THE DEVELOPMENT AND IMPLEMENTATION OF INDUSTRIAL HYDROMETALLURGICAL GALLIUM RECOVERY OF THE CLARKSVILLE REFINERY WASTE RESIDUE

by

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Abstract

Todd Fayram, the Gordonsville Operation of Pasminco US Inc., and 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 gallium. This thesis describes the testing and engineering program that culminated in this successful recovery of gallium through process described herein.

Keywords:
Gallium, Germanium, Clarksville Residue, Clarksville Refinery, Ion Exchange, Electro-refining, Leaching, Sphalerite, Pasminco

Dedication

I wish to dedicate this thesis to my wife, Suzanne. She has pushed me to excel in the Mineral Processing, Metallurgy, and Mining fields while unfailingly supporting these endeavors, projects, and relocations.

Acknowledgements

I would like to thank the Center for Advanced Mineral and Metallurgical Processing of Montana Tech and Dr. Corby Anderson for his detailed metallurgical knowledge and know-how that made this and other projects we have worked on, very successful.

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Glossary of Terms

%	percent
”	inch
A/O	aqueous/organic phase ratio
Al	Aluminum
atm	atmosphere
˚C	degree Celsius
Ca	Calcium
Cd	Cadmium
CO_3	Carbonate
Cu	Copper
EW	Electrowinning
Fe	Iron
Ga	Gallium
Ge	Germanium
Gms	Grams
H	Hydrogen
HAL	Hot Acid Leach
IX	Ion Exchange
Kg	kilogram
l	liter
m	meter
M	molar
m^2	meters squared
Mg	Magnesium
min	Minute
Na	Sodium
NaOH	Sodium hydroxide (caustic)
NO_2	Nitrite
NR	Not recovered
NSC	Nitrogen Species Catalyzed Leach
O	Oxygen
OH	Hydroxide
OPAP	Octyl Phenyl Acid Phosphate
org	Organic
oz	Ounce avoirdupois (troy)
Pb	Lead
PO_4	phosphate
ppm	Parts per million
SO_4	Sulfate
SX	Solvent Extraction
tons	Short tons
µm	micrometer
USD	United States Dollars
w/	With
WAL	Weak Acid Leach
Zn	Zinc

1. Introduction

The Gordonsville Zinc Mine and Mill, located in Gordonsville, Tennessee has produced zinc sulfide (sphalerite) flotation concentrates almost continuously since the early 1960s, when zinc was discovered in the Gordonsville, Tennessee area. The mine typically produces approximately 95,000 tons of low iron, extremely high-grade zinc concentrate of 65.5% zinc by weight nearly approaching the theoretical sphalerite concentration limits of 67.1% zinc by weight per year. This zinc concentrate is sent to the Clarksville Zinc Refinery where the zinc is leached from the sphalerite using a weak acid leach process, electrowon, melted, and poured into high purity zinc ingots (>99.99% zinc).

Within the sphalerite concentrate, several byproduct elements were found to be significantly concentrated including gallium. The gallium concentration in the sphalerite concentrate was found to approach approximately 300 parts per million(1) or a quantity of approximately 40 tons of gallium per year. The gallium typically replaced zinc and other metals within the crystal lattice structure of the sphalerite(2) and was concentrated in the flotation concentrate in the same manner as the sphalerite.

During the hydrometallurgical zinc-processing at the Clarksville Refinery, a leach residue is typically formed that contains a majority of the impurities including the gallium that would otherwise contaminate or hinder the zinc refining process. Approximately 7,000 tons of residue is formed annually containing approximately 0.6% gallium(1) along with significant quantities of iron (10%), zinc (17%), copper (0.4%), germanium (0.4%), silica (1.0%) and lead (15%). The metals for the residue are typically found as oxides although there are significant unreacted zinc sulfides. This residue was typically sold for the germanium value. Until recently, no revenue for the gallium was obtained from the sale of the residue.

The goals of the gallium recovery project were to:

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

The results of the testwork and pilot study are identified and presented in this thesis.

2. Technology Review and Initial Flowsheet Development

As part of reviewing the feasibility of gallium removal, a technology assessment was completed which comprised searching and reviewing associated technology, literature, and recovery methods for gallium. The literature search is listed in its entirety and separately in the bibliography(1-82).

During this assessment, a consultation was held with the Clarksville Refinery personnel to identify methods that may or may not be used for recovering the gallium. Due to environmental issues identified by the site personnel relating to Bevill Exclusion requirements, (In 1980 RCRA (Resource Conservation and Recovery Act) was amended by adding section 3001(b)(3)(A)(ii), known as the Bevill exclusion, to exclude "solid waste from the extraction, beneficiation, and processing of ores and minerals" from regulation as hazardous waste under Subtitle C of RCRA(3)). No Hot Acid Leach scenarios could be developed or used for any recovery of gallium from Clarksville residue (in the case of Clarksville, a hot acid leach or HAL is any leaching with acid where the leaching process starts at a temperature of 80° Celsius or higher). Based on this comment, the following alternatives were identified and researched:

- Weak acid and alkali hydrometallurgical leaching were identified for gallium dissolution.
- Ion exchange, solvent extraction, cementation, and precipitation methods were explored to selectively recover gallium.
- Electrorefining methods were explored for final recovery of the gallium.

Based on the literature and technology review, basic flowsheets were identified for each of the processes to use as a template for testing. The following identifies the results of the review.

2.1. Weak Acid Leaching/Solvent Extraction

The literature review identified two gallium recovery processes that had been developed based on Clarksville residue(4,5). Both gallium recovery processes were similar and used the following methods:

- A weak acid leach circuit to dissolve the gallium, typically

  $Ga_2O + 3H_2SO_4 + O_2 \leftrightarrow Ga_2(SO_4)_3 + 3H_2O$
- Conversion of the leached iron from ferric to ferrous iron(21), typically

  In pH <3.5, $2Fe^{+3} + Zn_{(metal)} \leftrightarrow 2Fe^{+2} + Zn^{+2}$

  $Zn^{+2} + H_2SO_4 \leftrightarrow ZnSO_4 + H_{2(gaseous)}$
- Precipitation and filtration of other metals using, sodium sulfide and sodium carbonate

  Germanium Sulfide Precipitation Example:

  $Ge^{+2} + Na_2S \leftrightarrow GeS + 2Na^{+}$

  Lead Carbonate Precipitation Example:

  $Pb^{+2} + NaCO_3- \leftrightarrow PbCO_3 + Na^{+}$
- Recovery of the gallium with a solvent extraction approach using,

OPAP (Octyl Phenyl Acid Phosphate, $C_{14}H_{23}O_4P$), in the following reactions(6):

$Ga^{3+} + (3\text{-}S1)HM_{(org)} = GaM_3 \cdot S1HM_{(org)} + 3H^{+}$

$Ga^{3+} + (3\text{-}S2)HD_{(org)} = GaM_3 \cdot S2HD_{(ORG)} + 3H^{+}$

Where HM denotes mono-OPAP and HD denotes di-OPAP.

- Strip of the gallium from the solvent extraction chemical, and
- Electrowinning of the strip solution to create a crude gallium metal for sale.

Based on a review of the two processes, a block flowsheet was developed. This included an acidic nitrogen species catalyzed (NSC)(7) pressure leach step. Figure 1 illustrates the proposed testing flowsheet.

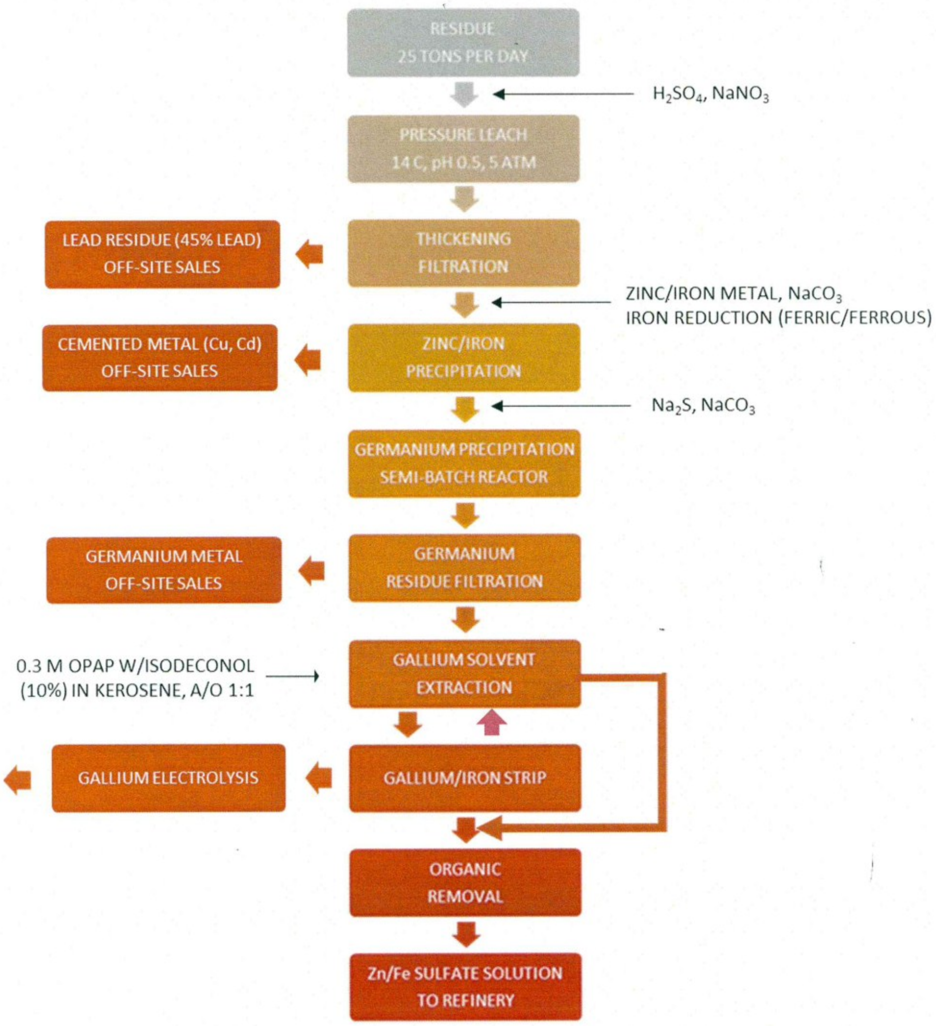


Figure 1: Weak Acid Leach/Solvent Extraction Flowsheet

2.2. Alkaline Leaching/Precipitation Flowsheet

The literature review identified two alkaline gallium leaching processes. The processes identified were being developed by Dowa(8,9) and Cominco(10). Both of the processes were nearly identical and included the following:

- Alkaline leaching using sodium hydroxide to remove iron and form a jarosite ($NaFe_3(OH)_6(SO_4)_2$) residue,
- Precipitation and filtration of aluminum, cadmium, and zinc from leach solutions with calcium hydroxide,
- Precipitation and filtration of germanium from leach solutions with magnesium hydroxide,
- Neutralization of leach solutions with sulfuric acid and further precipitation and filtration of iron lead, and zinc, and
- Addition of sodium hydroxide to increase alkalinity of solution and recovery of gallium by electrowinning.

The proposed alkaline leach flowsheet follows:

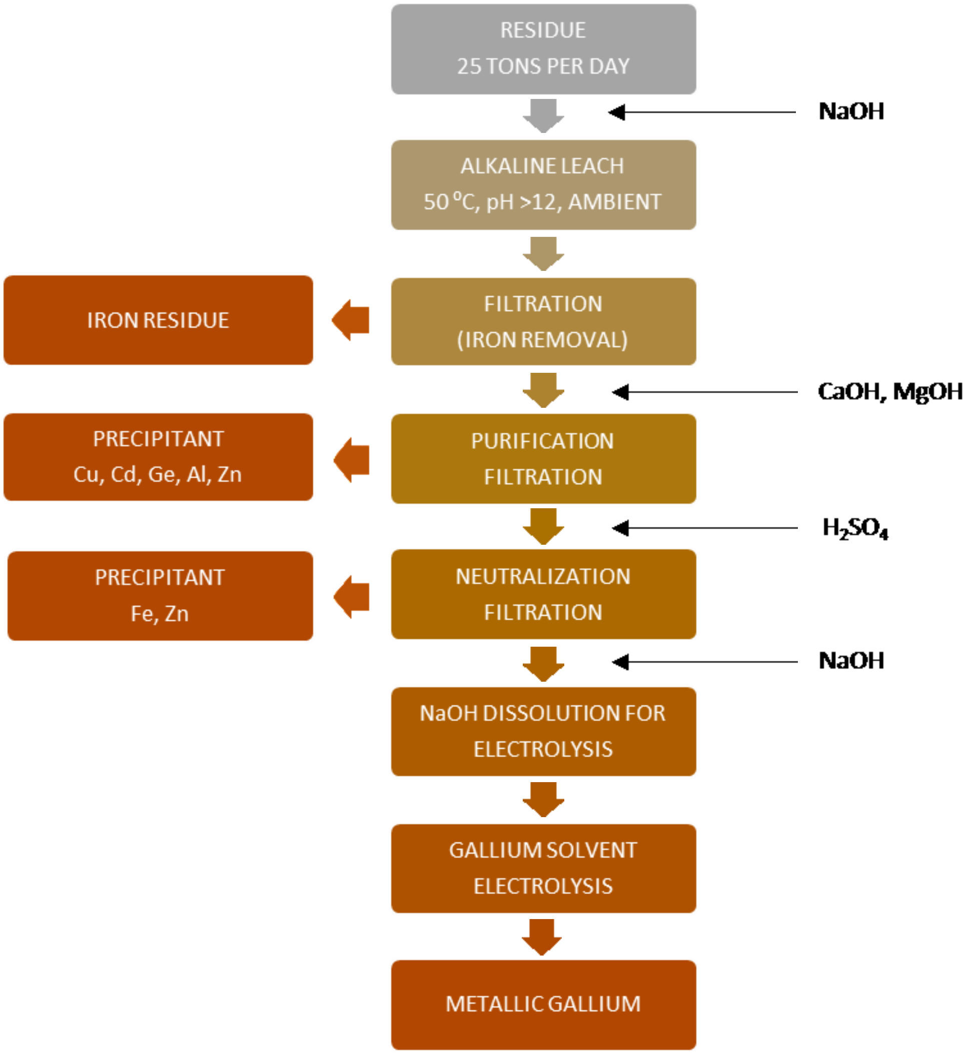


Figure 2: Alkaline Flowsheet

2.3. Ion Exchange

Instead of using Solvent Extraction for removal of Gallium, several ion exchange resins that contained iminodiacetic acid (dicarboxylic acid amine - $C_4H_7NO_4$) as the active component were tested to recover gallium(11,12). Figure 3 illustrates an ion exchange flowsheet.

