyanex 302	0	0	TBP	0	1
Cyanex 923	1	1	TOPO	0	0
Cyanex 925	5	0	Tri-octylamine	0	3
DEHPA	0	0	Versatic Acid	0	0
KELEX 100	99	58	JMT	9	7
LIX 63	41	25			

aqueous to organic (A:O) volume ratios of 1:1. The results in Table 2 show that only three of the organics extracted over 20% (i.e. distribution ratios greater than 0.25) of the germanium: Kelex 100 (from Sherex Chem. Co.), LIX 63 (from Henkel Corp.), and Cyanex 301 (bis (2,4,4-trimethylpentyl) dithiophosphinic acid from American Cyanamid Co.).

The selectivity of these three extractants for germanium was then tested using filtrate B, an actual leach solution containing 60 g/L H_2SO_4. As before, A:O ratios of 1:1 and contact times of 30 min were used. Table 3 shows that LIX 63 extracted little germanium when interfering ions were present in solution. Although KELEX 100 and Cyanex 301 extracted over 80% of the germanium, each had a significant drawback. Cyanex 301 was not

TABLE 3. SOLVENT EXTRACTION RESULTS TESTING VARIOUS EXTRACTANTS

Organic Extractant	Ext., %					
	Cd	Cu	Fe	Ga	Ge	Zn
LIX 63, 10 vol %	1.8	2	2.3	6	4	2.9
KELEX 100, 10 vol %	0	49	10	0	84	0
Cyanex 301, 40 vol %	>30	98	4	5	86	98.8

selective for germanium, high amounts of copper and zinc were also extracted. As previously mentioned, KELEX 100 is already patented for germanium solvent extraction. Therefore, other possible extractants were sought.

Often when two extractants are mixed, a synergistic effect occurs whereby the combination of extractants is capable of extracting more of a metal than either organic alone. This was shown by Demopoulos and Gevfert for extracting ferrous iron (10) and by De Schepper (11) for increasing germanium extraction by mixing KELEX 100 and LIX 26. In the current study, various extractants were grouped by two's and mixed with kerosene as the diluent. Each combination was then contacted with leach filtrate B for 30 min at an A:O ratio of 1:1. Select results in Table 4 showed that two combinations, 0.3$\underline{M}$ OPAP (octylphenyl acid phosphate obtained from Albright & Wilson Americas)/10% LIX 63 and 0.3$\underline{M}$ OPAP/10% KELEX 100, extracted over 40% of the germanium. However, according to Table 3, 10% KELEX 100 alone extracted an equally high amount of germanium as the mixture of OPAP and KELEX 100. Thus, the addition of OPAP to KELEX 100 was of no advantage for germanium extraction. By contrast, the 0.3$\underline{M}$ OPAP/10% LIX 63 organic combination exhibited a truly synergistic effect. Therefore, work on this combination was expanded.

Germanium Loading

Effect of Copper and Iron

Because germanium extraction from an actual leach solution averaged only 40% when using the OPAP/LIX 63 mixture, methods to

TABLE 4. TESTING VARIOUS ORGANIC COMBINATIONS

Combination	Ge ext., %
.3M OPAP/10% Cyanex 272	0
.3M OPAP/10% TOPO	0
.3M OPAP/10% KELEX 100	85
10% DEHPA/.3M OPAP	0
.3M OPAP/10% LIX 63	49
10% DEHPA/10% LIX 64N	6
10% DEHPA/10% JMT	9
10% DEHPA/10% Adogen	8

TABLE 5. EFFECT OF COPPER AND IRON ON GERMANIUM EXTRACTION

Cu	Fe	Ge ext., %
yes	++	72
yes	+++	41
no	++	76
no	+++	32

increase extraction were examined. LIX 63 was originally developed as a copper extractant (12) and OPAP is known to extract ferric iron (13); therefore, a series of tests was performed to determine the effect of aqueous copper and iron on germanium extraction when using the .3M OPAP/10% LIX 63 mixture. Table 5 shows that highest germanium extraction was possible when the leach solution was free of copper and the iron was in the reduced state. These objectives can be accomplished by contacting the leach solution with metallic iron as shown in reactions A and B.

$$Cu^{++} + Fe = Cu + Fe^{++} \qquad (A)$$

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

All further tests were performed using solutions contacted with metallic iron.

