



The development and implementation of industrial hydrometallurgical gallium and germanium recovery

by T.S. Fayram* and C.G. Anderson*

Synopsis

The Gordonsville Operation of Pasminco US Inc. along with the Center for Advanced Mineral and Metallurgical Processing (CAMP) at Montana Tech studied, developed and implemented a pilot-scale hydrometallurgical facility for the industrial recovery of germanium and gallium. This paper describes the joint testing and engineering programme that culminated in this successful process.

Introduction

The Pasminco US Inc. (PAS), Gordonsville Operation, has been producing zinc concentrate continuously since 1975. Within the zinc concentrate, several by-product elements were found to be significantly concentrated, including gallium and germanium. The gallium and germanium replace zinc and other metals within the crystal lattice structure of the zinc mineral (sphalerite) and are concentrated in the same manner as the zinc mineral. This concentrate is then sent to the Pasminco Clarksville Zinc Refinery for further processing. Within the hydrometallurgical zinc-processing plant at Clarksville, a residue is formed that contains a majority of the impurities that would otherwise contaminate or hinder the zinc process. Approximately 5 000 tons of residue is formed annually containing approximately 0.80% gallium and 0.60% germanium along with significant quantities of iron, zinc, silica, and lead. Pasminco currently sells this residue for the germanium value. Until recently, no revenue for the gallium was obtained from the sale of the residue.

The goals of this project were to:

- Review the feasibility of gallium removal from the refinery residue prior to germanium recovery
- Identify and lab test the commercial process
- Pilot test the commercial process
- Develop a preliminary capital and operating cost estimate.

Technology review

A technology review was completed by both Pasminco and the Center for Advanced Mineral and Metallurgical Processing (CAMP) and comprised searching and reviewing associated technology and recovery methods for both gallium and germanium. The literature search is listed in its entirety as courtesy to the reader¹⁻⁶⁸. Both acid and alkali leaching alternatives were reviewed. Ion exchange was also reviewed as an option to selectively recover gallium along with solvent extraction.

Acid leaching

The review of the literature identified two gallium recovery processes that had been developed based on Clarksville gallium/germanium residue^{1,2}. The gallium recovery processes used the following methods:

- An acid leach circuit to dissolve the gallium and germanium
- Conversion the leached iron from ferric to ferrous
- Recovery of the gallium with a solvent extraction approach
- Strip of the gallium from the solvent extraction chemical
- Electrowinning of the strip solution to create a crude gallium metal.

Based on a review of the two processes, a block flowsheet was developed. This included an acidic nitrogen species catalyzed (NSC)⁶⁹ pressure leach step. Figure 1 illustrates the proposed flowsheet.

* The Center for Advanced Mineral and Metallurgical Processing, Montana Tech of the University of Montana, USA.

© The Southern African Institute of Mining and Metallurgy, 2008. SA ISSN 0038-223X/3.00 + 0.00. This paper was first published at the SAIMM Symposium, Lead & Zinc 2008, 25-29 February 2008.

The development and implementation of industrial hydrometallurgical gallium

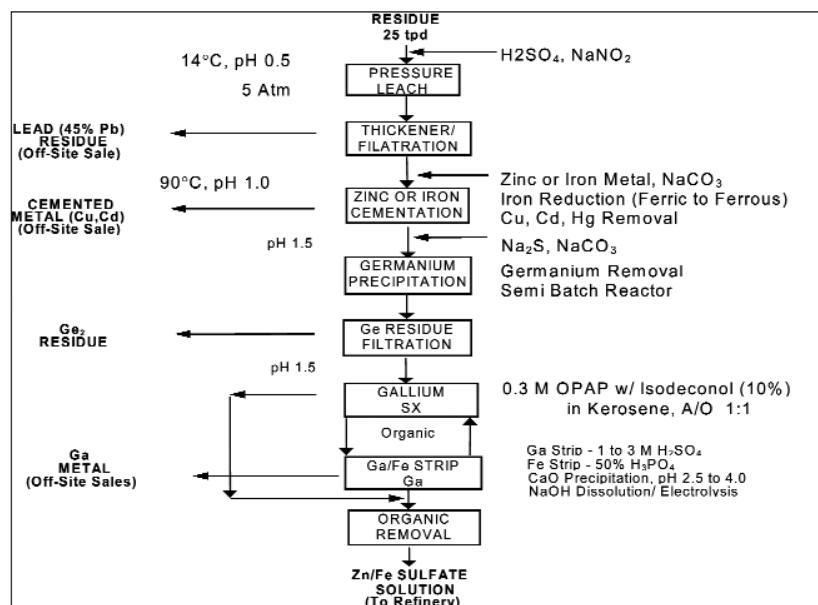


Figure 1—Acid leach flowsheet

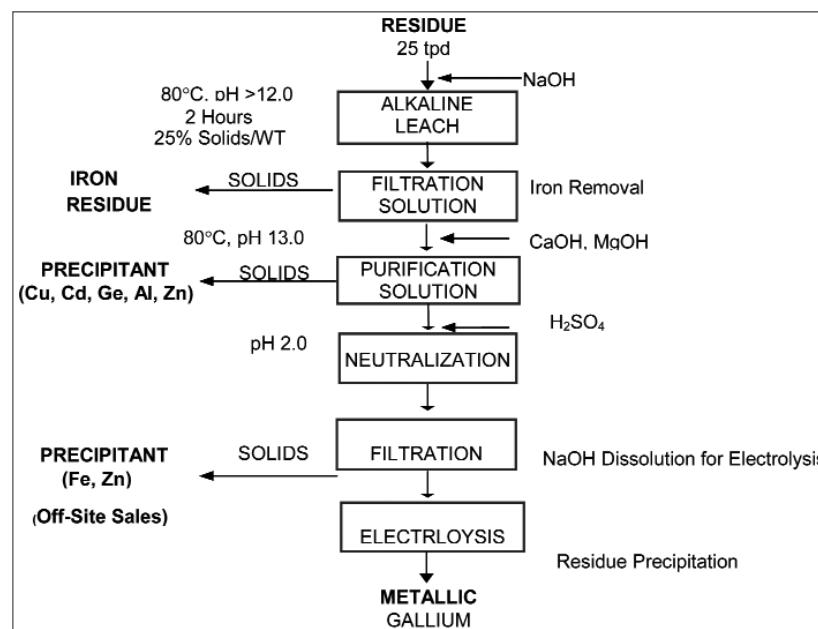


Figure 2—Alkaline leach flowsheet

Alkaline leaching

The two alkaline leaching processes identified were from Dowa³ and Cominco⁴. Both of the processes were nearly identical to each other and include the following:

- Alkaline leaching using sodium hydroxide to form a jarosite residue
- Precipitation of aluminum, cadmium, and zinc with calcium hydroxide
- Precipitation of germanium with magnesium hydroxide,
- Recovery of gallium by electrowinning.