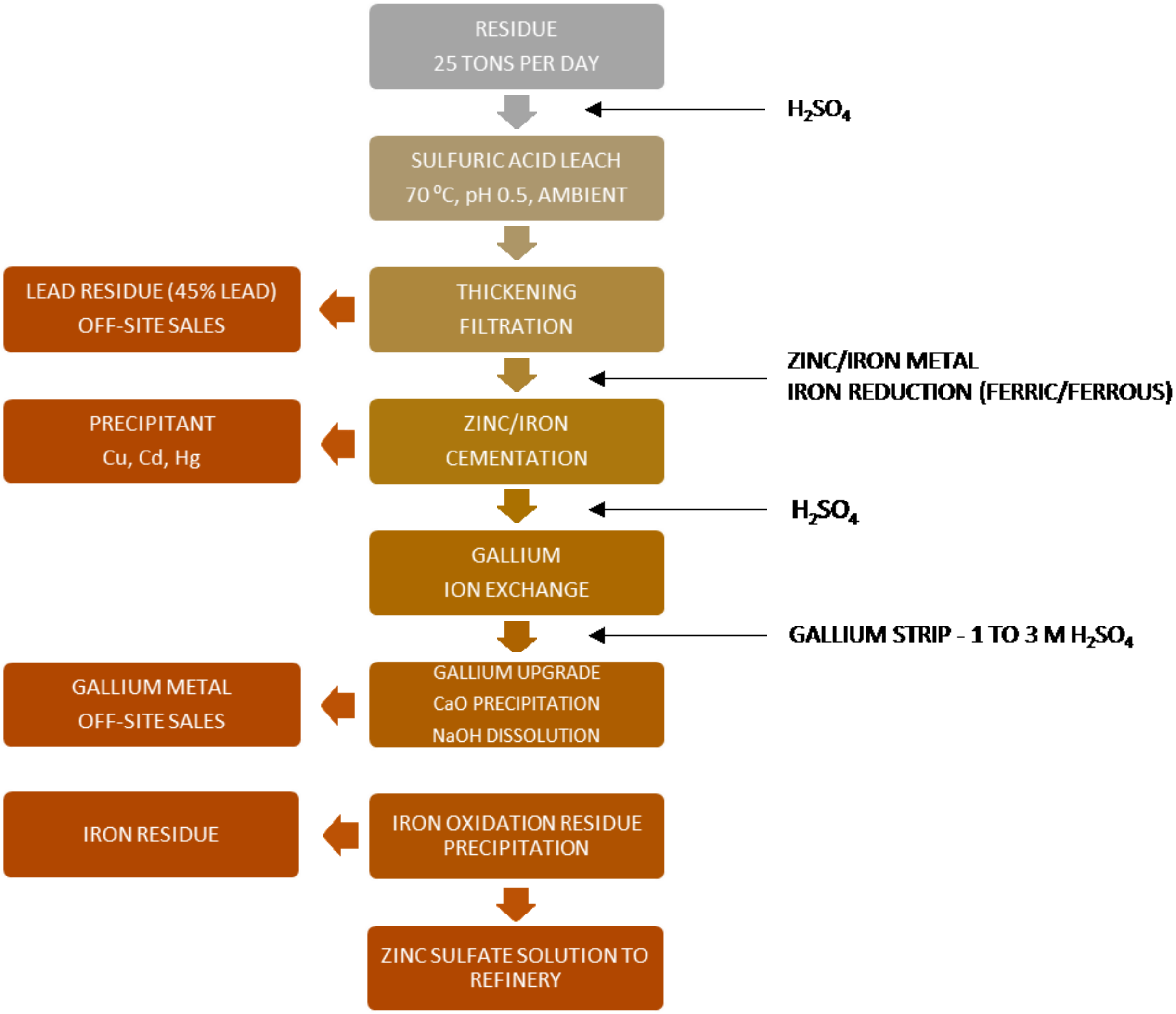


Figure 3: Ion Exchange and Electrowinning Flowsheet

3. Laboratory Testing

Bench scale testing of the Clarksville residue was used to identify the parameters required for pilot testing. Individual testing of each process 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 was completed using acid/alkaline leaching, cementation, solvent extraction, ion exchange, and electrowinning. Each area of testwork is identified below. The gallium was assumed to be a gallium oxide when testing started.

3.1. Alkaline Leaching

Gallium is highly soluble within alkaline solutions and typically forms a gallate in the form of $Ga(OH)^{-\,4}$(13). The Alkaline leaching was dismissed as a viable process due to the solubility of lead oxide to soluble hydroxoplumbates (II)(14) within the alkaline solutions. In a review of the literature, lead was found to interfere with the recovery of the gallium in both solvent extraction and ion exchange. Alkaline leaching was also dismissed as a process due to the extensive availability of sulfuric acid and acid proof materials and equipment.

3.2. 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 for sulfur removal,
- Germanium Slag—Slag product containing gallium after germanium removal, and
- Clarksville Germanium Residue—Final residue created at Clarksville refinery. (This residue was processed for germanium recovery.)

Testing consisted of weak acid leach (WAL), hot acid leach (HAL), and a nitrogen species catalyzed leach (NSC)(7), all using sulfuric acid as the leachate. The test parameters were identified in Table I (Pasminco Test for Total Acid can be found in Appendix A).

Table I: Acid Leaching Parameters

Parameter	HAL	WAL	NSC
Slurry Density (% solid by weight)	15%	15%	15%
Temperature (℃)	90	70	105
Time (hours)	5	5	2
Acid Strength, H_2SO_4 (gms/l)	150	~5	150
Pressure (atm)	ambient	ambient	6
Mixing (shear w/propeller)	constant	constant	constant
Sodium Nitrite Addition	no	no	yes

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

Table II: Gallium Leach Recovery

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

3.3. Cementation

The cementation step was originally undertaken to do the following:

- Identify zinc dust requirements to convert the ferric iron to ferrous iron, and
- Raise the pH to 2.1 to allow for solvent extraction or ion exchange.
  Note that the 2.1 pH level was arbitrarily identified based on a review of the many different references. Although no isotherms were able to be identified: gallium, in a pH 2.0 sulfate system, was identified as preferentially absorbing on a wide range of ion exchange resins or is extracted in solvent exchange solutions over ferrous iron. Based on the reference review, testwork arbitrarily used the pH 2.0 value as base point.

Subsequent testwork used the parameters shown in Table III with final cementation test results identified in Table IV.

Table III: Initial Cementation Parameters

Parameters	Leach Solution
pH	0.50
Iron Content, Fe^{+3} (gms/l)	6.5
Acid Strength, H_2SO_4 (gms/l)	150
Pressure (atm)	ambient
Temperature (℃)	ambient
Mixing, shear w/propeller	constant

Table IV: Final Cementation Results

Parameters	Leach Solution
pH	2.1
Iron Content, Fe^{+3} (gms/l)	0.0
Acid Strength, H_2SO_4 (gms/l)	3
Zinc Added (gms/l)	43
Temperature (℃)	45
Mixing, shear w/propeller	constant

All ferric iron was converted to ferrous iron (Pasminco Test Procedure for Ferrous and Total Iron can be found in Appendix B. Note that sodium carbonate was added to bring pH from 0.5 to 1.0 at a rate of 75 grams/liter. Sodium carbonate use was found to minimize the amount of precipitant formed over the use NaOH.

3.4. Solvent Extraction

Solvent extraction was identified by the U.S. Bureau of Mines(15) as an extraction technique for recovering gallium using Octylphenyl Acid Phosphate (OPAP). The initial test work was on residue material from Clarksville and which subsequently identified a solvent extraction flow sheet to remove gallium. Solvent extraction test work completed at CAMP for this project paralleled the Bureau's work.

The test work consisted of leaching Clarksville gallium residue with hot sulfuric acid and completing the cementation work as noted above. 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 (see Figure 4 for the set-up).

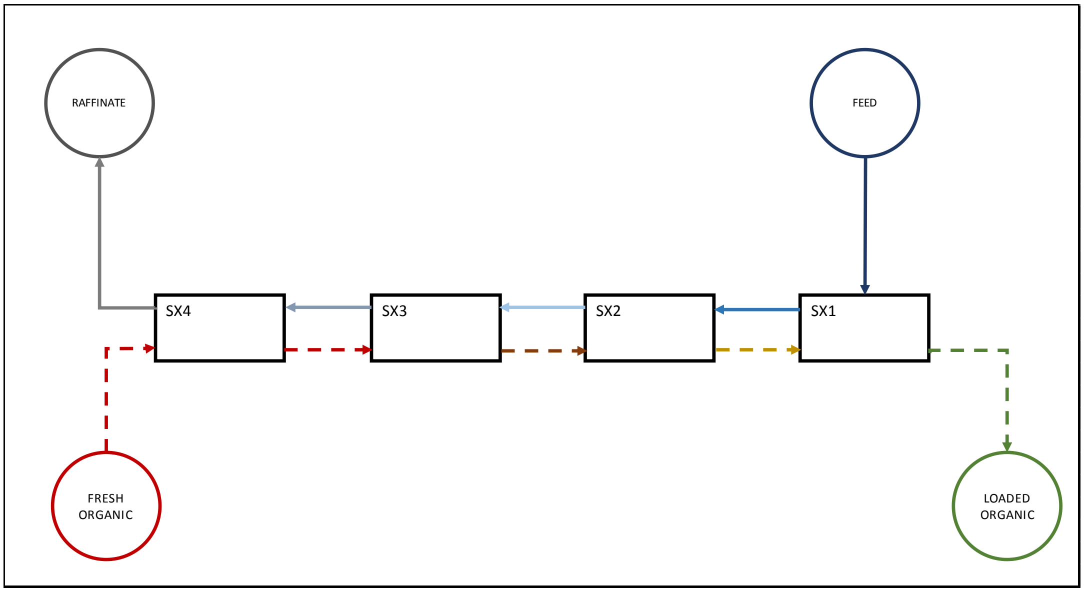


Figure 4: SX Testing Flowsheet

In the laboratory, four separatory funnels were placed in a series and the feed solution was added to the first funnel with the initial organic. The flow was then advanced by hand in a countercurrent manner so the highest grade feed the highest grade organic. Table V lists the bench scale solvent extraction test parameters.

Table V: Solvent Extraction Test Parameters

Parameters	**Leach Solution**
pH	2.1
Iron Content, Fe^{+3} (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, Isododeconal (% by vol)	10
Organic	Kerosene
Mixing	shaker

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. Both organic and aqueous fractions were hand transferred. The results listed in Table VI were obtained (See Appendix C for solvent extraction test work results.).

Table VI: Solvent Extraction Test Results

Parameters	Leach Solution
Gallium Recovery (%)	90+
Germanium Recovery (%)	0
Temperature (℃)	ambient
Mixing (shear w/propeller)	constant

3.5. 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 Incorporated(11,12) that was subsequently tested (Test report performed by Purity Systems is identified in Appendix D). The resin parameters were identified as shown in Table VII.

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

Testing consisted of adding zinc powder to the leach liquor for impurity cementation, pH adjustment and ferric reduction. Following precipitant filtration, ion exchange was performed. Several leach liquors including residue leach liquor, 1st 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 with the results listed in Table IX provided by testing at Purity Systems labs.

Table VIII: Initial Ion Exchange Parameters

Parameters	Leach Solution
pH	2.1 - 2.5
Temperature (℃)	ambient
Iron Content, Fe^{3+} (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 Ion Exchange Recovery

Test	Ga Recovery (%)	Ge Recovery (%)	Fe Recovery (%)	Zn Recovery (%)
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.

Upon completion of the initial test work, further work was completed using a hot acid leach solution of the leach residue 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 and the results are listed in Table XI.

Table X: Hot Acid Leach Ion Exchange Testing Parameters

Parameters	Leach Solution
pH	2.1 - 2.5
Temperature (°C)	ambient
Iron Content, Fe^{+3} (gms/l)	0.0
Acid Strength, H_2SO_4 (gms/l)	1 - 3
IX Flow Rate (bed volumes/minute)	0.833 upflow
Strip Solution, H_2SO_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 (grms Ga/kg resin)	4.8
Attrition	none
Strip Time (bed volumes)	1.5

3.6. 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(1).

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 re-dissolved using 200 gram per liter 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-zinc-minor metal hydroxide solution ready for electrowinning.

3.7. Electrowinning

Electrowinning of solution purification hydroxide solutions was tested using purchased gallium and zinc in simulated process solutions (See Appendix E for testing report). The parameters of Table XII were used for testing. Parameters for testing were identified from US Patent 3,966,568(16) and 6319483(9). Testwork was repeated and confirmed by CAMP.

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 (℃)	30
Flow Rate (l/min)	1

Based on the reference review, high current densities and voltages are normal in the gallium industry. The high current densities support higher purity gallium forming. In the testing, a single cathode was placed between a two anodes. 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. No pitting was identified on either the anodes or cathodes. The results of the electrowinning test are shown in Table XIII.

Table XIII: Electrowinning Test Results

Variables	Parameters
Current Density (amps/m^2)	1000
Cell Voltage (volts)	4.0 to 4.1
Gallium Recovery (%)	93 to 99
Anode Deposition	None
Cathode Deposition	Ga Droplets,
Zn Dendrites	Yes, floating
Cell Temperature (℃)	31 to 38
Flow Rate (l/min)	1

Note: Ga was easily removed from the cathode

Current efficiency was not identified in the above testing due to the fact that with amount of gallium to be produced (approximately 7,000 kg/year), high or low current efficiencies would have limited effect on the operating cost to produce a kilogram of gallium. The test was completed to ensure that gallium would indeed plate on stainless and be effectively removed.

4. 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 to ultimately 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 100:1. Piloting consisted of testing the following systems:

- Hot Acid Leaching,
- Cementation,
- Ion Exchange,
- Precipitation, and
- Electrowinning.

Figure 4 is the flowsheet as developed and used for the pilot testing at Clarksville.

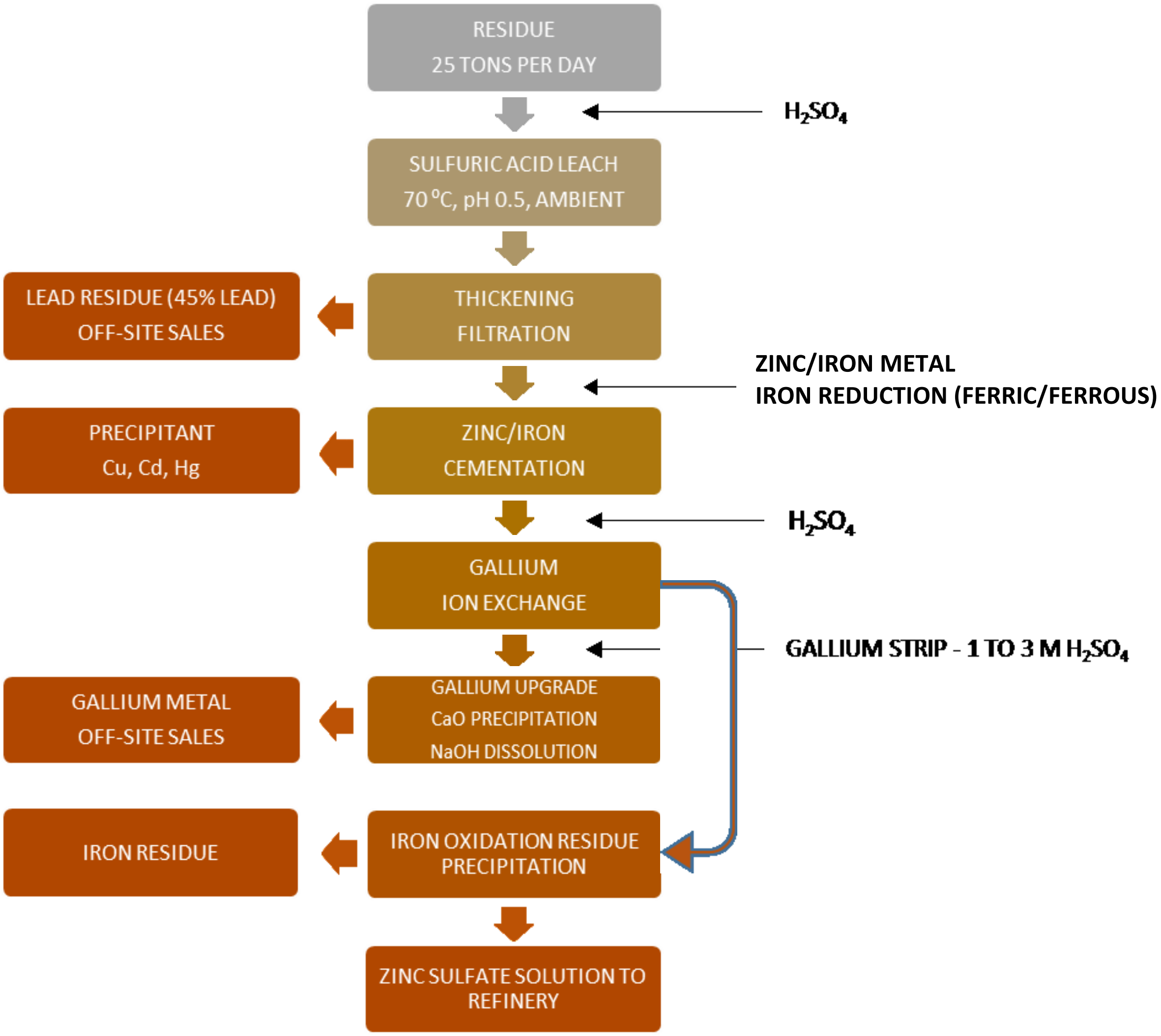


Figure 5: Ion Exchange and Electrowinning Pilot Plant Flowsheet

4.1. 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.

Table XIV: Acid Leaching Test Parameters

Parameter	HAL
Slurry Density (% solid by weight)	15
Temperature (℃)	90
Time (hours)	5
H_2SO_4 Acid Strength (gms/l)	150
Pressure (atm)	1
Mixing (shear w/propeller)	constant
Other (Sodium Nitrite Addition)	no

For the pilot test, approximately 1,050 kilograms of Clarksville residue was added to 4,000 liters of water under high agitation. Approximately 1,000 liters of water was not 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℃. Once at temperature, the solution was leached in H_2SO_4 for 5 hours and then filtered. The results are listed in Table XV.

Table XV: Pilot Hot Acid Leach (HAL) Results

Element	Residue Head Grade (%)	Filtrate Grade (gms/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.

Filtration of the solution was completed in a plate and frame filter using 215 square feet of filter cloth. Filter cloth used was a 10.5 oz polypropylene with a porosity of 3 to 5 cubic feet per minute under 1-inch water pressure designed to trap 1-micron particles or larger. The filter rate of the material was approximately 20 liters/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.