Synergism

Table 6 more clearly shows the synergistic effect obtained when various OPAP/LIX 63 combinations were used for germanium

TABLE 6. SYNERGISTIC EFFECT OF OPAP/LIX 63 MIXTURE

Extractant	Ge ext., %	Ga ext.,%
0.3M OPAP	0.0	77.7
10% LIX 63	8.7	0
10% LIX 63 and 0.3M OPAP	57.0	61
20% LIX 63	21.0	NA
20% LIX 63 and 0.3M OPAP	80.5	NA
30% LIX 63	30	0
30% LIX 63 and 0.2M OPAP	83	8

NA not analyzed.

extraction. Filtrate C with 60 g/L free acid and A:O ratios of 1:1 were used in these tests. An organic phase containing 10% LIX 63 in kerosene extracted only 8.7% of the germanium; however, with an organic phase containing 0.3M OPAP/10% LIX 63 in kerosene, germanium extraction increased to 58%. As another example, germanium extraction increased from 30 to 83% with the 0.2M OPAP/30% LIX 63-kerosene as compared to the 30% LIX 63-kerosene solvent.

Table 6 also demonstrates that the concentrations of LIX 63 and OPAP are important variables in obtaining high germanium extraction. By increasing the LIX 63 concentration from 10 to 20% in the 0.3M OPAP in kerosene organic, germanium extraction increased 23.5%.

An interesting phenomenon was observed in the data reported in Table 6. The OPAP/LIX 63 mixture has the ability to co-extract gallium along with germanium. A literature survey revealed that such a process has not previously been reported. Co-extraction of germanium and gallium was pursued on a limited scale with some pertinent results given later in this paper.

Effect of Acid Concentration

Table 7 shows the importance of solution acidity on germanium extraction with the OPAP/LIX 63 combination. As seen, germanium extraction increased with increasing free acid.

TABLE 7. EFFECT OF SOLUTION ACIDITY

Free acid concentration, g/L	Ge ext., % 30% LIX 63 0.2M OPAP	 20% LIX 63 0.3M OPAP
22.5	71.2	64.7
32.5	75.7	71.8
42.5	78.6	75.9
52.5	81.4	79.6
62.5	84.8	81.9

TABLE 8. EFFECT OF VARIOUS STRIPPING LIQUORS

Reagent	Ge stripped, %
1.5M H_2SO_4	28.4
Distilled Water	41.9
0.5M NaOH	63.6
1.0M H_3PO_4	35.9
1.0M Na_2SO_4	40.2
1.0M Na_2CO_3	12.0
10% HCl	19.5
1 g/L $FeSO_4$	38.5

Germanium Stripping

Once the organic was loaded with germanium, a proper stripping agent was needed to make solvent extraction complete. Several possible strip liquors were tested to remove germanium from a loaded OPAP/LIX 63 organic mixture. Table 8 shows the results obtained using contact times of 1 hr and A:O ratios of 1:1 to treat a loaded 0.3M OPAP/10% LIX 63 organic solvent.

As anticipated, NaOH stripped a high percentage of the germanium. However, germanium stripping using distilled water was surprisingly high. Because water is inexpensive and easy to handle, further testing was performed. In particular, table 9 shows that increasing water temperature from 25 to 75 °C increased germanium stripping from 41.9 to 73.9%.

TABLE 9. EFFECT OF INCREASING WATER TEMPERATURE ON STRIPPING

Temperature, °C	Ge stripping, %
25	41.9
60	64.6
75	73.9

With this background information, a study of continuous germanium solvent extraction was proposed using OPAP/LIX 63 for loading and hot water for stripping. For such an investigation, it was necessary to perform basic rate and equilibrium tests.

GERMANIUM RATE AND EQUILIBRIUM ANALYSIS

Rate and equilibrium analyses were conducted using a 0.2M OPAP/30% LIX 63 mixture for loading, and 75 °C water for stripping. Two samples of filtrate C were tested: one with the free acid adjusted to 40 g/L, the other with the free acid adjusted to 60 g/L. These tests were used to determine the number of loading and stripping stages, as well as the retention time needed in a continuous solvent extraction operation.

Germanium Loading

Figure 1 shows equilibrium data obtained after one contact of aqueous with organic. A contact time of 20 min was deemed sufficient for loading germanium onto the extractant for a multi-contact system.