The proposed alkaline leach flowsheet is shown in Figure 2.

Ion exchange

Several ion exchange resins that contained aminodiacetic acid as the active component were tested to recover gallium. Figure 3 illustrates an ion exchange flowsheet.

Bench-scale testing

Bench-scale testing was used to identify the parameters required for pilot testing. Process testing was completed to fill in gaps from the available data, confirm previous testing and ensure specific processes would work under the parameters given. Initial bench-scale testing by CAMP was completed using acid/alkaline leaching, cementation, solvent extraction, ion exchange, and electrowinning.

The development and implementation of industrial hydrometallurgical gallium

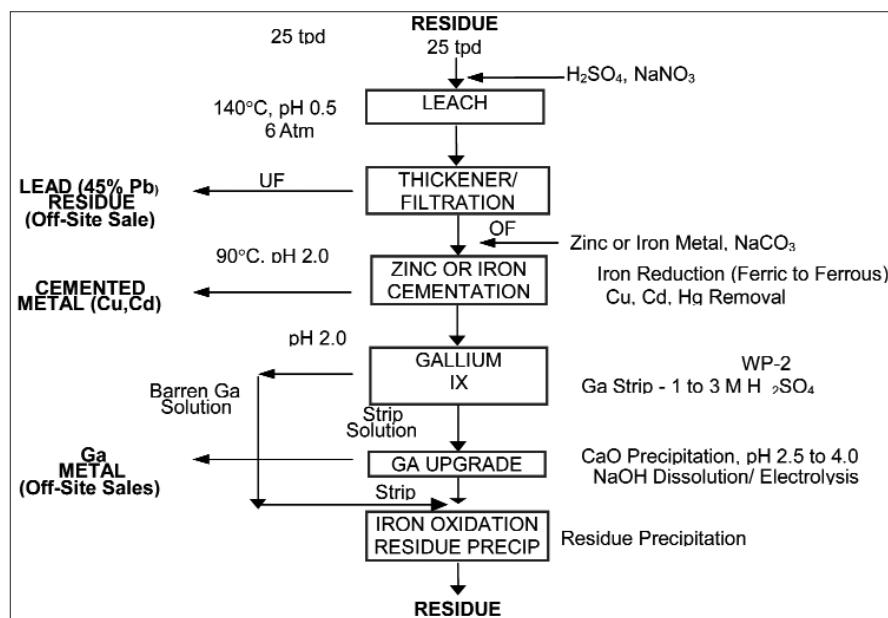


Figure 3—Ion exchange and electrowinning flowsheet

Alkaline leaching

Alkaline leaching was dismissed as a viable process due to the solubility of lead within the alkaline solutions. Lead was found to interfere with the recovery of the gallium.

Acid leaching

In finding the optimum process to extract gallium from the final Clarksville leach residue, several gallium-laden materials were leached under varying conditions including:

- 1st Primary Filter Leach Cake – Weak acid leach residue prior to flotation sulfur removal,
- Germanium Slag – Slag product after germanium removal, and
- Clarksville Germanium Residue - Final residue created at Clarksville refinery.

The latter residue is currently processed for germanium recovery. Testing consisted of weak acid leach (WAL), hot acid leach (HAL), and a nitrogen species catalyzed leach (NSC). The test parameters were identified in Table I.

Due to the high Ga recoveries from existing PAS processes and facilities, NSC testing was not completed due to the need for a pressure vessel. However, NSC testing was completed on the Germanium slag. Table II summarizes the gallium recoveries for each test.

Cementation

The cementation step was originally undertaken to do the following:

- Identify zinc dust requirements to convert the ferric iron to ferrous iron
- Raise the pH to 2.1 to allow for solvent extraction or ion exchange.

Subsequent testwork used parameters shown in Table III, with the results shown in Table IV.

All ferric iron was converted to ferrous iron. Note: sodium carbonate was added to bring the pH from 0.5 to 1.0 at a rate of 75 grams/litre.

Table I
Acid leaching test parameters

Gallium recovery from leach type			
Parameter	HAL	WAL	NSC
Slurry density, % solid by weight	15%	15%	15%
Temperature, °C	90	75	105
Time, hours	5	5	2
Acid strength, gms/l	150	~5	150
Pressure, atmospheres	ambient	ambient	6
Mixing, shear w/propeller	constant	constant	constant
Sodium nitrite addition	no	no	yes

Table II
Gallium leach recovery

Gallium recovery from leach type			
Material	HAL	WAL	NSC
1st Primary filter leach cake	96%	91%	NT
Clarksville germanium residue	92%	90%	NT
Germanium slag	NT	NT	75%
NT: no test			

Table III
Initial cementation parameters

Parameters	Leach solution
pH,	0.50
Iron content, ferric gms/l	6.5
Acid strength, H_2SO_4 gms/l	150
Pressure, atmospheres	ambient
Temperature, °C	ambient
Mixing, shear w/propeller	constant

The development and implementation of industrial hydrometallurgical gallium

Table IV Final cementation parameters	
Parameters	Leach solution
pH,	2.1
Iron content, ferric gms/ℓ	0.0
Acid strength, H_2SO_4 , gms/ℓ	3
Zinc added, gms/ℓ	43
Temperature, °C	145
Mixing, shear w/propeller	constant

Table V Solvent extraction test parameters	
Parameters	Leach solution
pH,	2.1
Iron content, ferric gms/ℓ	0.0
Acid strength, H_2SO_4 , gms/ℓ	3
O/A ratio,	1:1
Loading time, min	8
Extractant, OPAP molar	0.3
Modifier, isododecanol % by Vol	10
Organic, kerosene	
Mixing	shaker

Solvent extraction

Solvent extraction was identified by the US Bureau of Mines⁴¹ as an extraction technique for recovering gallium using octylphenyl acid phosphate (OPAP). The initial test work was on residue material from Clarksville and subsequently identified a solvent extraction flowsheet to remove gallium. Solvent extraction test work completed at CAMP for this project paralleled the Bureau's work.

In the bench-scale work, four mixing/settlers were used in counter current to imitate the flow of the pregnant leach liquor through several mixing settlers. Table V lists the bench-scale test parameters.

It is important to note that the OPAP was received as a hardened solid and required heating to melt the material prior to mixing with isododecanol and kerosene. As a liquid, the OPAP mixed well to form a coherent organic. The results listed in Table VI were obtained.

Ion exchange

Ion exchange was not an initial option for recovery. Contact with resin manufacturers indicated that they had resins that would possibly work for gallium, but they had limited or no experience in gallium recovery. CAMP identified a silica based resin, WP-2, produced by Purity Systems Incorporated⁷⁰⁻⁷⁵ that was subsequently tested. The resin parameters were identified as shown in Table VII.