4.2. 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, zinc powder from the Clarksville refinery 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 powder was added as needed until pH 2.1 was obtained. The test results are shown in Table XVI.

Table XVI: Zinc Powder Cementation Testing Result

Parameters	Leach Solution
pH	<0.5
Zinc Usage* (gms/l)	240
Temperature (ºC)	21 to 54
Iron Content, Fe^{+3} (gms/l)	0.0
Acid Strength, H_2SO_4 (gms/l)	200 to 3.0
Color	clear to reddish black

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. Flowrates 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. Collected cementation material is removed and sent to the Clarksville refinery impurity section for further processing of salable elements.

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.

Table XVII: Pilot Plant Zinc Powder Cementation Results

Element	Pre Cementation Solution Grade (gms/l)	Post Cementation Solution Grade (gms/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			

A review of the testing identified that the gallium was not precipitated. Gallium in the filter cake was soluble gallium and was not washed from the cake due to inefficiencies 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 out 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 1000 ppm. The iron level remained relatively the same but all of the ferric iron converted to ferrous iron.

Pilot testing 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 out, 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 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 a 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 Clarksville zinc was completed in the laboratory to see if the results could be duplicated. Parameters recorded included E_H, pH, temperature, free acidity, and zinc addition. In the test, the amount of zinc used was approximately 230 grams/liter of zinc powder, which was equivalent to the pilot cementation testing. Laboratory test 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 with the lead increase was due to the lead in the zinc powder added by the Clarksville Refinery to their powered zinc.

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

Upon achieving the same results as the pilot test, sodium carbonate was added in various amounts until the amount of zinc use was cut in half. Ultimate test runs at 180 grams/liter sodium carbonate, dropped the zinc usage to about 120 grams/liter. 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.

Table XIX: Cementation Results
With 180 Gram/Liter 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

4.3. Ion Exchange

The main focus of the pilot testing was to test gallium recovery with ion exchange using Purity Systems WP-2 ion exchange resin. 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.

Table XX: Pilot Plant Ion Exchange Column Parameters

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

Pilot testing consisted of three columns operating in series followed by one strip column. The highest Ga-loaded column would then be stripped and readied for loading again. The strip solution consisted of 200 gram/liter H_2SO_4 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).

Table XXI: Typical Ion Exchange Results

Time	Ga Conc (gms/l)	Strips	Ga Conc (gms/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

In the initial testing, the gallium solution concentration would start at a level, then increase, and finally drop back to some lower level at which point the gallium solution 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 of the problem identified that a hydrogen ion was being released back into the recycled solution as the gallium replaced the hydrogen ion on the hydrogen based ion exchange resin. This hydrogen ion effectively lowered the recycled solution pH below the absorption threshold for gallium for this particular ion exchange resin causing the recycled cementation solution to drop below pH 1.8. Essentially, the gallium was stripped from the resin of gallium as fast as the gallium loaded. To minimize the potential for precipitation, 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.

Table XXII: Typical Ion Exchange Results

Time (minutes)	Ga Conc (gms/l)	Strips	Ga Conc (gms/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 > pH to 2.1
**Added H_2SO_4 to maintain 200 gm/l free acidity.

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.

Table XXIII: Final Pilot Ion Exchange Test Results

Element	Cementation Solution Head Grade (gms/l)	Ion Exchange Solution Tail Grade (gms/l)	Final Strip Solution Grade (gms/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

4.4. Precipitation

Upon completion of the pilot ion exchange testing, approximately 60 to 70 gallons of final strip solution was obtained for gallium recovery and contained approximately 200 grams/liter free acidity of H_2SO_4 that needed to be neutralized to basic conditions to allow for gallium electrowinning. Following the Clarksville refinery practice as identified in Section 3.6: 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 with the initial process testing various reagents included lime, sodium carbonate, and sodium hydroxide. Lime use was discontinued because of the overwhelming amount of unidentified 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 used 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/liter of 100% NaOH. As the solution was added, the solution temperature increased to approximately 70℃ 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 Clarksville refinery and literature.

Table XXIV: pH 4.1 Precipitation Results

Element	Final Strip Solution Grade (gms/l)	pH 4.1 Filtrate Grade (gms/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 next step was to leach the gallium from the filter cake using a pH 13 sodium hydroxide solution and create a Ga electrowinning electrolyte. Initial leaching of the precipitate cake was at ambient temperature for one hour. The solution was filtered and assayed. Approximately 12 liters of solution were used to bring the gallium back into solution and 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%.

Table XXV: pH 13 Gallium IX Strip Solution Precipitate Releach

Element	Initial pH 13 Filter Cake Grade (%)	Final EW Solution Grade (gms/l)	Final 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

4.5. 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 with the anode placed between the two cathodes. The testing cell was set up similar to that in Figure 6.

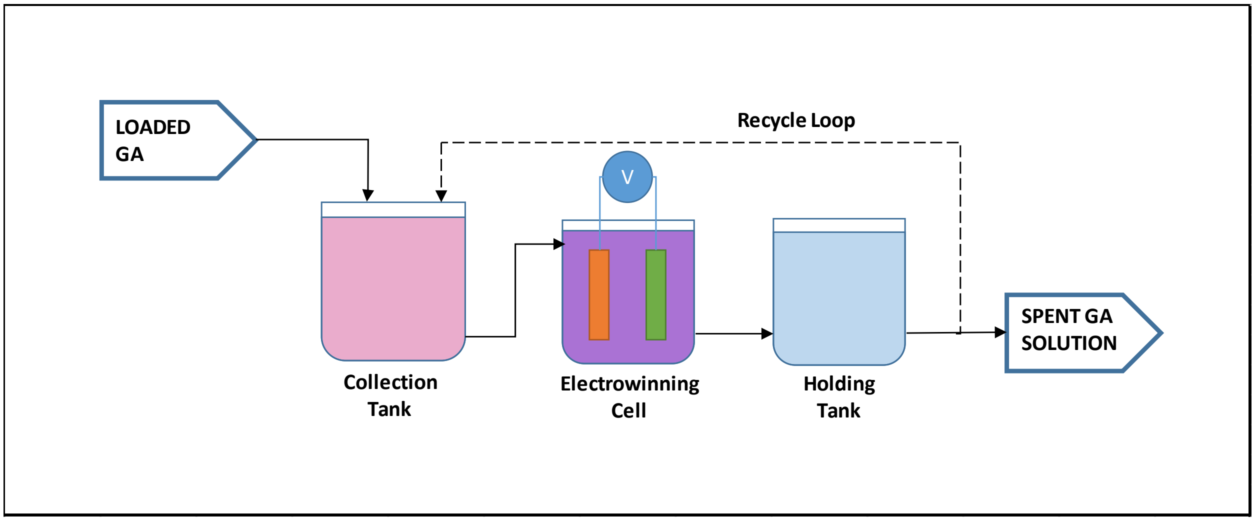


Figure 6: Electrowinning Test Set-up

The parameters listed in Table XXVI were used to run two tests: one using 1000 amps/square meter current density and all subsequent tests using 1500 amps/square meter. Test 1 was run for 12 hours. Test 2 was run for 45 hours. Table XXVII outlines the results of the tests.

Table XXVI: Electrowinning Test Parameters

Variables	Parameters
Current Density (amps/m^2)	1000
Cell Voltage (volts)	3.0
Current Efficiency (%)	25 to 50
Anode Material (stainless)	2 ea
Cathode Material (stainless)	1 ea
Electrolyte, NaOH (gms/l)	150
Cell Temperature (°C)	30
Flow Rate (l/min)	2

Table XXVII: Electrowinning Test Results

Element	Test 1-2 Head (gms/l)	Test 1 Tails (gms/l)	Test 2 Tails (gms/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

Upon completion of the testing, approximately 249 grams of gallium were obtained from the solutions. The current efficiency in the tests was approximately 27% with substantial gassing at both the anodes and cathodes. Cathode gassing occurred 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℃ and remained there during both tests. Upon increase of the temperature, a lead hydroxide 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. Ultimately, this material would be added back to the HAL and reprocessed.

Table XXVIII: EW Precipitate Analysis

Element	EW Precipitate (%)
Ga	0.72
Ge	<0.05
Zn	2.52
Cd	0.04
Cu	0.08
Pb	92.5
Fe	3.91

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.

5. 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(15) 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.

6. 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 Mines(15). Main changes to the flowsheets from previous work include the switch to hot acid leaching and the change to ion exchange from solvent extraction. A detailed flowsheet and mass balance can be found in Appendix F.

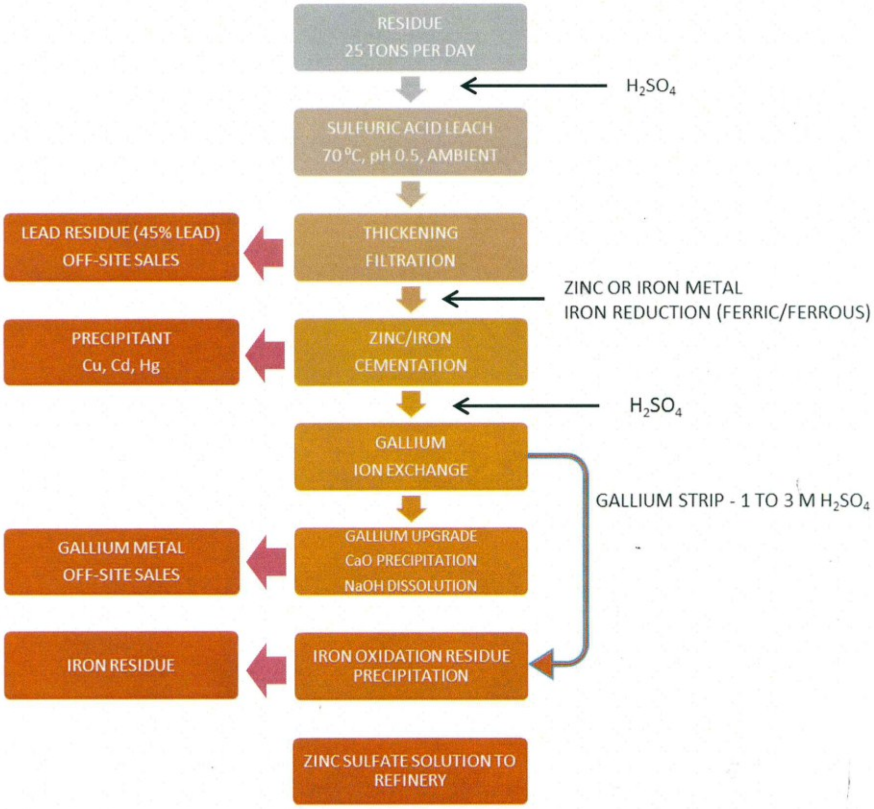


Figure 7: Proposed Gallium Recovery Flowsheet

7. Cost Estimates

Cost estimates to build a gallium facility were completed based on the conceptualized flowsheet and mass balance. Both a capital and operating cost estimate were completed.

7.1. Capital Cost Estimate

A capital cost estimate was completed using the mass balance for general design size and plant requirements. The following estimating materials were used:

- Plant Design and Economics for Chemical Engineers, Peters and Timmerhaus using a 1990 cost basis(17).
- Mine Cost Service – Costmine – 2010(18).
- Internal Pasminco Quotes

All costs were brought to 2012 dollars using the Marshall and Swift Equipment Cost Index. The process industry average was used for this estimate.

- 2010 cost factor—129.9 and
- 2012 cost Factor—165.5

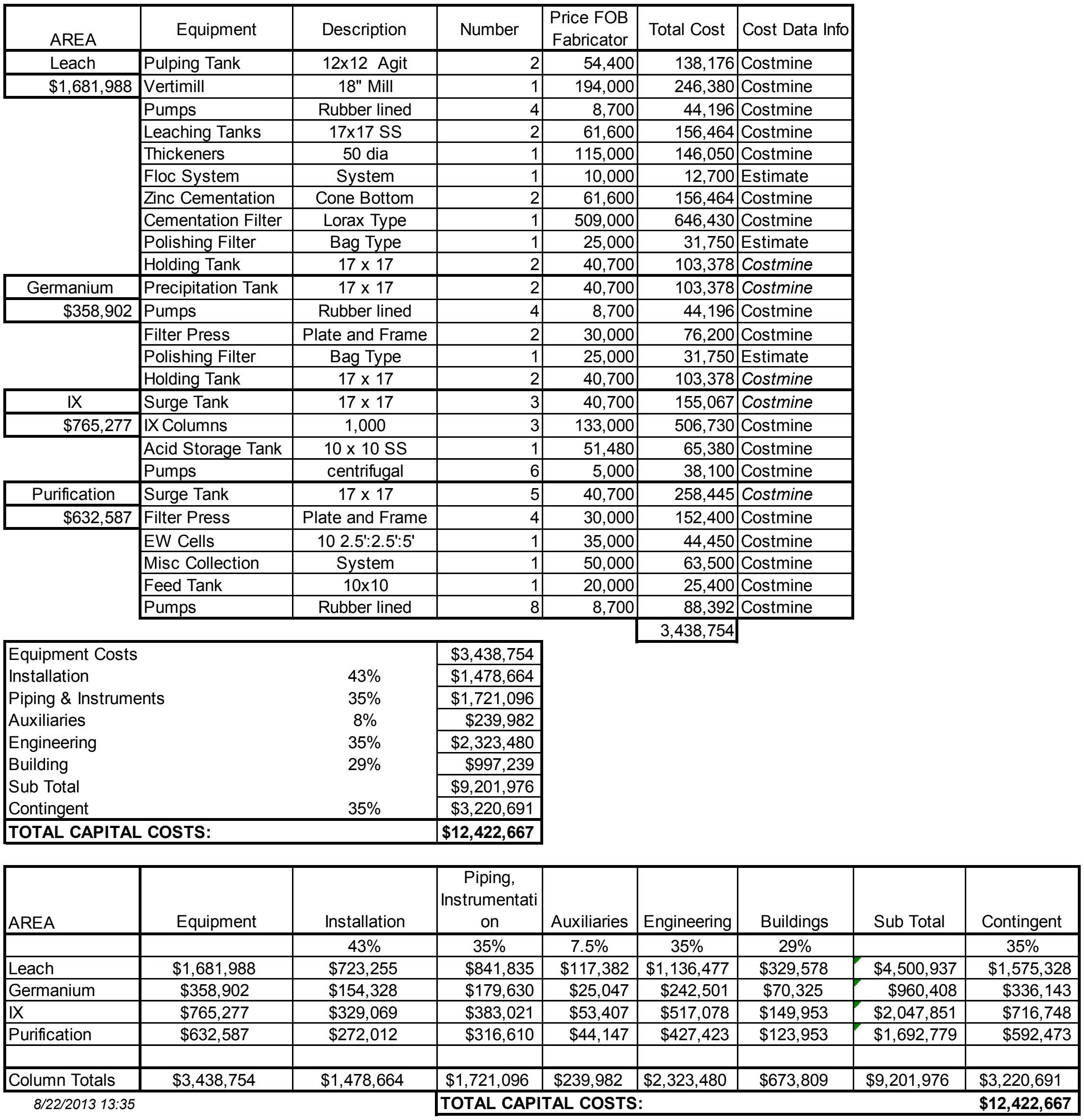
Based on this index difference, all costs developed using 2010 factors were increased by approximately 27%. The following established assumptions were used when developing the capital costs:

- All costs are estimated at +/- 35%,
- Estimated costs used the high value when multiple values were available,
- Because of the small size of the pumps associated with this estimate, all pump and associated equipment were valued at $8,700,
- All material used for this project would be 316 carbon steel unless otherwise noted,
- Agitator horsepower was estimated based on experience,
- IX column design was based on similar chemical exchange towers and hardware,
- Installation cost is estimated at 43% of the equipment cost,
- Piping and Instrumentation is estimated at 35% of the installed equipment cost,

- Auxiliaries are estimates at 7.5% of the installed cost,
- Engineering was estimated at 35% of the total cost and included freight,
- Building cost was estimated at 29% of the equipment cost and is an installed cost, and
- Contingency was estimated at 35%.

Table XXIX identifies the capital costs associated with this project.