Figure 2 shows a McCabe-Thiele analysis of the germanium loading isotherm for a filtrate with 40 g/L free acid. As seen, a loaded solvent containing 0.3 g/L Ge could be produced at an A:O ratio of 1:1 using four mixer-settlers. When the 60 g/L free acid filtrate was tested, the McCabe-Thiele analysis of the germanium loading isotherm, figure 3, revealed that a loaded organic containing 0.6 g/L Ge could be obtained at an A:O ratio of 2:1

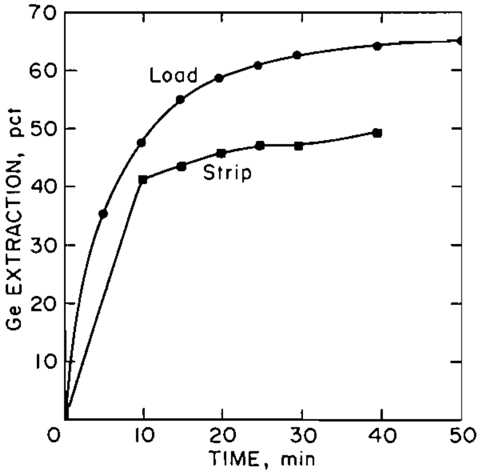

FIGURE 1. Effect of contact time on loading and stripping.

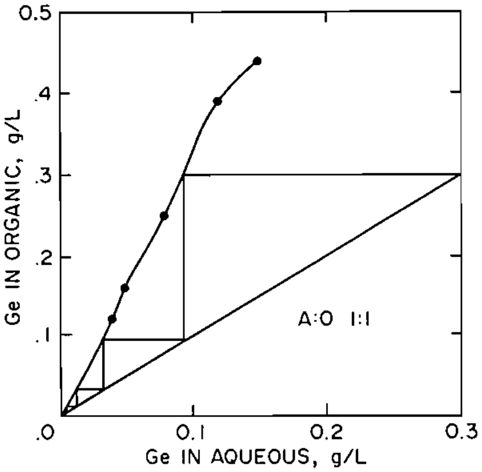

FIGURE 2. Germanium loading isotherm, 40 g/L H_2SO_4.

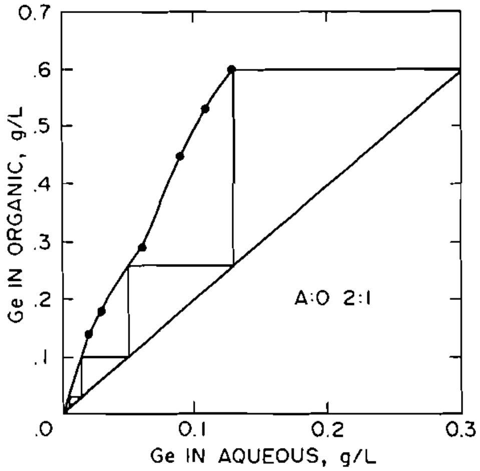

FIGURE 3. Germanium loading isotherm, 60 g/L H_2SO_4.

using four mixer-settlers. Therefore, by increasing the free acid concentration in solution from 40 to 60 g/L, germanium concentration of the loaded organic would double.

Germanium Stripping

Stripping germanium from a 0.3 g/L Ge loaded organic with 75 °C water reached equilibrium after a contact time of approximately 20 min, as seen in figure 1. A McCabe-Thiele analysis of the equilibrium stripping isotherm, figure 4, indicated that an organic phase containing 0.3 g/L Ge could be stripped in four stages at an A:O ratio of 1:1 to produce a strip liquor containing 0.3 g/L Ge, while an organic phase containing 0.6 g/L Ge could be stripped in four stages at an A:O ratio of 1:1 to produce a strip liquor containing 0.6 g/L Ge.

Iron Scrubbing

Analysis of the organic phase after germanium loading and stripping revealed that up to 8 g/L Fe was present, even when the

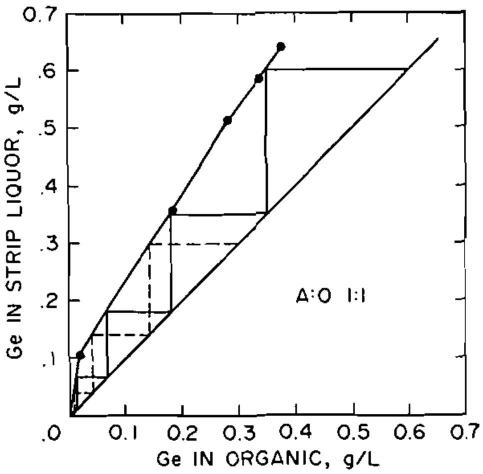

FIGURE 4. Germanium stripping isotherm using 75 °C water.

iron in the filtrate was maintained in the ferrous state. If the 8 g/L Fe organic phase were recycled, this much iron would hinder germanium loading. To avoid this problem, iron scrubbing was studied. Rate and equilibrium analyses for iron scrubbing were conducted using a loaded organic phase containing 7 g/L Fe and a 3<u>M</u> H_2SO_4 scrub solution. McCabe-Thiele analyses of the scrubbing isotherm, figure 5, showed that iron in the organic phase could be reduced from 7 to 2.4 g/L at an A:O ratio of 1:1 in two stages.