Testing consisted of adding zinc powder to the leach liquor for impurity cementation, pH adjustment and ferric reduction, precipitant filtration, followed by ion exchange. Several leach liquors including residue leach liquor, first primary filter cake leach liquor, and germanium slag leach solution were tested. The initial ion exchange test parameters were identified as shown in Table VIII.

The results listed in Table IX were provided by testing at Purity Systems labs.

Upon completion of the initial test work, further work was completed using a hot acid leach solution produced by CAMP. The ion exchange parameters listed in Table X were used for this test.

All ion exchange loading and strips were taken to completion. Based on this test, the results as presented in Table XI were obtained.

Table VI
Solvent extraction test results

Parameters	Leach solution
Gallium recovery, %	90+
Zinc recovery, %	8
Iron recovery, %	<0.5
Germanium recovery, %	0
Temperature, °C	ambient
Mixing, shear w/propeller	constant

Table VII
IX resin parameters

Parameters	Leach solution
Substrate	Silica gel/polyamine composite
Active agent	Iminodiacetic Acid
Particle size	60–80 mesh
Pore size	175 (μm)
Ionic form	Hydrogen
Swell	none

Table VIII
Initial IX parameters

Parameters	Leach solution
pH,	2.1–2.5
Temperature, °C	ambient
Iron content, ferric, gms/ℓ	0.0
Acid strength, H_2SO_4 , gms/ℓ	1–3
IX Flow rate, bed volumes/minute	0.5 upflow
Strip solution, gms/ℓ	200
Strip rate, bed volumes/minute	1

Table IX
Gallium IX recovery (%)

Test	Ga	Ge	Fe	Zn
WAL solution	87.3	1.6	0.75	0.09
1st primary filter cake solution (Test 5a)	79.9	7.6	0.44	3.71
1st primary filter cake solution – multiple passes (Test 5b)	88.6	NR	0.76	9.55
Germanium slag	78.7	NR	0.85	14.75
NR – Not recovered				

The development and implementation of industrial hydrometallurgical gallium

Table X

Hot acid leach ion exchange testing parameters

Parameters	Leach solution
pH,	2.1–2.5
Temperature, °C	ambient
Iron content, ferric gms/l	0.0
Acid strength, H ₂ SO ₄ gms/l	1–3
IX flow rate, bed volumes/minute	0.833 upflow
Strip solution, H ₂ SO ₄ gms/l	200
Strip rate, bed volumes/minute	0.1 upflow

Table XI

Ion exchange HAL recovery

Parameter	HAL solution
Gallium recovery, %	85.1
Resin capacity, grams Ga/kg resin	4.8
Attrition	none
Strip time, bed volumes	1.5

Note: Iron and zinc loadings were also found to be similar.

Solution purification

Because precipitation of gallium and other metals is standard practice within the Pasminco refinery, no initial bench-top precipitation and electrorefining work was completed. A review of the refinery mass balance shows the refinery currently precipitates almost 100% of the gallium, germanium, iron, lead, and other contaminate metals between a pH of 2.5 and 4.5.

Purification consisted of precipitating gallium from the ion exchange strip solutions at pH 4.1 using sodium hydroxide. At pH 4.1, the germanium, iron, lead, cadmium, aluminum, copper, and some zinc will also precipitate but these elements have mostly been removed in prior processing. The solution is then filtered and the filter cake washed. The filter cake, which contains the gallium, is redissolved using 200 gram per litre sodium hydroxide solution at 30% solids by weight. Gallium, being 100% soluble in a hydroxide solution, will go back into solution along with any remaining germanium, lead, cadmium, aluminum, copper, and zinc. Iron is insoluble as a hydroxide and will not dissolve into solution. Zinc is only sparingly soluble in high pH solutions. What remains is a high gallium and zinc hydroxide solution ready for electrowinning.

Electrowinning

Electrowinning of solution purification hydroxide solutions was tested using purchased gallium and zinc in simulated process solutions. The parameters of Table XII were used for testing.

Initial testing identified a large amount of gassing at both the anode and cathode. This gassing diminished as gallium started to plate on the cathode. Gallium formed on the cathode as small droplets of liquid gallium that eventually grew and dripped off the cathode. Residual gallium was easily removed from the cathode by brushing. Zinc formed

small dendrites that readily detached and floated within the solution. The results of the electrowinning test are shown in Table XIII.

Pilot testing

Pilot testing was completed to confirm the results identified from the bench-scale testing. Ion exchange, because of its ease of operation and positive bench-scale test results, was picked as the process ultimately to separate the gallium from the leach solutions. Because all the processes except the ion exchange process used commercially available and viable processes, the main focus of the pilot was to confirm gallium ion exchange recovery at larger scale. Additional testing was not completed unless pilot testing found variations from the bench-scale testing. The scale factor used for piloting was approximately 100 to 1. Piloting consisted of testing the following systems:

- Hot acid leaching
- Cementation
- Ion Exchange
- Precipitation
- Electrowinning.

Hot acid leaching

Hot acid leaching was completed separately from the pilot test. The leaching was completed at the Clarksville Cadmium plant using a 1 500 gallon agitated stainless steel tank designed for leaching. Hot acid leaching for the pilot test, used the parameters of Table XIV.

For the pilot test, approximately 1 050 kilograms of germanium residue was added to 4 000 litres of water under high agitation. Approximately 1 000 litres of water was not

Table XII

Electrowinning test parameters

Variables	Parameters
Current density, amps/m ²	500–1000
Cell voltage, volts	3.0
Current efficiency, %	30–50
Anode material	2 ea - stainless
Cathode material	1 ea - stainless
Cell temperature, °C	30
Flow rate, l/min	1

Table XIII

Electrowinning test results

Variables	Parameters
Current density, amps/m ²	1000
Cell voltage, volts	3.8
Current efficiency, %	29
Anode deposition	None
Cathode deposition	Ga Droplets,
Zn dendrites	
Cell temperature, °C	34
Flow rate, l/min	1

Note: Gallium was easily removed from the cathode.

The development and implementation of industrial hydrometallurgical gallium

Table XIV Acid leaching test parameters	
Parameter	HAL
Slurry density, % solid by weight	15%
Temperature, °C	90
Time, hours	5
Acid strength, gms/ℓ	150
Pressure, atmospheres	1
Mixing, shear w/propeller	constant
Other, sodium nitrite addition	no

Table XV Pilot hot acid leach (HAL) results					
Element	Germanium residue head grade, %	Filtrate grade g/ℓ	Final Leach residue grade, %	Pilot recovery, %	Bench recovery, %
Ga	0.83	2.1	0.17	93.3	92.0
Ge	0.61	0.8	0.21	88.8	84.4
Zn	11.91	32.8	4.24	88.4	48.8
Fe	12.76	26.5	3.22	91.7	96.5
Pb	14.87	NS	30.70	32.3	0.03
Cd	0.12	5.2	0.04	98.9	84.6
Cu	1.79	4.43	0.13	97.6	79.7

NS—No Sample. Pb results were back calculated based on residue grade.

added to allow for steam condensation and extra water addition during leaching. The leach residue was allowed to mix thoroughly in the leach vessel. Upon agitation, steam was directly injected into the slurry to bring the temperature to between 80 and 90°C. Once at temperature, the solution was leached for 5 hours and then filtered. The results are listed in Table XV.