Table XXIX: Estimated Capital Costs



AREA	Equipment	Description	Number	Price FOB Fabricator	Total Cost	Cost Data Info
Leach	Pulping Tank	12x12 Agit	2	54,400	138,176	Costmine
$1,681,988	Vertimill	18" Mill	1	194,000	246,380	Costmine
	Pumps	Rubber lined	4	8,700	44,196	Costmine
	Leaching Tanks	17x17 SS	2	61,600	156,464	Costmine
	Thickeners	50 dia	1	115,000	146,050	Costmine
	Floc System	System	1	10,000	12,700	Estimate
	Zinc Cementation	Cone Bottom	2	61,600	156,464	Costmine
	Cementation Filter	Lorax Type	1	509,000	646,430	Costmine
	Polishing Filter	Bag Type	1	25,000	31,750	Estimate
	Holding Tank	17 x 17	2	40,700	103,378	*Costmine*
Germanium	Precipitation Tank	17 x 17	2	40,700	103,378	*Costmine*
$358,902	Pumps	Rubber lined	4	8,700	44,196	Costmine
	Filter Press	Plate and Frame	2	30,000	76,200	Costmine
	Polishing Filter	Bag Type	1	25,000	31,750	Estimate
	Holding Tank	17 x 17	2	40,700	103,378	*Costmine*
IX	Surge Tank	17 x 17	3	40,700	155,067	*Costmine*
$765,277	IX Columns	1,000	3	133,000	506,730	Costmine
	Acid Storage Tank	10 x 10 SS	1	51,480	65,380	Costmine
	Pumps	centrifugal	6	5,000	38,100	Costmine
Purification	Surge Tank	17 x 17	5	40,700	258,445	*Costmine*
$632,587	Filter Press	Plate and Frame	4	30,000	152,400	Costmine
	EW Cells	10 2.5':2.5':5'	1	35,000	44,450	Costmine
	Misc Collection	System	1	50,000	63,500	Costmine
	Feed Tank	10x10	1	20,000	25,400	Costmine
	Pumps	Rubber lined	8	8,700	88,392	Costmine
					3,438,754	

Equipment Costs		$3,438,754
Installation	43%	$1,478,664
Piping & Instruments	35%	$1,721,096
Auxiliaries	8%	$239,982
Engineering	35%	$2,323,480
Building	29%	$997,239
Sub Total		$9,201,976
Contingent	35%	$3,220,691
TOTAL CAPITAL COSTS:		**$12,422,667**

AREA	Equipment	Installation	Piping, Instrumentation	Auxiliaries	Engineering	Buildings	Sub Total	Contingent
		43%	35%	7.5%	35%	29%		35%
Leach	$1,681,988	$723,255	$841,835	$117,382	$1,136,477	$329,578	$4,500,937	$1,575,328
Germanium	$358,902	$154,328	$179,630	$25,047	$242,501	$70,325	$960,408	$336,143
IX	$765,277	$329,069	$383,021	$53,407	$517,078	$149,953	$2,047,851	$716,748
Purification	$632,587	$272,012	$316,610	$44,147	$427,423	$123,953	$1,692,779	$592,473
Column Totals	$3,438,754	$1,478,664	$1,721,096	$239,982	$2,323,480	$673,809	$9,201,976	$3,220,691
8/22/2013 13:35			**TOTAL CAPITAL COSTS:**					**$12,422,667**

7.2. Operating Cost Estimate

The operating cost estimate was based on the flow sheet mass balance and, where necessary, good operating practice. The following assumptions were used in developing the cost:

- All chemical costs were based on outside purchase of materials. No change in cost was made for internal availability and incremental costs of, for example, sulfuric acid and zinc powder,
- Personnel requirements were based on having 2 operators 24 hours per day with part time supervision of the area,
- Power was estimated by adding the required motor horsepower of the different equipment, lights, and electric steam generation. The cost per kilowatt was \$0.04/kilowatt hour (2012),
- Diesel cost for the loader was estimated at \$2.95/gallon using off-road diesel, and
- General maintenance costs were developed from Plant Design and Economics for Chemical Engineers, Peters and Timmerhaus using a 1990 cost basis(17). The maintenance cost was estimated at 9% of the capital cost per year.

Table XXX lists the operating cost estimate for this project.

Table XXX: Estimated Operating Costs

Item	$USD/tn Residue Processed	$USD/Kg Gallium Produced
Chemical Costs	427.6	58.6
Personnel	172.7	23.7
Power	1.7	0.2
Diesel	3.6	0.7
General Maintenance	39.0	5.3
Total Op Cost	644.6	88.5
Zinc recoup	234.7	32.2
Total Cost	409.9	56.3

8. Conclusion

The current price of Gallium is approximately $US 1,000 (2012) per kilogram. The residue is estimated to contain 0.6% gallium or approximately 6 kilograms of gallium per ton of Clarksville residue. Based on an estimated gallium recovery of approximately 85%, the value of a ton of residue is approximately $US 4,600. As the processed cost is approximately $US 410 per ton, there is a potential for a very significant profit associated with the recovery of gallium using the process herein.

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 economically recover gallium.

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Appendix A: Sulfuric Acid Content Procedure

PASMINCO CLARKSVILLE LABORATORY

Procedure Number

Issue Date 8/10/01

Chief Chemist F Burchwell

Revision Date

ACID

SCOPE: This procedure is used to determine the acid content as sulfuric acid in zinc sulfate solutions.

PRINCIPLE: This method is based on the strong acid / strong base reaction between sulfuric acid and sodium carbonate. The equivalence point is indicated by the presence of methyl orange indicator. The reaction is:

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2 \uparrow$$

REAGENTS:

1. Methyl Orange Indicator - 0.2%
2. Sodium Carbonate - 54 g/l or 10.7 g/l

PROCEDURE:

1. Pipette a 5 ml sample into a 250 ml Erlenmeyer flask, filtering if necessary.
2. Add approximately 75 ml of D.I. water and 3 drops of methyl orange indicator.
3. Titrate with Na_2CO_3 until the color changes from red-orange to yellow.

CALCULATION:

For 54 g/l Na_2CO_3: ml Na_2CO_3 x 10 = g/l H_2SO_4

For 10.7 g/l Na_2CO_3: ml Na_2CO_3 x 2 = g/l H_2SO_4

INTERFERENCES: An excess of ferric iron will mask the methyl orange endpoint causing a higher erroneous titration. To eliminate this interference, add several grams of KI plus several drops of starch indicator, then titrate with sodium thiosulfate until clear. Then proceed with titration as outlined above.

Appendix B: Ferrous Iron and Total Iron Procedure

PASMINCO CLARKSVILLE LABORATORY

Procedure Number____________________ Issue Date 8/10/01

Chief Chemist F Burchwell Revision Date________________

FERROUS IRON

SCOPE: This procedure is used to determine the amount of ferrous iron in zinc sulfate solutions.

PRINCIPLE: The ferrous (Fe+2) salts in cold acid solution are quantitatively oxidized to the ferric (Fe+3) oxidation state by potassium dichromate.

REAGENTS:

1. Potassium Dichromate solution - 4.4 g/L
2. Potassium Dichromate solution - 0.44 g/L
3. Sodium Diphenylaminesulfonate - 10 g/L
4. Acid Buffer Solution - 15% H_2SO_4, 15% H_3PO_4 to 1 liter with water.

PROCEDURE:

1. Pipette a 5 or 50 mL filtered sample into a 250 mL Erlenmeyer flask.
2. Add 50 mL acid buffer solution and 10 drops Diphenylamine Sulfonate indicator.
3. Titrate with Potassium Dichromate solution until color changes to purple or violet.

CALCULATION: 5 ml sample:

ml 0.44 g/L $K_2Cr_2O_7$ x 0.1 = g/L Fe^{++}

ml 4.4 g/L $K_2Cr_2O_7$ x 1.0 = g/L Fe^{++}

50 ml sample:

ml 0.44 g/L $K_2Cr_2O_7$ x 0.01 = g/L Fe^{++}

ml 4.4 g/L $K_2Cr_2O_7$ x 0.10 = g/L Fe^{++}

INTERFERENCES: Cu in quantities >1 mg assists the oxidation of Fe^{++} by air. As (III) raises results as it oxidized to As (V) by Dichromate.

PASMINCO CLARKSVILLE LABORATORY

Procedure Number

Issue Date 8/10/01

Chief Chemist F Bucknell

Revision Date

TOTAL IRON

SCOPE: This procedure is used in the determination of total iron in zinc sulfate solutions.

PRINCIPLE: The first reaction is the reduction of iron with a slight excess of stannous chloride $SnCl_2$. The excess $SnCl_2$ is oxidized readily on the addition of mercuric chloride.

$$2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}$$

$$Sn^{+2} + 2\,Hg^{+2} \longrightarrow Sn^{+4} + 2Hg^{-}$$

Thereafter, the method depends upon the quantitative oxidation of ferrous salts in cold acid solution to the ferric oxidation state by potassium dichromate.

$$6\,Fe^{+2} + Cr_2O_7 + 14\,H^{+} \longrightarrow 6\,Fe^{+3} + 2\,Cr^{+3} + 7\,H_2O$$

REAGENTS:

1. Stannous Chloride Solution - 15 g in 100 ml 1:1 HCl + piece of Sn
2. Mercuric Chloride Solution - Saturated solution (60-70 g/l)
3. Indicator - 10 g/L Diphenylamine sulfonate.
4. Potassium Dichromate Solution - 4.4 g/L and 0.44 g/l
5. Acid Buffer Solution - 150 mL H_2SO_4, 150 mL H_3PO_4 to 1 liter
6. 1:3 HCl

PROCEDURE:

1. Pipette a 5 mL or 50 mL sample into a 500 mL flask
2. Add 50 mL 1:3 HCl and bring to a boil.
3. Add $SnCl_2$ drop-wise until decoloration of solution, then add 2 drops in excess (maximum).
4. Add 200 mL D.I. water, 15 mL $HgCl_2$ solution, 15 mL Acid Buffer Solution and 10 drops indicator.
5. Titrate with $K_2Cr_2O_7$ solution until stable violet color results.

IRON - TOTAL (Continued)

CALCULATION: 5 mL Sample:

ml 0.44 g/L $K_2Cr_2O_7$ x .1 = g/L Fe

ml 4.40 g/L $K_2Cr_2O_7$ x 1.0 = g/L Fe

50 mL Sample:

ml 0.44 g/L $K_2Cr_2O_7$ x .01 = g/L Fe

ml 4.40 g/L $K_2Cr_2O_7$ x .10 = g/L Fe

INTERFERENCES: Cu in quantities greater than 1 mg assists the oxidation of ferrous iron by air. As (III) raises results as it is oxidized to As (V) by Potassium Dichromate.

Appendix C: Solvent Extraction Bench Scale Results

Pasminco Clarksville
SX Results - Bench Scale Results

	Ga Results, ppm	Solution Volume, ml	Mass, Grams	Grams, Ga	Sum	Recovery	Ge Results, ppm	Solution Volume, ml	Mass, Grams	Grams, Ga	Sum	Recovery
Pilot Head	552	8000		4.416			118	8000		0.944		
After Cementation	434	9025		3.917			116	9025		1.047		
Cementation Solids	21.6		87.89	0.190	4.107	95.2%	0.1		87.89	0.001	1.048	99.92%
After Sulfide Precipitation	402	9325		3.749		95.7%	1.5	9325		0.014		0.18%
Sulfide Solids	2.3		104.7	0.024	3.773	4.3%	90		104.7	0.942	0.956	99.82%
Head Solution, 5 Tests	402	2000		0.804	3.749		1.5	2000		0.003	0.014	
Raff #1	1	2000		0.002	0.009		1.5	2000		0.003	0.014	
Raff #1	1	2000		0.002	0.009		2	2000		0.004	0.019	
Raff #1	1	2000		0.002	0.009		1	2000		0.002	0.009	
Raff #1	1	1325		0.001	0.006	99.4%	4	1325		0.005	0.025	8.4%
Final Loaded Solution	370	9325		3.450			1	9325		0.009		

Appendix D: Purity Systems Test Results

INTRODUCTION

Due to the fact gallium has become a valuable commodity in the electronics industry, Pasminco Inc. contacted Purity Systems Inc. (PSI) for some experimental bench scale work on gallium recoveries from an acidic mine leach. The leach solution contained various metals including gallium, aluminum, iron, and zinc. For the acidic solution, various materials were tested and parameters were optimized for gallium recovery and selectivity.

This report is results of a comparison test between two separate ion exchange resins using the same iminoacetic acid functional group. The two resins are different by binding base matrix. HRC 748, from Rohm and Haas Inc., is a styrene based ion exchange resin, while WP-2, from Purity Systems Inc. (PSI), uses a silica based matrix. During the comparison testing, two separate PSI WP-2 silica gels were used, a laboratory made gel and a pilot plant testing gel made in China.

Secondly, we have developed a new resin with a gallium selective ligand. This material was also tested for gallium capacity and selectivity over other metals in the acidic leach solutions.

Pasminco Gallium Recovery

OBJECTIVE

Purity Systems Inc. (PSI) received an acidic pressure leach test solution, which contained gallium, iron, zinc, and aluminum, from Pasminco Inc. for testing of PSI silica technologies. The acidic test solution (pH=0.01) contained a high amount of zinc and iron, as ferric, with smaller amounts of gallium and aluminum. Overall concentrations can be observed in table 1. The overall goal was to separate and concentrate gallium from the other metals in solution.

Table 1. Metal Concentrations

Metal	Concentration (ppm)
Aluminum	345
Iron	7,171
Gallium	624
Zinc	8,279

Secondly, other PSI silica gel technologies were tested along with a common ion exchange resin for gallium capacities and selectivity over other metals in the system.

PSI BENCH SCALE WP-2 RESEARCH

PSI initially chose a silica resin called WP-2, which contains an iminoacetic acid functional group, for its initial testing of the pressure leach. The group should has a high affinity to bind metals along with proton exchange for removal of gallium from pressure leach test solutions. An initial drawback for using this resin is ferric binding in the system. As done in previous studies, the iminoacetic acid functional group has a high affinity for removal of ferric from solution, however, iron is not bound to the silica resin when it is in the reduced ferrous form. Due to this fact, the initial step is to reduce iron using elemental zinc. The overall reaction is as follows:

$2Fe^{+3} + Zn^{0} \rightarrow 2Fe^{+2} + Zn^{+2}$

Elemental zinc addition has two effects on the acidic solution. The zinc, not only reduces iron in the system, but also raises the pH of the solution. After reduction of ferric to ferrous, the next testing step for WP-2 was pH adjustment. As seen in previous studies, PSI WP-2 silica resin is pH dependant. Because of the high acidic conditions of the test solution, overall pH of the solution was raised to pH 2.1 for initial bench scale testing using sodium hydroxide (NaOH).

The WP-2 silica was placed into a 30 ml syringe column for testing. The flow rate of the system was calibrated using a peristalic pump to 5 ml per minute for the testing procedure. The test solution was loaded from bottom to top to minimize solution channeling. The flowthrough solution was captured for analysis and retreatment into the column. After the solution was pumped throught the column, 10 bed volumes (300 ml) of distilled water was pumped through the column. The column was then stripped with concentration sulfuric acid for gallium capture and recovery. After stripping, the column was regenerated with 5 bed volumes (150 ml) of distilled water. For all test solutions, both flowthrough and stripped columns, metal analysis were measured on an Inductively Coupled Plasma Spectrometer (ICP).

PSI BENCH SCALE WP-2 RESULTS

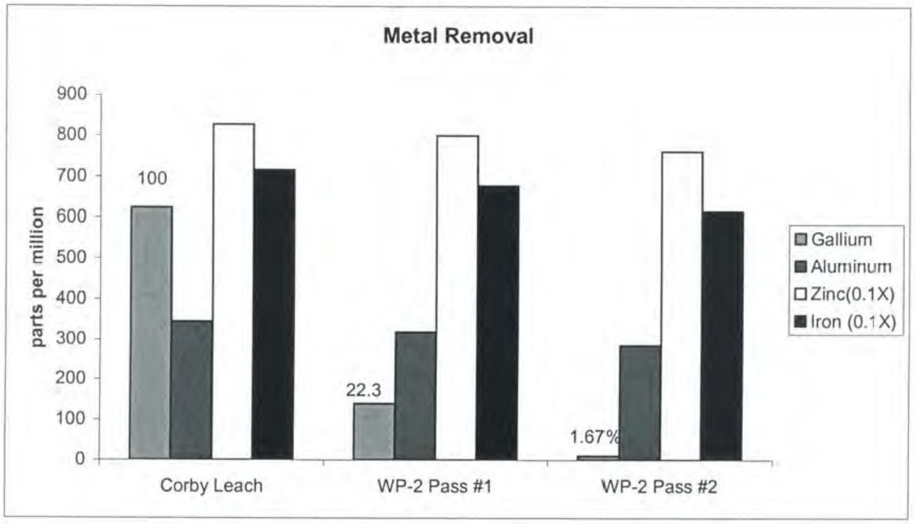
PSI technology (WP-2) has an excellent affinity for gallium over iron, zinc, and aluminum in acidic solutions. Flowthrough results can be observed in table 2. According to the data, iron, zinc, and aluminum are passed through the column, while gallium is selectively removed.