CONTINUOUS SOLVENT EXTRACTION OF GERMANIUM

With this background information, it was possible to operate a continuous germanium solvent extraction circuit using the OPAP/LIX 63 organic mixture for germanium extraction, hot water for germanium stripping, and H_2SO_4 for iron scrubbing.

System Design

A small-scale continuous system was constructed consisting of mixer-settlers arranged so that the organic was fed at the top of

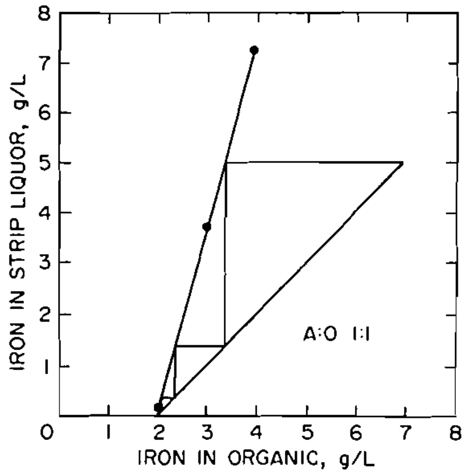

FIGURE 5. Iron stripping isotherm using 3$\underline{M}$ H_2SO_4.

the operation and cascaded down through the set-up. The mixer-settlers were divided into three sections: germanium extraction with four mixer-settlers, germanium stripping with four mixer-settlers, and iron scrubbing with two mixer-settlers. Pumps and flowmeters made it possible to adjust the aqueous 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 so that all solution entering the system passed through this column. The germanium stripping stage was maintained at 75 °C by circulating hot water through specially designed glass tubing placed in each settler.

System Operation

The continuous system was operated according to conditions determined by the McCabe-Thiele analyses for a 0.2$\underline{M}$ OPAP/30% LIX 63-kerosene extractant. The operation parameters and results of each test, along with any variables tested are given below.

Testing Leach Filtrate C Containing 40 g/L Free Acid

In these tests, germanium loading was operated at an A:O ratio of 1:1, as determined by the McCabe-Thiele analysis shown in figure 2. Germanium stripping with 75 °C water was conducted at an A:O ratio of 1:1 and iron scrubbing with 3M H_2SO_4 at an A:O ratio of 1:1. Organic and aqueous flow rates were set to maintain a retention time of at least 20 min in each stage of the loading and stripping sections. In the first 30 hr, the organic extractant was not recycled. Under these conditions, an average of 91% of the germanium extracted and 67% of this germanium was stripped from the organic extractant. When the organic was recycled, germanium extraction stayed consistent at 88%, while germanium stripping increased to 77%.

The results using a 40 g/L free acid filtrate were encouraging; however, even under optimum conditions, the final strip liquor would have the same germanium concentration as the initial leach filtrate. One method of increasing the germanium concentration of the strip liquor would be to recycle the aqueous solution to load the organic to capacity and to recycle the aqueous during the stripping cycle to improve concentration ratios. In some operations, up to 90% of the aqueous is recycled. However, this recycling increases operating costs and decreases the rate of output. A better alternative would be to increase solution acidity so higher amounts of metal initially load onto the organic.

Testing Leach Filtrate C Containing 60 g/L H_2SO_4

In these tests, all conditions remained the same as described for the 40 g/L H_2SO_4 solution except germanium loading was operated at an A:O ratio of 2:1. In the first 20 hr, the organic extractant was not recycled. Under these conditions, an average of 92% of the germanium extracted and 66% of this germanium was stripped from the organic extractant. These results are similar to those obtained using the 40 g/L H_2SO_4 filtrate, but the highest germanium concentration in the strip liquor was 0.54 g/L, as opposed to a high of 0.24 g/L for the 40 g/L free acid solution.

TABLE 10. EFFECT OF RECYCLING OPAP/LIX 63 EXTRACTANT

Condition	Ge Extraction,%	Ge Stripping,%	Iron Extracted, g/L
1st recycle	85	71	2.6
2nd recycle	85	79	2.8
3rd recycle	90	99	2.6

The system was then operated for 24 hr with the organic being recycled. Table 10 shows that germanium extraction remained relatively high at 85 to 90% and the iron level remained consistently around 2.6 g/L.

The fact that the amount of germanium stripped increased with each recycle indicates that an equilibrium amount of germanium remained in the organic phase, but did not affect subsequent germanium loading or stripping when the organic phase was recycled.