Filtration of the solution was completed in a plate and frame filter using 215 square feet of filter cloth. The cloth was a 10.5 oz polypropylene with a porosity of 3 to 5 cubic feet per minute under 1" water pressure. The filter is designed to trap 1 micron particles or larger. The filter rate of the material was approximately 20 litres/minute with the filtrate being slightly cloudy at the beginning of filtration and clearing in a short period of time after the cake began to build. A small polishing filter or filtrate recycle will be required in a full-scale application. Testing identified that HAL can effectively leach the gallium from the residue with the pilot test validating the results of the initial bench-scale testing.

Cementation

Cementation was completed in a 750 gallon stainless steel open top agitated vessel. Approximately 500 gallons of filtered HAL solution was added to the vessel. As identified previously, the main goals of the cementation process was to convert the ferric iron to ferrous iron, raise the pH to 2.1, and precipitate as many of the impurity elements as possible. In testing, the zinc powder was added to the agitated solution at ambient temperature from the top of the tank. Temperature and pH were monitored during the entire process. Zinc was added as needed until pH 2.1 was obtained. The test results are shown in Table XVI.

Upon completing the test, the cementation product was filtered through a 2 cubic foot plate and frame test filter. When initially filtering the material, the cementation product immediately blinded the filter cloth. At this point, a sample of the cementation product was sent to Eimco Process Equipment Company. Testing identified that the material was finely divided and would filter at a rate of only 0.125 gallons/square foot/hour.

Eimco identified several processes that would filter the cementation material. The first process was a vacuum filter with a precoat. Flow rates of 9 to 11 gallons/square foot/hour were obtained. The second process was to use a pressure filter such as a plate and frame filter and add a body-coat such as diatomaceous earth to the agitated cementation solution and mixed thoroughly. The diatomaceous earth builds up against the cloth along the finely divided cementation product and maintains porosity. Flow rates of 2 gallons/square foot/hour were obtained.

In the pilot test, a 7 plate, 56 square feet filtering capacity, plate and frame filter was purchased and set up to process the cementation product. A medium porosity, polypropylene filter cloth recommended by Eimco was installed. Approximately 25 pounds of diatomaceous earth was added to the cementation product, mixed and filtered. Upon filtering, approximately 400 gallons of material was filtered in 2.5 hours or a rate of 2.8 gallons/square foot/hour. The cementation product dropped relatively easily from the plates, although some scraping was required in the back end of the filter. Some of the material in the back end was relatively damp. The results of the cementation step are listed in Table XVII.

A review of the testing identified that the gallium was not precipitated. The gallium in the filter cake was soluble gallium and was not washed from the cake due to ineffi-

Table XVI
Zinc powder cementation testing result

Parameters	Leach solution
pH,	<0.5 to 2.0
Zinc usage*, gms/ℓ	240
Temperature, °C	21 to 54
Iron content, ferric gms/ℓ	0.0
Acid strength, H ₂ SO ₄ gms/ℓ	200 to 3.0
Color	clear to reddish black

Table XVII
Pilot plant zinc powder cementation results

Element	Pre cementation solution grade, g/ℓ	Post cementation solution grade, g/ℓ	Filter cake, %
Ga	2.0	1.73	0.19
Ge	0.7	0.049	4.87
Zn	29.7	57	12.63
Cd	7.4	2.3	3.13
Cu	4.23	0.005	32.00
Fe	25.5	20.0 (all as Fe ⁺²)	4.51
Pb	NS	NS	3.15

NS: No Sample

The development and implementation of industrial hydrometallurgical gallium

ciciencies in rinsing. The germanium completely precipitated along with the copper. The lead in the filter cake was found to be from the zinc powder used in the test. Clarksville adds lead to their zinc powder to help in their purification processes. Most of the cadmium precipitated but the solution temperatures were not high enough to bring the precipitation to completion. The zinc level increased due to the cementation process. Gaseous hydrogen also formed, which required proper ventilation and monitoring as the hydrogen levels gassing from the tank were above 1 000 ppm. The iron level remained relatively the same but all of the ferric iron converted to ferrous.

The pilot test was a success in that all of the goals were accomplished. The ferric iron was converted to ferrous iron, most of the impurity metals were precipitated, and the pH was increased to 2.1. But in the test, two issues arose. First, the amount of zinc consumed was considerably higher than expected and the germanium precipitated with the zinc. This did not happen in the bench-scale testing. To tackle the first problem of the high zinc consumption, several bench-scale tests were completed. These tests were used to confirm the pilot plant usage and identify an alternative to zinc to initially raise the pH to some point around pH 1.0 and still use zinc for cementation and raise the pH to its final point of 2.1. Initial tests used both sodium carbonate and sodium hydroxide to raise the pH.

In the first test, sodium hydroxide and sodium carbonate were added to the leach solution to bring the pH to 2.1. This was done to ensure that the addition of either material would not have any adverse effects on the solution. Based on this initial testing, sodium hydroxide was immediately eliminated as a precipitate started to form at approximately pH 1.3 to 1.5. Sodium carbonate showed no such precipitation.

A test using zinc was completed in the laboratory to see if the results could be duplicated. Parameters recorded included Eh, pH, temperature, free acidity, and zinc addition. In the test, the amount of zinc used was approximately 230 grams/litre of zinc powder. This was equivalent to the pilot cementation testing. The results are shown in Table XVIII. The increase in Ga and Fe grades was due to a slight decrease in solution volumes upon completion from taking samples. These results were similar to the pilot cementation results. The lead increase was due to the lead in the zinc powder.

Upon achieving the same results as the pilot, sodium carbonate was added in various amounts until the amount of zinc use was cut in half. Ultimate test runs at 180 grams/litre sodium carbonate, dropped the zinc usage to about 120 grams/litre. Germanium would be recovered from the zinc precipitant cake as needed. The results are identified in Table XIX and indicate that the cementation products stayed relatively the same but the zinc usage was cut in half. Sodium carbonate use was therefore incorporated into the final design.

Ion exchange

The main focus of the pilot testing was to test gallium recovery with ion exchange. Final filtered solution from cementation was used to run the ion exchange tests. The design parameters of the pilot ion exchange columns are listed in Table XX.

Pilot testing consisted of having three columns operating in series and with one strip column. The highest Ga loaded column would then be stripped and readied for loading again.