Table 2. Metal Flowthrough Results.

	Gallium (ppm)	Aluminum (ppm)	Zinc (ppm)	Iron (ppm)
Leach	780	774.8	9237	20150
FT 1	357.1	673.4	8980	18450
FT 2	149.1	642.9	8752	17850

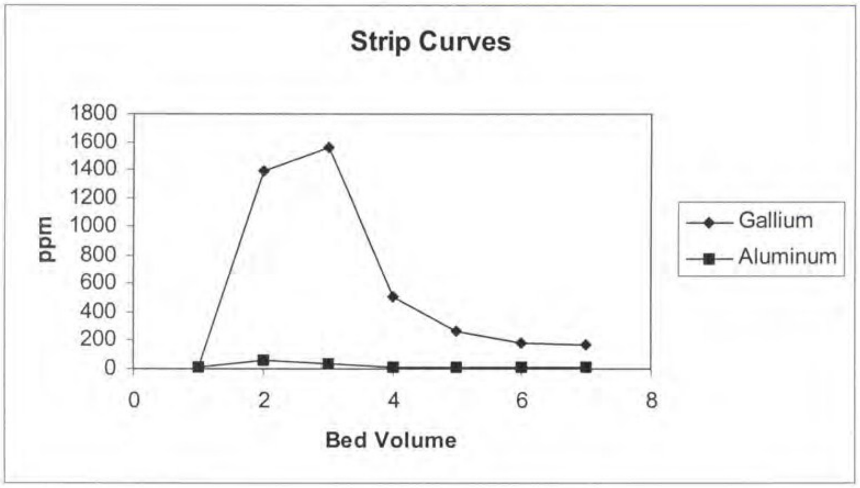
Approximately, 77% of the gallium is taken from the solution. After two passes through the WP-2 column, over 98% of the gallium is captured on WP-2.

Figure 1. Metal Recovery



The WP-2 column was selectively stripped using concentrated sulfuric acid. During the stripping process, samples were taken and analyzed to form a gallium-aluminum strip curve as seen in figure 2.

Figure 2. Metal Strip Curves using WP-2.



Conclusion

According to the figures and table data, WP-2, which uses an iminoacetic acid functional group has excellent affinity for removing gallium from aluminum, iron, and zinc in acidic solutions. The metal ordering affinity is as follows:

$Fe^{+3} > Ga^{+3} > Al^{+3} > Zn^{+2} > Fe^{+2}$

It is very important to uses elemental zinc to reduce the ferric ion to ferrous for gallium capturing using WP-2. The main reason for gallium recovery from other metals is two fold. The iminoacetic acid will have a higher affinity towards trivalent metals such as Fe^{+3}, Al^{+3}, and Ga^{+3}. Since ferric ion was reduced to ferrous using elemental zinc, only aluminum and gallium compete for the iminoacetic sites on the resin. Since gallium is a softer more polerizable metal than aluminum, the functional group has a higher affinity for the gallium metal ion from the solution. Because of this fact, gallium is selectively captured on the iminoacetic functional group over aluminum. The bench scale testing shows excellent results of gallium recovery from these acid leach solutions.

LEACH SOLUTION TESTING

A second leach solution was tested using WP-2 for gallium capture and recovery. The solution had increased metal concentration than previous bench scale testing solutions. Overall metal concentrations can be observed in Table 3.

Table 3. Pressure Leach Metal Concentrations.

Metal	Concentration (ppm)
Aluminum	2,626
Iron	43,350
Gallium	2,148
Zinc	51,450

OBJECTIVE

The overall of testing these solutions was two fold. Initially, using the higher metal concentrated solutions, PSI wanted to determine if WP-2 could effectively removed the gallium from the other metals. Secondly, using this solution, PSI wanted to know if the solution was pH dependent. Several tests were conducted to evaluate both metal affinity and pH variables for gallium recovery. The overall calculated data includes gallium capacity for WP-2 as well as gallium to other metal ratios in the strip solutions.

WP-2 HIGHER METAL CONCENTRATION TESTING

For the higher metal aqueous testing, WP-2 silica resin was placed into a 30 ml syringe column. The flow rate for all testing procedures was 5 ml per minute. Since the solution, had excess elemental zinc already in solution, it was assumed iron in the system was ferrous and no further elemental zinc was added into the system. The pH of the solution was raised to pH 2.1 with sodium hydroxide for initial testing procedures. Samples were taken every 20 milliliter and analyzed on the ICP for overall metal concentrations.

For gallium capacities, a head solution was initially analyzed, then flow through solutions were captured for analysis of the metals. Gallium capacities were calculated using head data then subtracting the flow through data in each sample. At the end, each of the samples was added up for gallium recovery and divided by the weight (in grams) for WP-2 gallium capacities (mg Ga/g WP-2).

For metal strip ratios, the strip solutions were used for calculation of data. The calculated data was used with respect to gallium versus the other metals in the strip solution such as Ga/Al, Ga/Fe, and Ga/Zn. The ratios were calculated as weight to weight ratios in the solution.

WP-2 RESULTS ON HIGHER METAL SOLUTIONS

For the initial testing of higher concentrated metal solution, 23.98 grams of pilot WP-2 was placed into the 30 ml syringe column. A sample of 25 ml of flow through solution was collected for each sample and analyzed on the ICP for specific metals. Results can be seen in Table 4.

From the flow through results, both gallium capacities and gallium to metal ratios were calculated. Results can be observed in table 5 for gallium weight and table 6 for capacity calculations and in table 7 for strip ratios.

Table 4. Pilot WP-2 Flow Through on Higher Metal Solution.

Pilot WP-2 (20 ml)	Al	Fe	Ga	Zn
1	538.7	8592	121.3	15,470
2	1,865	29,910	111.1	39,160
3	2,154	36,400	499	44,860
4	2,229	37,140	489	44,720
5	2,461	38,560	679	45,980
6	2,621	43,230	720	48,680
7	2,097	34,520	679	44,240
8	2,211	35,930	846	44,890
9	2,184	36,880	1,003	43,580
10	2,569	42,070	1,212	49,800
11	2,559	42,340	1,266	49,310
12	2,320	38,590	1,099	46,810
13	2,022	33,750	1,212	43,110
14	1,930	31,680	1,223	41,300
15	2,430	40,050	1,264	47,660

Table 5. Pilot WP-2 Gallium Weight Calculations.

Bed Volume = 20ml	Ga (ppm)	Ga (mg)
Head	2,148	
1	121.3	40.534
2	111.1	40.738
3	499	32.98
4	489	33.18
5	679	29.38
6	720	28.56
7	679	29.38
8	846	26.04
9	1,003	22.9
10	1,212	18.72
11	1,266	17.64
12	1,099	20.98
13	1,212	18.72
14	1,223	18.5
15	1,264	17.68
Total (mg)		395.932

Table 6. Pilot WP-2 Gallium Capacities.

Weight of Pilot WP-2	23.92
Total Gallium(mg)	395.932
Pilot WP-2 Capacity (mg/g)	16.51

Table 7. WP-2 Strip Ratios

Strip (20 ml)	Al	Fe	Ga	Zn
1	127	1,759	3,542	4,670
2	130.9	2107	4,197	5,339
3	50.53	468.1	1,942	1385
4	32.91	252.7	1,024	862.3
5	25.39	196.9	684.3	645.5
Total	7.3346	95.674	277.786	258.036
Ga/Metal Ratio	31.06	2.38	1	0.88

RESULTS

Data from the pilot WP-2 silica gel indicates excellent affinity for gallium in highly concentrated metal solutions in acidic environments. The WP-2 silica gel is able to separate gallium from other metals, as high as 50 g/l, in acidic conditions. The next laboratory step could be to take the strip and adjust to pH 2 with sodium hydroxide and run the solution through the column again. Doing this step would increase the gallium concentration in the solution as well as increase the gallium to metal ratios of the strips. Overall, the iminoacetic acid functional group is an excellent choice for gallium removal in acidic type leaches.

HIGHER METAL CONCENTRATION ACIDIC COMPARISON TESTS

After testing pilot WP-2 silica gel, other previously made WP-2 resins were also compared along with a styrene based iminodiacetic funtional group ion exchange resin (HRC 748) using the same parameters as previously tested pilot WP-2 technology. These parameters include using a 30 ml syringe column, a flow rate of 5 ml per minute, samples taken every 20 ml, strip solutions taken every 20 ml, capacities calculated from flow through, and gallium to metal ratios calculated from strip solutions. Finally, a new gallium specific ligand placed onto silica gel was tested.

HRC 748

A styrene based ion exchange resin from Rohm & Haas called HRC 748 was used for testing purposes. The amount of ion exchange resin placed into the syringe column was 22.15 grams. As previously stated the same parameters were used for comparison. Table 8 shows the HRC 748 metal flow through results. Table 9 indicates HRC gallium weight calculations. Table 10 specifies gallium capacities for HRC 748 while table 10 shows the final gallium to metal strip ratios.

Table 8. HRC 748 Flow Through on Higher Metal Solution.

HRC 748	Al(ppm)	Fe(ppm)	Ga(ppm)	Zn(ppm)
1	0	0.963	43.88	2,092
2	639.8	13,890	36.67	24,090
3	1,347	28,750	162.2	40,710
4	1,315	27,630	284.4	39,580
5	1,230	25,970	363.2	38,250
6	1,252	26,220	412.2	38,700
7	1,294	26,990	531	39,700
8	1,300	26,770	600	39,920
9	1,270	25,800	652	39,510
10	1,287	27,120	737.4	39,780
11	1,208	25,400	687.7	38,550
12	1,311	27,990	922.1	40,260
13	1,241	26,880	898.6	38,840
14	1,267	27,810	958	39,490
15	1,411	29,400	1,117	42,560

Table 9. HRC Gallium Weight Calculations.

HRC 748	Ga(ppm)	Ga(mg)
Head	2,148	
1	43.88	43.0024
2	36.67	43.1466
3	162.2	40.636
4	284.4	38.192
5	363.2	36.616
6	412.2	35.636
7	531	33.26
8	600	31.88
9	652	30.84
10	737.4	29.132
11	687.7	30.126
12	922.1	25.438
13	898.6	25.908
14	958	24.72
15	1,117	21.54
Total		490.073

Table 10. HRC 748 Gallium Capacities.

Weight of Pilot WP-2	22.15
Total Gallium(mg)	490.073
HRC 748 Capacity (mg/g)	22.12

Table 11. HRC 748 Gallium to Metal Strip Ratios.

Strip(20 ml)	Al	Fe	Ga	Zn
1	128.4	2,212	1,036	8,468
2	162.6	1,472	5,623	5,264
3	53.31	700.7	3,832	776
4	26.24	656.7	3,057	343
5	15.28	296.7	1,003	171.3
Total(mg)	7.7166	106.762	291.02	300.446
Ga/Metal Ratio	37.71	2.73	1	0.96

RESULTS

According to the data, HRC 748 showed excellent results for removal and selectivity of gallium from the acidic solution. The styrene based resins gallium capacity was measured at 22.12. Since the functional group of HRC 748 contains an iminodiacetic group, it has a high affinity for gallium over the other metals in the system. For gallium recovery, the functional group plays an important role regardless of the base matrix, either styrene or silica. This data shows the important role of the functional group.

Lab WP-2

A second previously laboratory made WP-2 was tested using the same parameters as the previously two tested materials. The silica matrix used for WP-2 was called Nanjing (60 to 80 mesh). The functional group used for the testing of the gel is still an iminoacetic acid group. Analysis results can be observed in tables 12 to 15.

Table 12. Lab WP-2 Flow Through on Higher Metal Solution.

Lab WP-2	Al	Fe	Ga	Zn
1	36.13	538.4	0.4085	741.1
2	739	12,320	133.4	7,640
3	1,299	20,920	288.9	10,340
4	1,351	21,080	503.1	10,660
5	1,441	21,970	314.7	10,600
6	1,341	21,060	644	10,680
7	1,361	21,020	772.5	10,750
8	1,413	21,370	842.3	10,600
9	1,409	21,590	926.3	10,590
10	1,360	20,520	920.7	10,500
11	1,371	21,150	1,012	10,550
12	1,358	20,910	1,036	10,540
13	1,307	20,150	1,133	10,440
14	1,341	20,140	1,222	10,380
15	1,485	21,670	1,425	10,470

Table 13. Lab WP-2 Gallium Weight Calculations

Lab WP-2	Ga (ppm)	Ga (mg)
Head	2148	
1	0.4085	42.95183
2	133.4	40.292
3	288.9	37.182
4	503.1	32.898
5	314.7	36.666
6	644	30.08
7	772.5	27.51
8	842.3	26.114
9	926.3	24.434
10	920.7	24.546
11	1,012	22.72
12	1,036	22.24
13	1,133	20.3
14	1,222	18.52
15	1,425	14.46
Total		420.91383

Table 14. Lab WP-2 Gallium Capacities.

Weight of Pilot WP-2	20.81
Total Gallium(mg)	420.91
Lab WP-2 Capacity (mg/g)	20.22

Table 15. Lab WP-2 Gallium to Metal Strip Ratios.

Strip (10ml)	Al(mg)	Fe(mg)	Ga(mg)	Zn(mg)
1	21.45	287	292.8	905.2
2	61.86	731	4,616	2,839
3	58.8	758.1	5,590	2,847
4	45.53	734.1	6,320	2,630
5	47.73	332.5	6,277	1,446
6	47.73	727.9	3,472	2,169
7	14.34	157.5	1,203	454
Total	2.97	37.28	277.71	132.90
Ga/Metal Ratio	93.36	7.44	1	2.09

RESULTS

According to the data, Lab WP-2 had similar results to HRC 748 with respect to gallium capacity. It should be noted that the Lab WP-2 was more selective in gallium to metal ratios with respect to aluminum and iron in the system than the HRC 748. This silica gel is an excellent choice to remove and separate gallium from other metals in acidic type environments.

GaRAM Series

Recently, PSI has developed a silica based technology capable of removing gallium from acidic solutions. Two separate technologies have been developed and tested for galllium recovery and selectivity. The technology still is silica based, however, the specific ligand has a high affinity for gallium over other metals in the system. GaRAM (Gallium Recovery from Aqueous Media) and GaRAM2 was tested using the same parameters as HRC 748, except flowthrough bed and strip volumeschanged from 20 ml to 25 ml, and the WP-2 series. Results can be observed in Tables 16 through 19.

Table 16.GaRAM Flow Through on Higher Metal Solutions.

Sample Name	Al	Fe	Ga	Zn
1	167.1	1,149	0.63	30,76
2	1,533	27,130	0.63	49,550
3	1,544	27,290	4.02	48,560
4	1,715	29,480	4.15	49,560
5	1,614	25,950	6.17	49,680
6	1,714	27,680	10.69	50,000
7	1,639	26,840	273.7	49,650
8	1,615	27,150	849.4	49,870
9	1,526	26,250	1,145	49,250
10	1,571	27,010	1,389	49,430

Table 17. GaRAM Gallium Weight Calculations.

Bed Volume (25ml)	Ga (ppm)	Ga (mg)
1	0.63	53.68425
2	0.63	53.68425
3	4.02	53.5995
4	4.15	53.59625
5	6.17	53.54575
6	10.69	53.43275
7	273.7	46.8575
8	849.4	32.465
9	1145	25.075
10	1389	18.975
Total		444.9153

Table 18. GaRAM Gallium Capacities.

Weight of GaRAM	17.13
Total Gallium(mg)	444.92
GaRAMCapacity (mg/g)	25.97

Table 19. GaRAM Gallium to Metal Strip Ratios.

BV (25ml)	Al (ppm)	Fe (ppm)	Ga (ppm)	Zn (ppm)
1	6.29	40.97	2.94	61.09
2	241.7	2377	235.78	64.42
3	76.33	1469	97.2	6.24
4	7.93	32.12	1.50	14.45
Total (mg)	8.30625	97.97725	337.4163	3.655
Ga/Metal Ratio	40.62	3.44	1	92.31

Results

GaRAM results show excellent recovery and selectivity of gallium from the other metals in solutions. Of all the materials tested, GaRAM was the best in capacity and selectivity. One concern may be the amount of iron in the strip solution, however, since the overall testing of the solution has taken some time, some of the ferrous in solution may have oxidized to ferric and bound to the GaRAM material. Overall, this is an excellent choice for removal of gallium from acidic solutions.

GaRAM 2

A second material with the gallium specific ligand was placed onto a silica based matrix. Testing was completed using the same acidic leach solution and the same parameters as previous GaRAM material. Results can be observed in tables 20 through 23.

Table 20. GaRAM2 Flow Through on Higher Metal Solutions.