GERMANIUM AND GALLIUM CO-EXTRACTION

There is currently no available technology for the simultaneous solvent extraction and selective recovery of germanium and gallium from acidic solutions. This is significant because germanium and gallium often occur together in nature and can be leached using the same reagents. By extracting both metals at the same time, many processing steps could be eliminated.

Germanium and gallium co-extraction was tested using OPAP/LIX 63 combinations in conjunction with filtrate B at A:O ratios of 1:1 and contact times of 60 min. The results in table 11 show that if the acid concentration of the aqueous and the strength of the extractant are properly controlled, appreciable amounts of both gallium and germanium can be extracted simultaneously.

TABLE 11. CO-EXTRACTION OF GALLIUM AND GERMANIUM. (SOLUTION FREE OF Cu AND Fe^{+++})

Organic	Free acid g/L	Ext., % Ga	Ge
0.3M OPAP & 10% LIX 63	40	58	55
	60	57	61
	80	28	69
	100	26	77
0.2M OPAP & 30% LIX 63	30	21	80
	50	16	82
	60	8	83

TABLE 12. CO-EXTRACTION FROM A ZINC PROCESS SOLUTION

Free acid g/L	Ext., % Ga	Ge
1.5	60	84
11.5	36	90
50.5	18	92

Selective stripping of the loaded organic phase showed that a water strip at 75 °C using an A:O ratio of 1:1 removed 96% of the germanium. A subsequent strip of the organic phase with 3M H_2SO_4 removed greater than 95% of the gallium. More importantly, less than 1% of each metal contaminated the other.

Industrial Application

During the processing of certain zinc concentrates, germanium and gallium are solubilized in a pH 1.5 H_2SO_4 leach. These solutions typically contain over 200 g/L Zn and approximately 0.28 g/L Ga and 0.30 g/L Ge. Co-extraction using the 0.2M OPAP/30% LIX 63 mixture was tested on such a solution with the results shown in Table 12. With just one contact of aqueous phase with organic phase, 60% of the gallium and 84% of the germanium were extracted. High germanium extraction from a pH 1.5 solution is quite

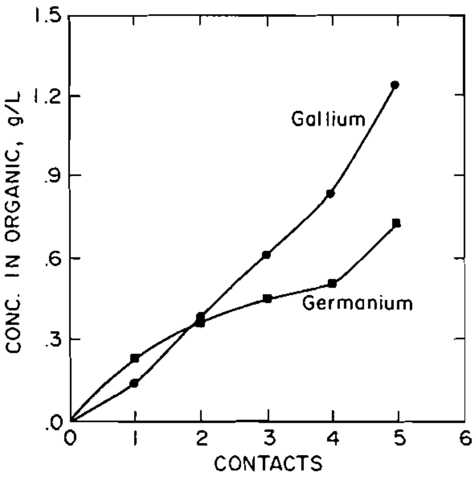

FIGURE 6. Germanium and gallium loading with multiple contacts.

significant. Table 12 also shows that when increasing amounts of sulfuric acid were added to the solution, germanium extraction increased while gallium extraction decreased.

Results of multiple contacts of aqueous with organic are shown in figure 6. As seen, germanium and gallium continue to load without crowding either one off the organic.

These results imply that a OPAP/LIX mixture could be used to recover gallium and germanium during zinc processing, before these metals report to the waste residue. Such technology would greatly increase the supply of these critical metals.

SUMMARY

The goal of this research was to identify organic reagents capable of extracting germanium from sulfuric acid solutions and to test such extractants in a continuous circuit. The results of this investigation are summarized as follows:

1. Over 70 potential extractants and combinations of extractants were screened. Of these, the organic mixture of OPAP/LIX 63 was found to synergistically extract over 40% of the germanium after one contact with actual leach solution.

2. Germanium extraction increased to over 80% when copper was removed from solution and when iron was reduced to the ferrous state. Copper removal and iron reduction were accomplished by contacting the leach solutions with metallic iron.

3. Germanium was effectively stripped from the loaded organic extract using only 75 °C water.

4. The amount of residual iron in the organic phase was reduced to acceptable levels using sulfuric acid scrub solutions.

5. A continuous germanium solvent extraction circuit using OPAP/LIX 63 for germanium extraction, water at 75 °C for germanium stripping and sulfuric acid for iron scrubbing extracted over 90% of the germanium from leach solutions.

Testing showed that the OPAP/LIX 63 combination could also co-extract over 50% of both germanium and gallium from a 40 g/L H_2SO_4 solution. Germanium and gallium were sequentially stripped from the loaded organic phase, thus providing a simple method for recovering both metals.

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