The strip solution consisted of 200 gram/litre H₂SO₄ running upflow through the column at approximately 1/10 of a bed volume per minute. The solution was recycled until stripping was complete. Typically, stripping was extremely fast, taking only 1/10 the time of loading. Upon completion of stripping, the column was drained of strip solution (which was added back to the strip solution container) and rinsed with water. The water was added back to the leach solution make-up circuit. The strip solution was not changed during the entire process to build the gallium tenor.

Initial testing focused on the ability of the resin to collect gallium and identify its characteristics. During these tests, the resin did not react quickly enough requiring all tails solutions from the ion exchange columns to be captured for re-circulation (see Table XXI).

In the initial testing, the gallium solution concentration would start at some level, then increase, and finally drop back to some lower level at which point the gallium solution

Table XVIII
Cementation results – zinc only

Element	Pre cementation solution grade, mg/l	Post cementation solution grade, mg/l
Ga	812	867
Ge	131	0.9
Zn	15469	228011
Cd	102	41
Cu	979	2
Fe	8095	10814
Pb	0.8	7.5

Table XIX
Cementation results (with 180 gram/Litre sodium carbonate addition)

Element	Pre cementation solution grade, mg/l	Post cementation solution grade, mg/l
Ga	812	732
Ge	131	59.2
Zn	15469	127248
Cd	102	29.2
Cu	979	2.0
Fe	8095	10884
Pb	0.8	0.9

Table XX
Pilot plant ion exchange column parameters

Variables	Parameters
Columns	4
Recovery columns (in series)	3
Strip columns	1
Size	H – 1.3 m D – 0.20 m
Flow	Upflow, countercurrent
Expansion, %	100
Flow rate (all), bed volumes/min	1/10

The development and implementation of industrial hydrometallurgical gallium

level would stay relatively constant for several hours. The solution was being recirculated from the cementation head tank back at this time. After several tests with the same results, and some success with loading and stripping, the loading curve showed gallium loading at a rate of approximately 2 to 3 grams of gallium per kilogram of resin. This was well below the bench testing and at times there was no gallium to strip.

A review identified the problem as the recycled cementation solution dropping below pH 1.8 and essentially stripping the resin of gallium as fast as the gallium loaded. Sodium carbonate was added to the solution to ensure the pH was maintained between 2.1 and 2.5. Table XXII identifies typical results using pH control. Loading rates for this test were approximately 12 grams per kilogram of resin. This was well above the loading rates identified in the testwork.

Upon redesigning the pilot system for recirculation and pH control, a test was completed with the remaining fresh cementation solution. The test used approximately 200 gallons of fresh solution recirculated through the ion exchange columns maintaining a pH at 2.1. Three columns were on line at one time while one column was stripping. Approximately 60 to 70 gallons of strip solution was used for the test. Final results shown in Table XXIII identified gallium recovery at 94% with good selectivity towards zinc, cadmium and iron. The amount of copper, germanium, and lead were insignificant. These tests identified that the ion exchange process could be effectively used and incorporated into the final design.

Precipitation

Upon completion of the pilot ion exchange testing, approximately 60 to 70 gallons of final strip solution was obtained for gallium recovery. This solution contained approximately 200 grams/litre free acidity of H_2SO_4 that needed to be neutralized to basic conditions to allow gallium electrowinning. The first step of the precipitation process involved some laboratory work to bring the pH of the strip solution to a pH of 4.2. The initial process tested various reagents included lime, sodium carbonate, and sodium hydroxide. Lime use was discontinued because of the overwhelming amount of solids precipitated. Sodium carbonate use was also discontinued because of the amount of chemical required to achieve pH 4.2 and the excessive amount of precipitate formed. Sodium hydroxide was ultimately chosen because the amount of precipitate formed was not excessive, the amount of chemical use was not excessive, and the reaction readily created heat that improved precipitation. Although a hydroxide cake was formed, it was readily filtered.

In the pilot test, approximately 10 gallons of 50% sodium hydroxide was slowly added to the strip solution in an agitated tank. This was equivalent to adding approximately 110 grams/litre of 100% NaOH. As the solution was added, the solution temperature increased to approximately 70°C with a precipitate forming at ~ pH 2.5. The pH was slowly increased to 4.1 where sodium hydroxide addition stopped. At this point the solution was filtered through a plate and frame filter. The filtrate was clear with approximately 2 kg of reddish brown precipitate formed. Table XXIV illustrates the results of the precipitation. As expected, the gallium completely precipitated while a majority of the other elements stayed in solution. This was consistent with what had been identified in the PAS refinery and literature.

Table XXI

Typical ion exchange results

Time	Ga conc, g/ℓ	Strips	Ga conc, g/ℓ
0	.704		
1	.721		
2	.815	1	.365
3	.986		
4	.965	2	.508
5	NS		
6	.811	3	.637
7	.782	4	.892
8	.681	5	.812
9	.713	6	.955
10	.759	7	.934

Table XXII

Typical ion exchange results

Time	Ga conc, g/ℓ	Strips	Ga conc, g/ℓ
0	1.30		3.10
2.0	0.92	1	3.45
3.5	0.60	2	3.60
5.5*	0.50	3	4.14
7.5	0.35	4**	4.00
8.5	0.24	5	4.50

Notes: *Added sodium hydroxide to increase pH to 2.1

**Added H_2SO_4 to maintain 200 gm/l free acidity

Table XXIII

Final pilot ion exchange test results

Element	Cementation head grade, g/ℓ	Ion exchange tail grade, g/ℓ	Final strip solution grade, g/ℓ
Ga	1.73	0.135	3.68
Ge	0.05	0.05	0.04
Zn	57	52	22
Cd	2.3	1.9	1.01
Cu	0.005	0.005	0.018
Fe	20	22.8	5.8
Pb	ns	.002	.003

Table XXIV

pH 4.1 precipitation results

Element	Final strip solution grade, g/ℓ	pH 4.1 filtrate grade, g/ℓ	pH 4.1 filter cake grade, %
Ga	3.68	0.061	13.9
Ge	0.04	0.023	0.07
Zn	22	9.6	4.49
Cd	1.01	0.47	0.19
Cu	0.018	0.068	0.06
Fe	5.8	2.79	6.35
Pb	.003	0.006	<0.01

The development and implementation of industrial hydrometallurgical gallium

The next step was to leach the gallium from the filter cake using a pH 13 sodium hydroxide solution. This would create a Ga electrowinning electrolyte. Initial leaching of the precipitate cake was at ambient temperature for one hour. The solution was filtered and assayed. The amount of solution used to bring the gallium back into solution was approximately 12 litres. The amount of precipitate obtained was 1.2 kilograms. Table XXV shows the results of the initial filter cake leaching. As expected, almost all the impurities were removed from the final electrowinning solution. Further tests increased the leaching time and temperature and removed the gallium level in the filter cake to below 0.5%.