BV (25ml)	Al(ppm)	Fe(ppm)	Ga(ppm)	Zn(ppm)
1	319.9	36540	0	49,450
2	1,525	27,220	2.39	49,690
3	1,542	26,970	0.13	49,580
4	1,579	26,730	6.04	50,210
5	1,729	28,460	7.04	49,630
6	1,655	26,650	27.02	49,560
7	1,644	26,770	2.01	49,230
8	1,653	26,640	22.87	49,870
9	1,644	27,610	113	49,810

Table 17. GaRAM2 Gallium Weight Calculations.

BV(25 ml)	Ga(ppm)	Ga(mg)
1	0	53.7
2	2.39	53.64025
3	0.13	53.69675
4	6.04	53.549
5	7.04	53.524
6	27.02	53.0245
7	2.01	53.64975
8	22.87	53.12825
9	113	50.875
Total		478.79

Table 18. GaRAM2 Gallium Capacities.

Weight of GaRAM2	19.15
Total Gallium(mg)	478.79
GaRAM2 Capacity (mg/g)	25.00

Table 19. GaRAM2 Gallium to Metal Strip Ratios.

BV (25ml)	Al (ppm)	Fe (ppm)	Ga (ppm)	Zn (ppm)
25	75.85	1071	3047	2193
25	83.14	1714	7218	161.1
25	23.53	646.6	6335	60.31
25	0	33.7	267.7	61.93
Total (mg)	4.563	86.6325	421.69	61.9085
Ga/Metal Ratio	92.41	4.86	1	6.811

RESULTS

As seen in GaRAM, GaRAM shows excellent recovery and selectivity of gallium from the other metals. Observation of the data, reveals a high capacity and excellent selectivity from other metals.

COMPARISON CONCLUSIONS

Capacities

For the materials tested (Table 20), the GaRAM series had the best gallium capacity of all the materials. It should be noted that even though HRC 748 had the good gallium capacity, the PSI WP-2 series was relatively close in gallium capacity. At slower flow rates, the material (HRC 748) is suitable for removing gallium from acidic solutions. PSI technology, however, shows excellent potential in recovering gallium from solution. A major advantage for using PSI technology over styrene based technology is longevity of the material. Previous studies have indicated, silica gel matrix last many times longer in acidic environments than styrene based technology. Secondly, further testing was complete at higher flow rates for gallium capacities using the WP-2 and HRC 748 materials.

Table 20. Material Capacity for Each Material.

Testing Material	Capacity (mg Ga/g Material)
Pilot WP-2	16.51
HRC 748	22.12
Lab WP-2	20.22
GaRAM	25.97
GaRAM2	25.00

Gallium to Aluminum Selectivity

For the tested material, the lab WP-2, followed closely by GaRAM2, had the best gallium to aluminum strip ratio. The other materials had similar gallium to aluminum ratios.

Table 21. Gallium/Aluminum Selectivity for Each Material.

Testing Material	Ga/Al Ratio
Pilot WP-2	31.06
HRC 748	37.71
Lab WP-2	93.36
GaRAM	40.62
GaRAM 2	92.41

Gallium to Iron Selectivity

As seen before for metal separations, the lab WP-2 had the best gallium to iron selectivity (Table 22). The other results were similar is separating gallium from the iron in the acidic environment.

Table 22. Gallium/Iron Selectivity for Each Material.

Testing Material	Ga/Fe Ratio
Pilot WP-2	2.38
HRC 748	2.73
Lab WP-2	7.44
GaRAM	3.44
GaRAM2	4.86

Gallium to Zinc Selectivity

As with the other gallium to metal selectivities, GaRAM had the best gallium to zinc ratio. Compared to the other materials, GaRAM has tremendous potential to separate gallium for the other metals. The other materials results are seen in Table 23.

Table 23. Gallium/Zinc Selectivity for Each Material.

Testing Material	Ga/Zn Ratio
Pilot WP-2	0.88
HRC 748	0.96
Lab WP-2	2.09
GaRAM	92.31
GaRAM2	6.81

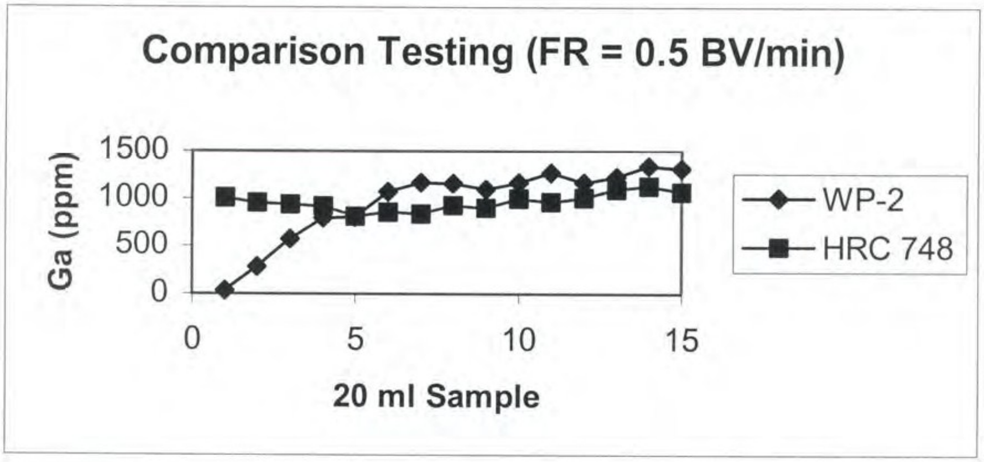
HIGHER FLOW RATE TESTING

A further study was initiated for gallium capture using the HRC 748 and lab WP-2. The purpose of the kinetic study was evaluating the materials at a higher flow rate. For both tests, the same 30 ml syringe column was used for the testing procedure. The flow rate was increased from 5 ml, in previous studies, to 15 ml per minute. A 20 ml flowthrough sample was taken and analyzed for metal analysis. Results can be observed in figure 3 and in table 24.

Table 24. Gallium Analysis and Higher Flow Rate.

Sample (20ml)	WP-2 Ga FT (ppm)	HRC 748 FT (ppm)
1	36	1,005
2	284.4	954.7
3	572.5	931.1
4	796.5	915
5	799.3	813.5
6	1,064	852
7	1,163	842.3
8	1,158	929.9
9	1,096	896.2
10	1,168	996.1
11	1,274	957.4
12	1,167	1,002
13	1,224	1,098
14	1,338	1,132
15	1,313	1,064

Figure 3. Higher Flow Rate Breakthrough Curve.



According to the data, WP-2 has substantially lower gallium breakthrough than HRC 748. Even after one bed volume, 50% breakthough occurs in the styrene based ion exchange resin. Silica based WP-2 has a tremendous advantage over HRC 748.

WP-2 pH TESTING CURVE

Additional testing also occurred on lab WP-2. The overall goal was to see how much pH affected the gallium capacity on the silica gel. The procedure involved adjusting the pH of the acidic solution with sodium hydroxide. After adjustment was made, the syringe column was loaded with gallium with pH adjusted solution. After loading the column, three bed volumes of distilled water was placed through the column to remove any additional loading solution. The column was then stripped with concentrated sulfuric acid to ensure all gallium on the solution. For calculation purposes, an initial head and stripped solution was analyzed for gallium recovery with respect to pH. Final results can be seen in table 25 and figure 4.

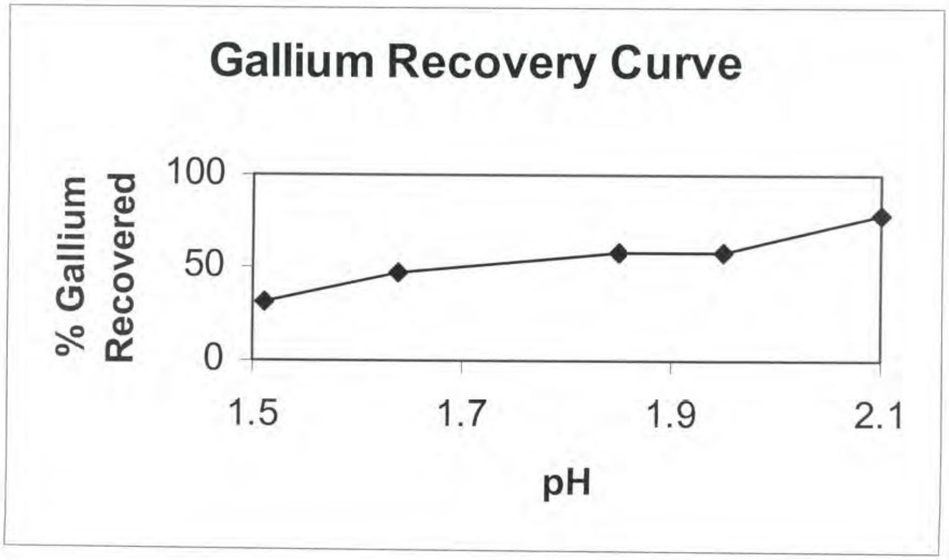
Table 25. pH Curve on Gallium Recovery.

pH	Percent Recovery
1.51	31.79
1.64	47.19306
1.85	57.06983
1.95	58.18804
2.1	77.7

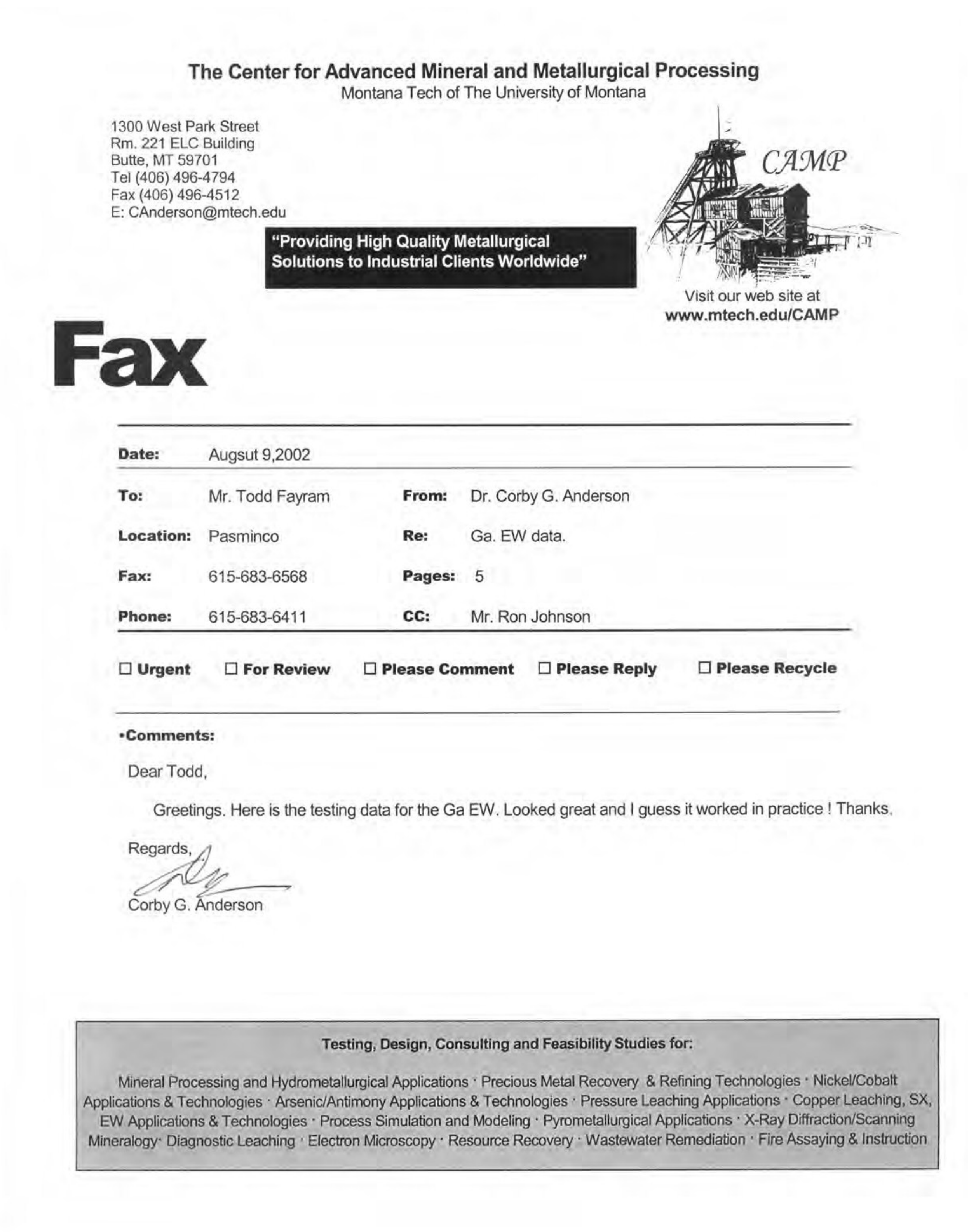
RESULTS

According to the data, WP-2 is pH dependent for removal and recovery of gallium from acidic solutions. The solution pH should be above 2.0 for optimal removal of gallium. Close pH controls of the system should be implemented for proper utilization of the resin and for greater recoveries of the metal.

Figure 4. Gallium Recover Curve.



Appendix E: Electrowinning Test Results



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Fax

Date:	Augsut 9,2002		
To:	Mr. Todd Fayram	**From:**	Dr. Corby G. Anderson
Location:	Pasminco	**Re:**	Ga. EW data.
Fax:	615-683-6568	**Pages:**	5
Phone:	615-683-6411	**CC:**	Mr. Ron Johnson

☐ **Urgent** ☐ **For Review** ☐ **Please Comment** ☐ **Please Reply** ☐ **Please Recycle**

•Comments:

Dear Todd,

Greetings. Here is the testing data for the Ga EW. Looked great and I guess it worked in practice ! Thanks.

Regards,

Corby G. Anderson

Testing, Design, Consulting and Feasibility Studies for:

Mineral Processing and Hydrometallurgical Applications · Precious Metal Recovery & Refining Technologies · Nickel/Cobalt Applications & Technologies · Arsenic/Antimony Applications & Technologies · Pressure Leaching Applications · Copper Leaching, SX, EW Applications & Technologies · Process Simulation and Modeling · Pyrometallurgical Applications · X-Ray Diffraction/Scanning Mineralogy· Diagnostic Leaching · Electron Microscopy · Resource Recovery · Wastewater Remediation · Fire Assaying & Instruction

TEST, T_1 10 g Ga METAL @ START. IN 200g/L NaOH.

T_{1-0} 89.0°F = 31.67°C 4 V 6 AMPS 200 mL INITIAL VOLUME
12:35p

T_{1-2} 89.5°F = 31.94°C 4 V 6 AMPS 154 mL FINAL Volume *
2:35p

T_{1-4} 90°F = 32.2°C 4.1 V 6 Amps 46 mL LOSS EVAPORATION & GASSING.
4:50p
ELAPSED TIME: 2hr 15min

T_{1-6} 101°F = 38.3°C 4.1 V 6 amps
6:35p

* ADDED 100 mL DISTILLED H_2O TO FINAL SOLN
ACTUAL VOLUME: 254 mL

CATHODE INITIAL: 42.89 g CATHODE FINAL: 43.81 g

Ga METAL DRIP BEAD Wt: 8.37 g Ga METAL

RECOVERED Wt: 9.29 g Ga METAL

ANALYTICAL RESULTS:

T_{1-0} 400 mg/L 2 mL per 250 mL Soln.
T_{1-2} 161 mg/L " "
T_{1-4} 48.9 mg/L " "
T_{1-6} 4169 mg/L IN 254 mL soln.

% REC (BASED ON 10 g Ga METAL) = (9.29/10) × 100 = 92.9%

TEST, T_2 10g Ga METAL @ START IN 200g/L NaOH.

T_{2-0} 11:00A	88°F = 31.1°C	4v	6Amps	200mL INITIAL Volume
T_{2-2} 1:00p	88°F = 31.1°C	4.1V	6Amps	155 mL final Volume
T_{2-4} 3:00p	91°F = 32.78°C	4.3v	6amps	45 mL LOSS
T_{2-6} 5:00p	95°F = 35°C	4.4 VOLTS	6Amps	

16.55 g (DRY) $Ga(OH)_3$ IN 200mL NaOH Soln

@ 120.744 g/mole $Ga(OH)_3$; Ga^{+++} .57742 mole frac.

16.55g × 0.57742 = 9.56g Ga^{+++} ✓ok

CATHODE INITIAL: 42.89 g CATHODE FINAL: 44.69g

Ga METAL DRIP BEAD wt: 7.25g Ga METAL

RECOVERED wt: 9.05 g Ga METAL

% REC (BASED ON 10g Ga METAL) = (9.05/10)*100 = 90.5%

% REC (@ 9.56g Ga METAL) = (9.05/9.56)*100 = 94.7%

ANALYTICAL RESULTS

T_{2-0}	443 mg/L	2mL PER 250 mL SOLN.
T_{2-2}	179 mg/L	" "
T_{2-4}	50.5 mg/L	" "
T_{2-6}	1919 mg/L	IN 155mL SOLN.