Electrowinning

Electrowinning tests were conducted with a small rectifier using three 7" x 5" stainless steel plates. Two of the plates were used as anodes and one plate was used as a cathode. The parameters listed in Table XXVI were used. Two tests were run using 1 000 amps/square metre current density and all subsequent tests using 1 500 amps/square metre. Test 1 was run for 12 hours. Test 2 was run for 45 hours. Table XXVII outlines the results of the tests.

Upon completion of the testing, approximately 249 grams of gallium were obtained from the solutions. The current efficiency in the tests was approximately 27%. There was substantial gassing at both the anodes and cathodes. The cathode gassed until gallium started to form. Gallium formed as liquid balls on the cathode and dripped off the cathode. Minor amounts of zinc formed as dendrites. These dendrites broke from the cathode and floated in the solution. Filtering will be required to collect this material as it leaves the cell. Temperature was maintained using the joule heat from cell inefficiency. The solution temperature reached 35°C and

remained there during both tests. Upon increase of the temperature, a precipitate formed. Table XXVIII is an elemental analysis of the electrowinning precipitate. Small amounts of gallium found in this material were from the electrowon gallium being pumped into the collection tank and collected with the precipitate. This precipitate was a lead hydroxide and is only sparing soluble in low temperature and insoluble at elevated temperatures. This material would be ultimately added back to the HAL.

Both precipitation and electrowinning testing went as expected. The final flowsheet will recycle most of the materials from this section to ensure maximum recovery from the final plant.

General testing issues

Testing of the gallium pilot was designed to review the ion exchange capabilities of the resin, prove the validity of previous work, and prove the validity of the U.S. Bureau of Mines testwork. Although several tests were run on the material available and a number of problems were worked out of the system, only one HAL batch was completed due to the environmental issues associated with doing a hot acid leach at Clarksville and the Bevill implications. Although all the piloting work results were similar or exactly as the bench-scale predicted and previous work predicted, some unforeseen problems might arise in the full-scale plant because of the small scale of the test work.

Proposed flowsheet

The proposed flowsheets for gallium recovery were developed based on previous and current verification test work and are similar to that of the Bureau of Mines⁴¹. The main changes to the flowsheets from previous work include the switch to hot acid leaching and the change to ion exchange from solvent extraction.

Table XXV

pH 13 gallium IX strip solution precipitate releach

Element	pH 13 filter cake grade, %	Final EW solution grade, g/ℓ	pH 13 filter cake grade, %
Ga	13.9	18.1	8.0
Ge	0.07	<0.010	<0.05
Zn	4.49	0.328	16.7
Cd	0.19	0.003	0.80
Cu	0.06	<0.005	0.61
Fe	6.35	0.004	28.20
Pb	<0.01	0.002	0.08

Table XXVII

Electrowinning test results

Element	Test 1 head, g/ℓ	Test 1 tails, g/ℓ	Test 2 tails, g/ℓ
Ga	18.1	13.4	3.31
Ge	<0.010	<0.010	<0.010
Zn	0.33	0.19	0.06
Cd	0.003	0.003	0.001
Cu	<0.005	<0.005	<0.005
Fe	0.004	0.002	0.003
Pb	0.002	0.001	0.001

Table XXVI

Electrowinning test parameters

Variables	Parameters
Current density, amps/m ²	500–1000
Cell voltage, volts	3.0
Current efficiency, %	25–50
Anode material	2 ea—stainless
Cathode material	1 ea—stainless
Electrolyte, NaOH, g/ℓ	150
Cell temperature, °C	30
Flow rate, ℓ/min	2

Table XXVIII

EW Precipitate Analysis

Element	EW Precipitate, %
Ga	0.72
Ge	<0.05
Zn	2.52
Cd	0.04
Cu	0.08
Fe	3.91
Pb	64.50

The development and implementation of industrial hydrometallurgical gallium

Conclusion

Based on information previously identified and data confirmed through lab and pilot-scale testing, an acidic leach ion exchange gallium recovery plant could be engineered and installed to recover gallium and germanium. For treatment of 5 000 tons per year of feed, the CAPEX was estimated in 2003 to be \$5 M USD and the OPEX to be \$55 USD/kg of Ga produced.