TEST, T_3 10 g Ga METAL @ START IN 150g/L NaOH.

T_{3-0} 2:05p 76°F = 24.44°C 4V 6AMPS 200mL INITIAL Volume

NOTE: MORE-HYDROGEN GAS GENERATION - POPPING OBSERVED.

T_{3-2} 4:05p 83°F = 28.33°C 4V 6AMPS 158mL FINAL Volume

NOTE: NOT MUCH Ga METAL YET

T_{3-4} 6:05p 92°F = 33.33°C 4.1V 6AMPS 42mL LOSS

NOTE: GOOD. Ga BEADS FORMING.

T_{3-6} 8:05p 101°F = 38.33°C 4.1V 6AMPS

NOTE: GOOD Ga DRIP BEADS + GOOD DEPOSIT ON

17.04g (DRY) $Ga(OH)_3$ IN 200mL NaOH soln

17.04g * 0.57742 = 9.84 g Ga METAL

CATHODE INITIAL : 42.89 g CATHODE FINAL : 45.81 g

Ga METAL DRIP BEAD WT: 6.79 g Ga METAL

RECOVERED WT : 9.71 g Ga METAL

% REC (BASED ON 10g Ga METAL) = (9.71/10)*100 = 97.1%

% REC (BASED ON 9.84g Ga METAL) = (9.71/9.84)*100 = 98.7%

ANALYTICAL RESULTS :

T_{3-0} 412 mg/L 2mL PER 250mL soln.

T_{3-2} 132 mg/L " "

T_{3-4} 19.1 mg/L " "

T_{3-6} 284 mg/L IN 158 mL SOLN.

TEST, T_4 10g Ga METAL @ START IN 200g/L NaOH.
plus 2.5g ZnO.
(EQUIV. TO 12.5g ZnO/L) = (EQUIV. TO 10g Zn/L)

T_{4-0} 11:00A	88°F = 31.11°C	4V	6amps	200mL INITIAL Volume
T_{4-2} 1:00p	90°F = 32.2°C	4V	6amps	150mL FINAL Volume
$T_{4-4.5}$ 3:30p	93°F = 33.89°C	4V	6amps	50mL LOSS
$T_{4-6.15}$ 5:15	102°F = 38.89°C	4.1V	6amps	

16.98g (DRY) $Ga(OH)_3$ IN 200mL NaOH soln

16.98g * 0.57742 = 9.805g Ga METAL

CATHODE INITIAL: 42.9g CATHODE FINAL: 52.8g

Ga METAL DRIP BEAD wt: 1.80g Ga. METAL

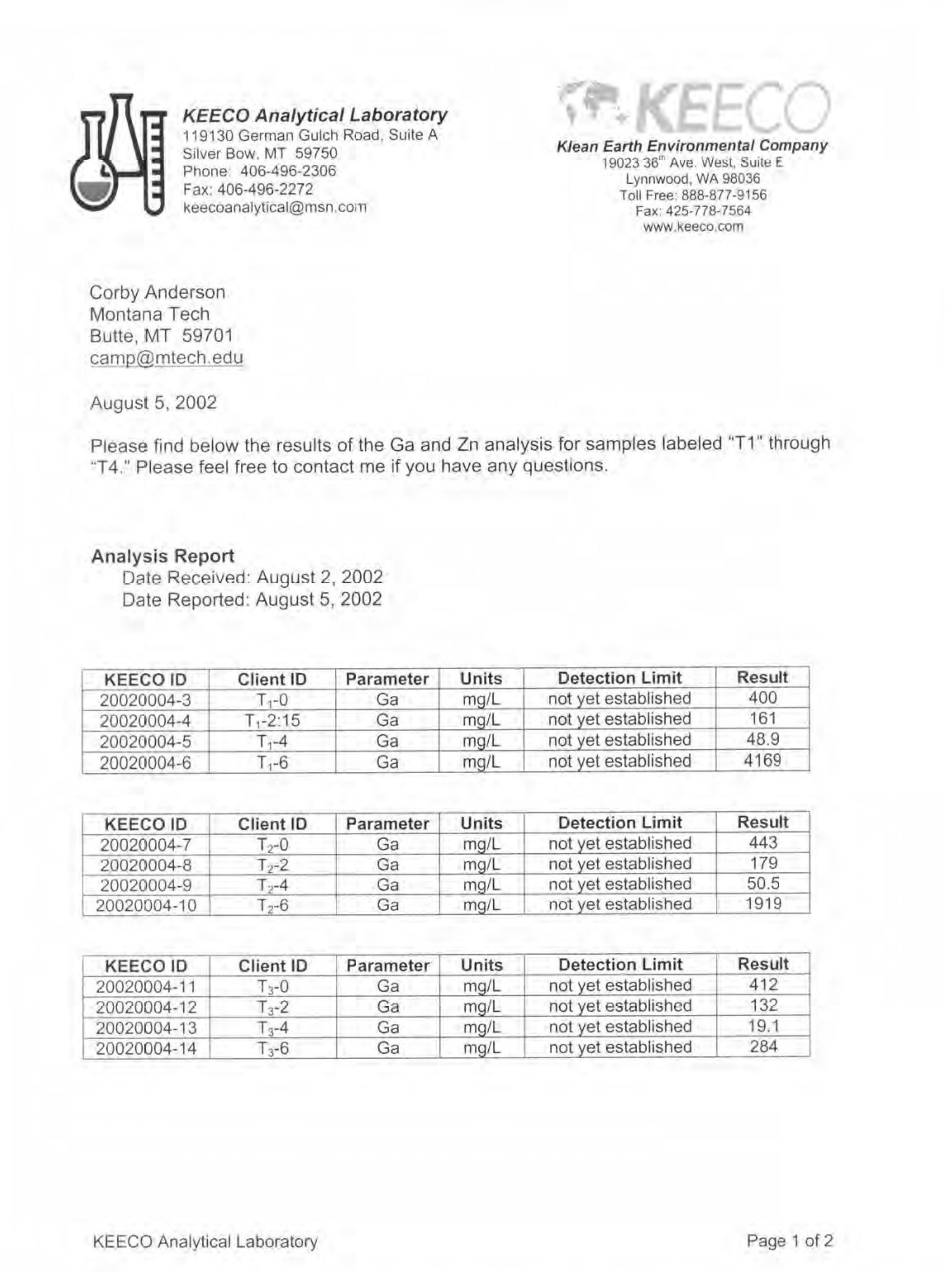
RECOVERED wt: 11.70g Ga/Zn METAL

%REC (BASED ON 10g Ga METAL) (11.70/12)*100 = 97.5%

% REC (BASED ON 9.805g Ga METAL) (11.70/11.805)*100 = 99.1%

ANALYTICAL RESULTS

T_{4-0}	Ga	465 mg/L	2mL per 250mL soln
	Zn	83.6 mg/L	
T_{4-2}	Ga	137 mg/L	" "
	Zn	12.1 mg/L	
$T_{4-4.5}$	Ga	0.62 mg/L	" "
	Zn	0.097 mg/L	
$T_{4-6.15}$	Ga	13.2 mg/L	IN 150mL soln
	Zn	1.8 mg/L	



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Corby Anderson
Montana Tech
Butte, MT 59701
camp@mtech.edu

August 5, 2002

Please find below the results of the Ga and Zn analysis for samples labeled "T1" through "T4." Please feel free to contact me if you have any questions.

Analysis Report
Date Received: August 2, 2002
Date Reported: August 5, 2002

KEECO ID	Client ID	Parameter	Units	Detection Limit	Result
20020004-3	T_1-0	Ga	mg/L	not yet established	400
20020004-4	T_1-2:15	Ga	mg/L	not yet established	161
20020004-5	T_1-4	Ga	mg/L	not yet established	48.9
20020004-6	T_1-6	Ga	mg/L	not yet established	4169

KEECO ID	Client ID	Parameter	Units	Detection Limit	Result
20020004-7	T_2-0	Ga	mg/L	not yet established	443
20020004-8	T_2-2	Ga	mg/L	not yet established	179
20020004-9	T_2-4	Ga	mg/L	not yet established	50.5
20020004-10	T_2-6	Ga	mg/L	not yet established	1919

KEECO ID	Client ID	Parameter	Units	Detection Limit	Result
20020004-11	T_3-0	Ga	mg/L	not yet established	412
20020004-12	T_3-2	Ga	mg/L	not yet established	132
20020004-13	T_3-4	Ga	mg/L	not yet established	19.1
20020004-14	T_3-6	Ga	mg/L	not yet established	284

KEECO ID	Client ID	Parameter	Units	Detection Limit	Result
20020004-15	T_4-0	Ga	mg/L	not yet established	465
20020004-15	T_4-0	Zn	mg/L	0.039	83.6
20020004-16	T_4-2	Ga	mg/L	not yet established	137
20020004-16	T_4-2	Zn	mg/L	0.039	12.1
20020004-17	T_4-4	Ga	mg/L	not yet established	0.62
20020004-17	T_4-4	Zn	mg/L	0.00039	0.097
20020004-18	T_4-6	Ga	mg/L	not yet established	13.2
20020004-18	T_4-6	Zn	mg/L	0.0039	1.8

Ga SRM 1:
Measured Value: 56 μg/L
True Value: 50 μg/L
Recovery: 112%

Ga SRM 2:
Measured Value: 272 μg/L
True Value: 250 μg/L
Recovery: 109%

Ga SRM 3:
Measured Value: 551 μg/L
True Value: 500 μg/L
Recovery: 110%

Zn SRM 1:
Measured Value: 48 μg/L
True Value: 50 μg/L
Recovery: 95%

Zn SRM 2:
Measured Value: 230 μg/L
True Value: 250 μg/L
Recovery: 92%

Zn SRM 3:
Measured Value: 467 μg/L
True Value: 500 μg/L
Recovery: 93%

Analyzed by: Julie Gress
Julie Gress

Reported by:
Marcee Cameron

$Ga(OH)_3$

Ga^{+++}

$$\begin{array}{l|l} & \underline{\text{At wt}} \\ 1\text{-Ga} & 69.72 \\ \text{O} & \left.\begin{array}{l}3\times16\\3\times1{,}008\end{array}\right\} 51{,}024 \\ \text{H} & \\ \hline & 120.744\text{ g/mole}\end{array}$$

$$\frac{69.72}{120.744} = .57742$$

$$\frac{51{,}024}{120.744} = .42258$$

Recovered 4,04 g $Ga(OH)_3$ + ?

Wt ORIGINAL Ga = 2.57 g

$$4.04 * .8039$$

$$\begin{array}{r} = 2.333\text{ g} \\ -\ 2.57 \\ \hline -\ 0.2372 \end{array}$$

$$\frac{2.33\text{ g Ga}}{\underline{1{,}7072\text{ g }OH^-}}$$

$I = 6$ amp $\qquad Ga^{+++} + 3e^- \rightarrow Ga_{(s)}$

$E = 23.24 \qquad E = \frac{69.72}{3} = 23.24g$

$$W = \frac{(23.24g)(6amp)(t_{hr})(3600 sec/hr)}{96{,}500 \text{ amp} \cdot sec}$$

$W(t) = 5.20191\ g\ (t_{hR})$ @ 100% C.Eff.

$$\frac{5.20191\ g}{100\%} = \frac{X(t)}{24.7\%}$$

$X(t) = 1.2849\ g\ (t_{hR})$

for 10g $\quad$ 7.783 hrs

$Ga(OH)_3$ IN (200g/l NaOH soln.)

EQUIVALENT to; 50g/l Ga = 10g/200ml

Go to 6AMPS

1000 amp/m^2

$$\frac{1000\ a}{m^2} = \frac{6\ a}{x^2}$$

$$x^2 = \frac{6\cancel{a}\ m^2}{1000\cancel{a}}$$

$$x^2 = 0.006\ m^2$$

$$x = \sqrt{0.006}\sqrt{m^2}$$

$$x = 0.07746\ m = 7.746\ cm \times 7.746\ cm$$

7.75cm x 7.75cm

60 cm^2 SA_{TOTAL}

30 cm^2 per SIDE

@ 2 SIDES

T4

CATHODE INITIAL wt 42.90 gms

50g/L Ga + 10g/L Zn USING ZnO_2

$Zn(OH)_2$

200g/L NaOH IN 200mL soln.

~~AT~~ wt

Zn 65.39 × 1 65.390
O 15.999 × 2 = 31.998
H 1.008 × 2 2.016

99.404 molwt

Zn × 1 = 65.390
O × = 15.999

81.389

10 g/L Zn

∴ 12.45 g ZnO/L

= 2.5g/200mL

ZnO

$\frac{65.390}{81.389} = 0.8034$

$\frac{x_g}{200mL} = \frac{12.45g}{1000mL}$

$x_g = \frac{(12.45)(200)}{1000}$

$x_g = 2.49 g$

9.805 + 2.0 = 11.805 TOTAL Ga+Zn metal

$x(.8034) = 10$

$x = \frac{10}{.8034} = 12.447$

RESULTS:

1.80 gm DRIP BEAD

52.80 CATH. FINAL
42.90 CATH. INITIAL

9.90 g Deposit

11.70 g TOTAL

16.98 gm $Ga(OH)_3$ * 0.57742 = 9.805 g Ga metal

T_{4-0}	88°F = 31.11°C	4v	6Amps	@ 11:00A
T_{4-2}	90°F = 32.2°C	4v	6amps	@ 1:00p
$T_{4-4.5}$	93°F = 33.89°C	4v	6amps	@ 3:30p
T_{4-6}	102°F = 38.89°C	4v	6amps	@ 5:15p

SULT RECOVERY / $\frac{11.70 \text{ g Recovered}}{11.805 \text{ INITIAL}} * 100$ = 99.11 % Rec. @ 6 hours

T#-0 THRU T#-4 { 2ml Ga/NaOH E.W. Soln } in { 250ml SLIGHTLY ACID. Soln. DISTILLED H_2O }

T#-6 ALL NON-DILUTED Ga/NaOH E.W. Soln.