References

1. HOFFMANN, J.E. Advances in the Extractive Metallurgy of Selected Rare and Precious Metals, *JOM*, April 1991, pp. 18–23.
2. MIHAYLOV, I. *et al.* Gallium Solvent Extraction in Hydrometallurgy : An Overview, *Hydrometallurgy*, vol. 28, 1992, pp. 13–27.
3. OLSEN, T.M. *et al.* Gallium and Germanium Extraction from a Primary Source, *Proceedings '88, 18th Hydromet. Meeting of CIM*, May 1988, Paper 12, pp. 1–16.
4. HWA YOUNG LEE *et al.* Process for Recovery of Gallium from Zinc Residues, *Trans IMM*, C, vol. 103, Jan–April, 1994, pp. 76–79.
5. WARDELL, M. P. *et al.* Acid Leaching Extraction of Ga and Ge, *JOM*, June 1987, pp. 39–41.
6. HARBUCK, D.D. *et al.* Sulfuric Acid Leaching of a Germanium-Gallium Ore, *Min. Eng.*, Nov. 1991, pp. 1361–1364.
7. ALFONSO DE MAGALHAES, M.E. *et al.* Recovery Gallium from Residual Bayer Process Liquors, *JOM*, June 1991, pp. 37–39.
8. HARBUCK, D.D. *et al.* Optimization of Gallium and Germanium Extraction from Hydrometallurgical Zinc Residue Light Metals, 1989, pp. 984–989.
9. TIAN RUNG-CANG, *et al.* New Technology for Indium, Germanium and Gallium Recovery in an Electrolytic Zinc Plant, *Mineral Processing and Extractive Metallurgy*, IMM, Kunming, Nov. 1984, pp. 615–624.
10. ZUOREN HUANG. The Recovery of Silver and Scarce Elements at Zhuzou Smelter, *Lead Zinc '90*, pp. 239–250.
11. KRAMER, D.A. *Gallium and Gallium Arsenide: Supply, Technology and Uses*, IC 9208, 1988, US Bur. Mines.
12. THAILI ZHOU, *et al.*, Recovering Tin, Ge and Ga for Zinc Residues, *JOM*, June 1989, pp. 36–40.
13. SCHEPPER, A.D. Liquid-Liquid Extraction of Gallium by TBP, *Hydrometallurgy* 4, 1979, pp. 285–290.
14. BAUTISTA, R.G. Gallium Metal Recovery, *JOM*, June 1989, pp. 30–31.
15. ROSI, F.D. A Survey of a Market, Supply and Availability of Gallium, *Materials & Society*, vol. 4, no. 3, 1980, pp. 349–365.
16. KATRAK, F.E. *et al.* Gallium : Long-Run Supply, *JOM*, Sept. 1981, pp. 33–36.
17. Roskill 1986, Gallium, Occurrence and Production, pp. 2–12, pp. 60–85.
18. PETKOF, B. Gallium Preprint from Bulletin 675, US Bur. of Mines, 1985.
19. ABE, H. *et al.* Recovery of Gallium and Indium at Dowa Mining, *Joint MMJ-AIME Meeting*, 1980, Tokyo, pp. 65–76.
20. OLSEN, M. *et al.* Gallium and Germanium Extraction from the Apex Mine Ore "Precious and Rare Metals Technologies", *Process Metallurgy* 5, Torma/Gundiler, 1989, pp. 531–545.
21. JACOBSON, M. Special Features of Germanium and Gallium Supply and Demand, *Trans of IMM*, C, March, 1988, pp. 45–48.
22. CROWSON, P. *Mineral Handbook*, 1988–89: pp. 108–111; 1990–91: pp. 107–110
23. ANON. Metaleurop Sizes up for Strength and Flexibility, *MBM* June 1990, pp. 22–23.
24. DEMARTHE, J.M. *et al.* Recovery of Specialty Metals, Mainly Germanium and Indium, from Zinc Primary Smelting, *Lead-Zinc '90*, pp. 151–160.
25. PLUNKERT, P.A. Germanium Preprint from Bulletin 675, US Bur. of Mines, 1985.
26. HOFFMANN, J.E. Extraction and Refining of Germanium, *JOM*, June 1987, pp. 42–45.
27. CRUMP, M.E. A New Source of Gallium—Geothermal Mud, *Australasian IMM*, 1995, pp. 163–167.
28. ABISHEVA, Z.S. *et al.* Acid-extraction Technology of Rare Metals Recovery from Phosphorous Furnace, *Elsevier Applied Science for Society of Chemical Industry*, 1993, vol. 1, pp. 210–217.
29. RODIER, D.D. An Overview of Silver and Trace Element Recovery Strategies in the Zinc Industry, *Lead-Zinc '90*, pp. 57–85.
30. HANUSCH, K. Concentration of Germanium from Lead Production Slags. Part 1, *Erzmetall*, vol. 40, no. 6, June 1987, pp. 308–312.
31. COLLINS, M.J. *et al.* Impurity Control and Disposal in Hydrometallurgical Processes, *24th CIM Hydrometallurgical Meeting*, Toronto, 21–24 August 1994, pp. 291–301.
32. ABISHEVA, Z.S. *et al.* Development of Acid-extraction Process for Recovering Gallium from Fly Ash Produced by Coal Combustion., *Tsvetnye Metally*, no. 3, Mar. 1994, pp. 36–38.
33. GRANT, R.M. Emerging Developments in Zinc Extraction Metallurgy., *Proceedings, 2nd international symposium on metallurgical processes for the year 2000 and beyond and the 1994 TMS Extraction and process metallurgy meeting*, San Diego, California, 20–23 September 1994., The Minerals, Metals and Materials Society, 1994, vol. II, pp. 125–149.
34. KIKUCHI, S. Extraction and Separation of Gallium (III), Indium (III) and Aluminium (III) from Sulphuric Acid Solutions by Octylphenyl Phosphoric Acid in Benzene. *J. Min. Metall. Inst. Jpn.*, vol. 104, no. 1207, Sept. 1988, pp. 601–605.
35. JUDIN, V.P. *et al.* Extraction Equilibria in the System $\text{GaCl}_3\text{-AlCl}_3\text{-H}_2\text{O}$ -Tributyl Phosphate, *Metall. Trans. B*, vol. 17B, no. 2, June 1986, pp. 259–265.
36. WATANABE, H. *et al.* Extraction of Aluminum and Gallium from Basic Solutions Containing Organic Acid by High-molecular Weight Quaternary Ammonium Compound, *J. Min. Mater. Process. Inst. Jpn.*, vol. 106, no. 8, 1990, pp. 474–478.
37. SHAOQUAN XU, *et al.* Extraction of Ga from In- and Ga-containing Zinc Blende Mine Treated by Goethite Method, *Rare Met.*, vol. 10, no. 2, Apr. 1991, pp. 129–132.
38. HARBUCK, D.D. Gallium and Germanium Recovery from Domestic Sources, Rep. Invest. US Bur. Mines, no. 9419, 1992, 26 pp.
39. ABISHEVA, Z.S. *et al.* Gallium Recovering from Unconventional Sources of Raw Materials, *Proceedings of the 6th international mineral processing symposium*, Kusadasi, Turkey, 24–26 September 1996, pp. 503–507.
40. MIHAYLOV, I. *et al.* Gallium Solvent Extraction from Acidic Solutions with Octyl Phenyl Acid Phosphate (OPAP) Reagents, *Hydrometallurgy*, vol. 37, no. 2, Feb. 1995, pp. 221–234.
41. JUDD, J.C. *et al.* Gallium Solvent Extraction from Sulphuric Acid Solutions Using OPAP, *Prepr. Soc. Min. Engrs. AIME*, 1990, pp. 90–147.

The development and implementation of industrial hydrometallurgical gallium

42. ADAMS, J.H. *et al.* Germanium Products and Their Applications, Precious and Rare Metal Technologies, *Proceedings of a symposium on precious and rare metals*, Albuquerque, NM, USA, 6-8 April 1988, pp. 577-587.
43. QUENEAU, P.B. *et al.* Germanium Recovery from Fargo Oil's Lang Bay Property, *CIM Bull*, vol. 79, no. 886, Feb. 1986, pp. 92-97.
44. MORALES, P. *et al.* Germanium, Rhenium and Selenium: New Valuable By-products to be Recovered at Chuquicamata, Copper 91. *Proceedings of the international symposium*, Ottawa, Canada, 18-21 August 1991. vol. III Hydrometallurgy and electrometallurgy of copper, Pergamon Press, 1991. pp. 269-280.
45. OHWA, H. *et al.* High-purity Metals Production of Sumitomo Metal Mining Co., Ltd., *Extraction metallurgy 89*, London, 10-13 July 1989, proceedings. London: IMM, 1989, pp. 885-898.
46. HARBUCK, D.D. Increasing Germanium Extraction from Hydrometallurgical Zinc Residues, *Prepr. Soc. Min. Engrs. AIME*, no. 91-42, 1991.
47. TCHAVDAROVA, D. *et al.* Investigating the Conditions of Gallium Re-extraction from Saturated Organic Phases, *Metalurgia Sofia*, vol. 45, no. 1, Jan. 1990, pp. 10-11.
48. RUN-CANG TIAN, *et al.* New Technology for Indium, Germanium and Gallium Recovery in an Electrolytic Zinc Plant, *Mineral Processing and Extractive Metallurgy*, Kunming, Yunnan, China, 27 October-3 November 1984. London: IMM, 1984. pp. 615-624.
49. LEE, H.Y. *et al.* Process for Recovery of Gallium from Zinc Residues, *Trans. Instn. Min. Metall. C*, vol. 103, Jan.-Apr. 1994, pp. C76-C79.
50. HUBICKI, Z. Purification of Zinc Salts from Cd(II), Pb(II), Cu(II), Ni(II), Fe(III), In(III) and Ga(III) Using Chelating Ion Exchangers, *Rudy Metale Nizelaz.*, vol. 30, no. 2, 1985, pp. 54-57.
51. AFONSO DE MAGALHAES, M.E. *et al.* Recovering Gallium from Residual Bayer Process Liquor, *J. Metals*, vol. 43, no. 6, June 1991, pp. 37-39.
52. PESIC, B. *et al.* Recovering Gallium with Kelex 100, *J. Metals*, vol. 40, no. 7, July 1988, pp. 24-26.
53. JI WANG *et al.*, Recovering Germanium from Zinc Leaching Solution by Liquid-Liquid Extraction, *Nonferrous Met. Chin. Soc. Met.*, vol. 52, no. 2, May 2000, pp. 77-79.
54. RIVEROS, P.A. Recovery of Gallium from Bayer Liquors with an Amidoxime Resin, *Hydrometallurgy*, vol. 25, no. 1, June 1990, pp. 1-18.
55. AKKURT, S. *et al.* Recovery of Germanium and Other Metal Values from the Electrolyte Purification Precipitates of Cinkur Zinc Plant, IV. *International Mineral Processing Symposium*, Antalya, Turkey, October 20-22, 1992, proceedings, Middle East Technical University, 1992. vol. 2, pp. 679-690.
56. PESIC, B. *et al.* Recovery of Silver and Gallium from Flue Dust with Acidified Thiourea Solutions, *Prepr. Soc. Min. Engrs. AIME*, no. 86-27, 1986, 17 pp.
57. SATO, T. Solvent Extraction of Gallium (III) from Sodium Hydroxide Solution by Alkylated Hydroxyquinolene, *Hydrometallurgy*, vol. 16, no. 3, Aug. 1986, pp. 315-324.
58. KARVE, M.A. *et al.* Solvent Extraction Separation of Gallium and Indium from Associated Elements with Liquid Anion Exchangers from Ascorbate Media, Solvent Extraction in the Process Industries, papers presented at *ISEC '93 international solvent extraction conference*, held in York, UK, 9-15 September 1993, Elsevier Applied Science for Society of Chemical Industry, 1993. vol. 3, pp. 1347-1352.
59. SWINKELS, G.M. *et al.* The Apex Project: Development of a Primary Gallium and Germanium Producer, *Prepr. Soc. Min. Engrs. AIME*, 1986. pp. 86-153.
60. SATO, T.I. The Extraction of Some Metals from Alkaline Solutions by Alkylated Hydroxyquinoline, *International Solvent Extraction Conference*, 1983. New York: American Institute of Chemical Engineers, 1983, pp. 244-245.
61. HIBBARD JR., W.R. The Extractive Metallurgy of Old Scrap Recycle, *J. Metals*, vol. 34, no. 7, July 1982, pp. 50-53.
62. JOHAN, Z. Indium and Germanium in the Structure of Sphalerite: an Example of Coupled Substitution, *Mineralogy and Petrology*, 1988, vol. 39, pp. 211-229.
63. PHATEK, G. *et al.* Electrochemical Extraction of Gallium From Alkaline Gallium Solutions, *Transactions of the SAEST*, 1988, vol. 39, no. 4, pp. 287-290.
64. CROSSLEY, *et al.* Electrowinning of Gallium, U.S. Patent 3,966,568.
65. KUDO, *et al.* Gallium and/or Indium Separation and Concentration Method, U.S. Patent 6,319,483.
66. CHARLTON, *et al.* Process of Concentrating and Recovering Gallium, U.S. Patent 4,071,422.
67. COTE, G. *et al.* Liquid-Liquid Extraction of Ge with Oxine Derivatives, *Hydrometallurgy* 5, 1980, pp. 149-160.
68. SHAOCHUN CHEN *et al.* Study of the Behavior of Germanium in a New Reducing Process for Zinc Calcine, *Pyrometallurgy 87*. Papers presented at a symposium held in London, 21-23 September 1987. London: IMM, 1987, pp. 255-264.
69. ANDERSON, C.G. Treatment of Copper Ores and Concentrates with Industrial Nitrogen Species Catalyzed Pressure Leaching and Non-Cyanide Precious Metals Recovery, *Journal of Metals*, TMS, April 2003.
70. ROSENBERG, E., FISCHER, R.J. and HART, C. Removal of Low Level Mercury from Aqueous Streams Using Silica Polyamine Composites, *2003 EPD Proceedings—Mercury Management*, M.E. Schlesinger (ed.), 2003, p. 285.
71. ROSENBERG, E., FISCHER, R.J., DEMING, J., HART, C., MIRANDA, V. and ALLEN, B. Silica Polyamine Composites: Advanced Materials for Heavy Metal Recovery, Recycling and Removal, *Symposium Proceedings of the International Conference on Materials and Advanced Technologies*, T. White and D. Sun (eds.), Mat. Res. Soc., Singapore, 2001, vol. I, p. 173.
72. ROSENBERG, E., FISCHER, R., DEMING, J., and ANDERSON, C. Silica Polyamine Composites as Platforms for Green Ore Processing, *ALTA 2000 Technical Proceedings*, SX/IX-1, ALTA Metallurgical Services 2000.
73. BEATTY, S.T., FISCHER, R.J., HAGARS, D.L., and ROSENBERG, E. A Comparative Study Of the Removal of Heavy Metal Ions from Water Using a Silica-Polyamine Composite and a Polystyrene Chelator Resin, *Industrial and Engineering Chemistry Research*, 1999, vol. 38, 4402 p.
74. BEATTY, S.T., FISCHER, R.J., PANG, D., and ROSENBERG, E. Applications of Silica-Polyamine Composites II. Metal Ion Separation from Mine Waste Water and Soft Metal Ion Extraction Efficiency, *Sep. Sci. and Tech.* 1999, vol. 34, 3125 pp.
75. ROSENBERG, E. and PANG, D. System for Extracting Soluble Heavy Metals from Liquid Solutions, U. S. Patents No. 5,695,882 and No. 5,997,748. 1997 & 1999.
76. PETERS, M.S. and TIMMERHAUS, K.D. *Plant Design and Economics for Chemical Engineers*, McGraw-Hill, Inc., New York, 1991.
77. Mine and Mill Equipment Costs, Western Mine Engineering, Spokane, Washington, 1995. ◆