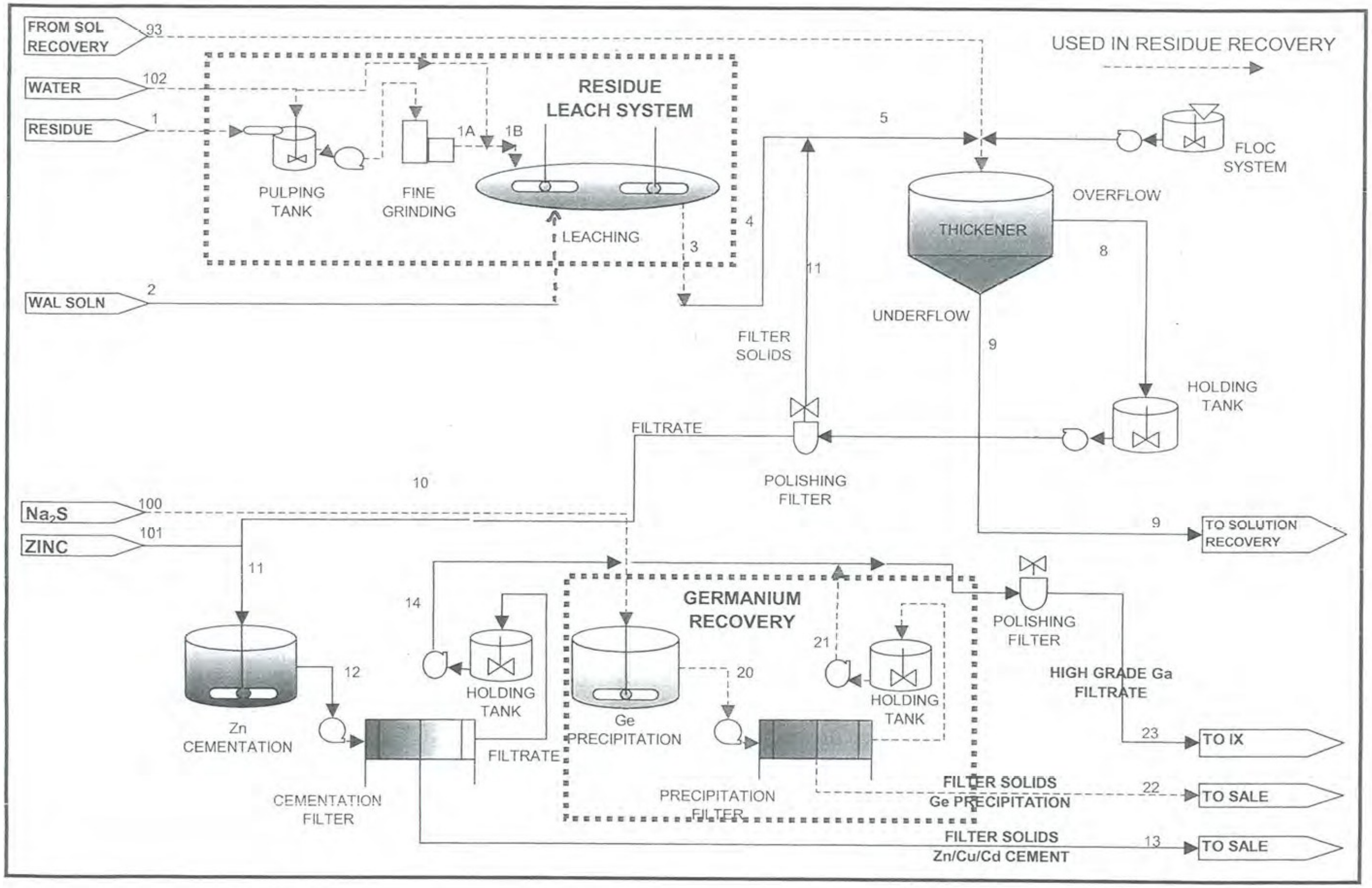
EXCEPTION: T_1-6 { WHICH CONTAINS SOME DISTILLED RINSE WATER ≈ 100mL }

T#-6 final Volumes

T_1	T_2	T_3	T_4
254ml	155ml	158ml	150ml
TEST FOR:			
Ga	Ga	Ga	Ga + Zn

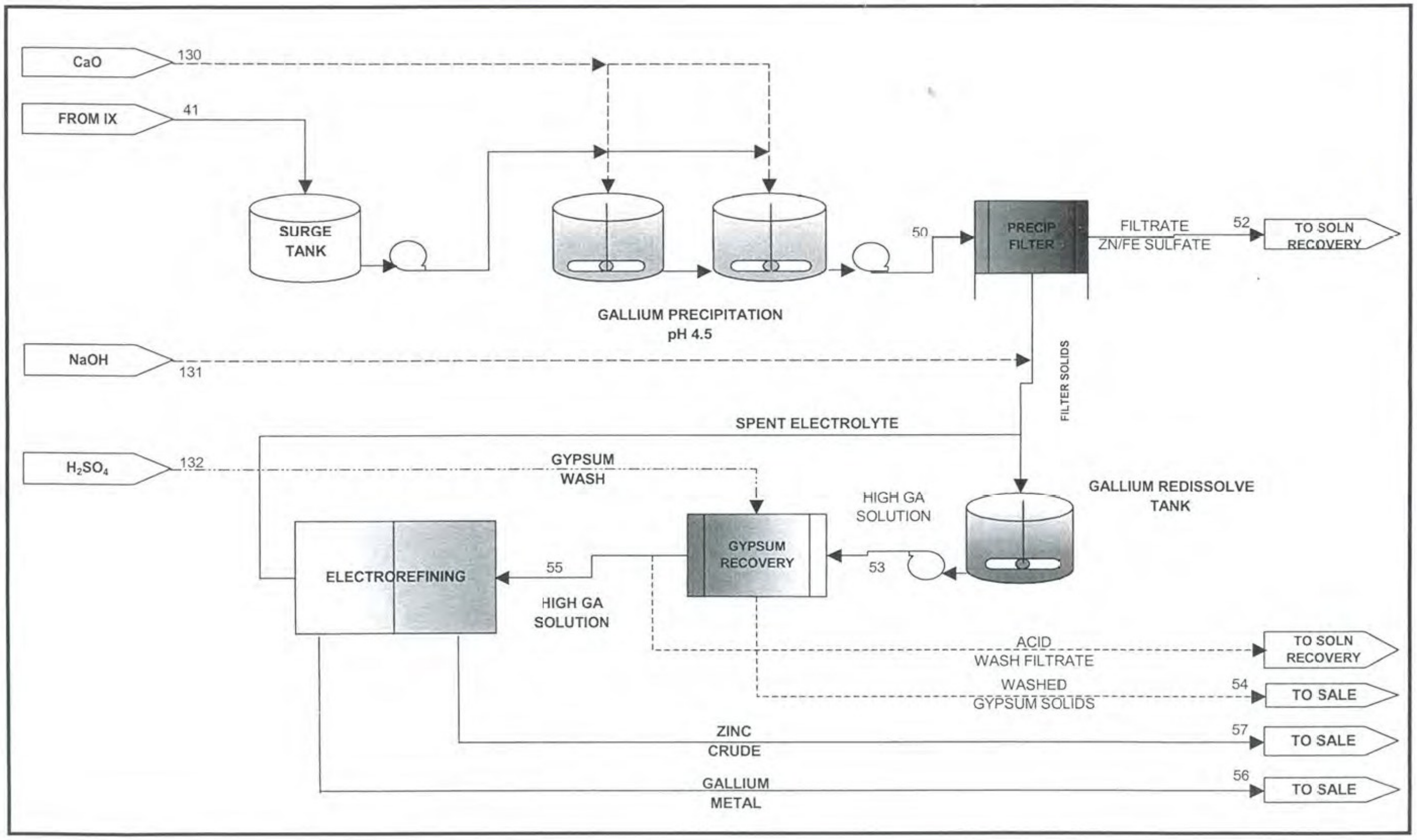
Appendix F: Final Mass Balance and Flowsheets

GORDONSVILLE RESIDUE LEACH CIRCUIT

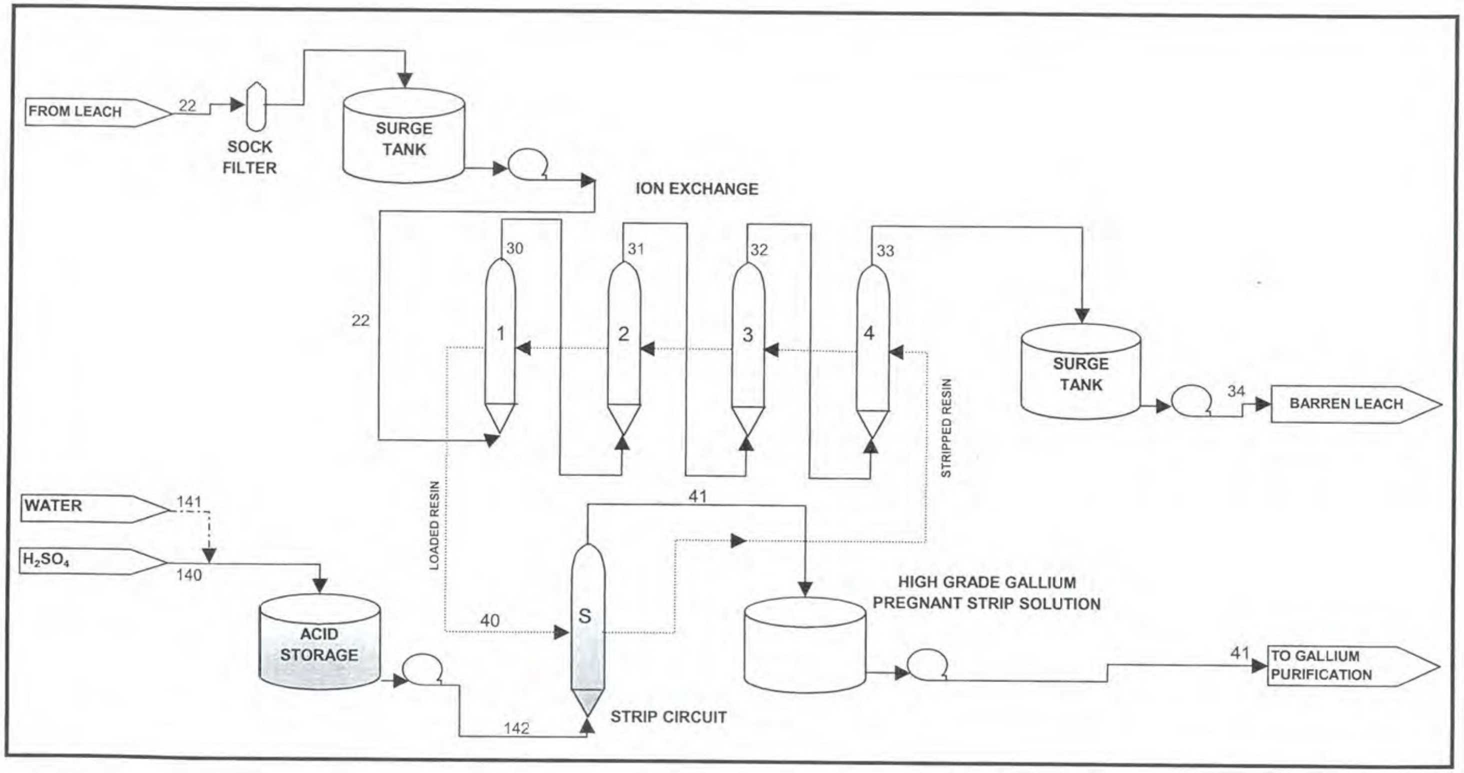


Ga-Ge Flowsheet IX/Leach Circuit

GORDONSVILLE RESIDUE GALLIUM PURIFICATION



GORDONSVILLE RESIDUE
ION
EXCHANGE CIRCUIT



GALLIUM RECOVERY FROM ZINC RESIDUES
MATERIAL BALANCE

REV 5/8/2013

PLANT CAPACITY TPY	4201	
CPERATING DAYS/YEAR	175	
CPERATING HOURS/DAY	16	
H2SO4 STRENGTH	93%	
AUTOCLAVE SIZE	9000	GALLON
ZINC ADDITION	0.02	TNS/TN SOLIDS
SULFIDE ADDITION	2	KG/KG GE FEED

	HEAD GRADE %	LEACH SOLUTION Recovery	RESIDUE GRADE Recovery	CU CEMENT REC Recovery	GE PRECIP Recovery
Gallium	0.2	90.0%	10.0%	0%	
Germ	0.44	75.0%	25.0%	0%	87.0%
Iron	12.4	95.0%	5.0%	0%	
Zinc	14.4	95.0%	5.0%	0%	
Copper	0.57	100.0%	0.0%	100%	
Lead	14.98	0.0%	100.0%	0%	
		% residue	34%		

STREAM	DESCRIPTION	MTPD SOLIDS	MTPD LICUID	MTPD TOTAL	Ga PPM	Ge PPM	Fe PPM	Zn PPM	Cu PPM	Pb PPM	% SOLIDS	KG Ga	KG Ge	KG Fe	KG Zn	KG Cu	KG Pb	GPD	LEACH/ DAY	KG H2SO4	NaNO3 kg/tn	G/L H2SO4	% H2SO4
1	Dry Residue/Grnd	24.0	24.0	48.0	2000	4400	124000	144000	5700	149800	50.0%	48.0	105.6	2976.0	3456.0	136.8	3595.2	6331		0			
102	Water Addition	0.0	96.0	96.0							0.0%							25324		0			
2	Acid Addition	0.0	20.6	20.6							0.0%							2059		20645		200	93%
1B	Leach Feed	24.0	140.6	164.6	2000	4400	124000	144000	5700	149800	14.6%	48.0	105.6	2976.0	3456.0	136.8	3595.2	33714	4.0	20645			
3	Leach Discharge	8.1	140.6	148.7							5.4%									7032		50	
5	Thickener Feed	8.1	143.6	151.7							5.3%	48.0	105.6	2976.0	3456.0	136.8	3595.2						
8	Thickener Overflow	0.0	139.2	139.2	310	569	20308	23583	983	0	0.0%	43.2	79.2	2827.2	3283.2	136.8	0.0						
9	Thickener Underflow	8.1	4.4	12.4							65.0%	1.3	2.4	85.8	99.6	4.1	3595.2						
96	Filtration Cake	8.1	1.4	9.5	504	2774	15638	18160	0	377834	85.0%	4.8	26.4	148.8	172.8	0.0	3595.2						
95	Filtrate	0.0	2.9	2.9							0.0%	0.9	1.6	57.7	67.0	2.8	0.0						
10	Thickener Overflow	0.0	139.2	139.2	310	569	20308	23583	983	0	0.0%	43.2	79.2	2827.2	3283.2	136.8	0.0						
101	Zinc Addition	0.5		0.5											480.0								
12	Zinc Tank Overflow	0.5	139.2	139.7	309	567	20238	26938	979	0	0.3%	43.2	79.2	2827.2	3763.2	136.8	0.0						
12	Zinc Filtration	0.5	0.1	0.6							85.0%				343.2	136.8							
13	Zinc Filtrate	0.0	139.1	139.1	310	569	20318	24579	0	0	0.0%	43.2	79.2	2827.2	3420.0	0.0	0.0						
18	ph Modification - 1.5																						
100	Sulfide Addition	0.16		0.16																			
20	Filter Feed	0.16	139.15	139.30								43.2	79.2	2827.2	3420.0	0.0	0.0						
22	GE Cake	0.16	0.03	0.19	100	369750	3048	3687	0	0	85.0%	0.0	68.9	0.6	0.7	0.0	0.0						
23	GA Solution	0.00	139.12	139.12	310	74	20318	24579	0	0	0.0%	43.2	10.3	2826.6	3419.3	0.0	0.0						

GALLIUM RECOVERY FROM ZINC RESIDUES
MATERIAL BALANCE

REV. 5/8/2013

PLANT CAPACITY TPY	4201
OPERATING DAYS/YEAR	175
OPERATING HOURS/DAY	16
% OPERATING UPTIME	0.85
H2SO4 STRENGTH	93%

LOADING	1
STRIPPING	0.05

PRIMARY

IX RECOVERY	
GA	55%
FE	0.5%
STRIP 1 RECOVERY	
GA	80%
FE	32%
SCRUB RECOVERY	
GA	0%
FE	95%

CLEANER

CLEANER EXTRACT RECOVERY	
GA	75%
FE	0.5%
CLEANER STRIP RECOVERY	
GA	98%
FE	32%

Extraction Recovery	
GA	95.9%
Strip Recovery	
GA	99.8%
Overall Recovery	
GA	95.6%

STREAM	DESCRIPTION	MTPD SOLIDS	MTPD LIQUID	ORGANIC	MTPD TOTAL	Ga PPM	Ge PPM	Fe PPM	Zn PPM	Cu PPM	Pb PPM	% SOLIDS	KG Ga	KG Ge	KG Fe	KG Zn	KG Cu	KG Pb	GPD	GPM	KG H2SO4	NaNO3 kg/tn	G/L H2SO4	% H2SO4
22	GA Solution	0.0	139.1		139.1	310.4	74.0	20318.2	24578.5	0.0	0.0	0.0	43.2	10.3	2826.6	3419.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	PRIMARY EXTRACTION																							
22	GA Tank Outlet	0.0	139.1		139.1	310.4	74.0	20318.2	24578.5	0.0	0.0	0.0	43.2	10.3	2826.6	3419.3	0.0	0.0	36697.8	45.0	0.0	0.0	0.0	0.0
	To IX Circuit			139.1																				
	Extraction 1	0.0	139.1	139.1	278.2	85.4		0.0					23.7		0.0									
	Extraction 2	0.0	139.1	139.1	278.2	123.8		45.7					34.4		12.7									
	Extraction 3	0.0	139.1	139.1	278.2	141.1		91.2					39.2		25.4									
	Extraction 4	0.0	139.1	139.1	278.2	148.8		136.5					41.4		38.0									
	Total Extraction	0.0	139.1	139.1	278.2	148.8		136.5					41.4		38.0									
34	**Barren Solution**	0.0	139.1	0.0	139.1	12.7		20045.2					1.8		2788.6									
	Strip Solution	0.0	0.0	139.1	139.1	297.7		273.1					41.4		38.0									
140	Add H_2SO_4 Soln.		7.0																					
	Strip 1	0.0	7.0	139.1	146.1	226.8		81.9					33.1		12.0									
	Strip 2	0.0	7.0	139.1	146.1	272.2		138.0					39.8		20.2									
	Strip 3	0.0	7.0	139.1	146.1	281.2		176.5					41.1		25.8									
	Strip 4	0.0	7.0	139.1	146.1	283.0		202.8					41.3		29.6									
	Total Strip	0.0	7.0	139.1	146.1	283.0		202.8					41.3		29.6									
	Organic	0.0	0.0	139.1	139.1	0.5		60.1					0.1		8.4									
41	**Strip Solution**	0.0	7.0	0.0	7.0	5934.3		3056.4					41.3		21.3									
41	**Strip Solution**	0.0	7.0	0.0	7.0	5934.3	0.0	3056.4	0.0	0.0	0.0	0.0	41.3	0.0	21.3									
	SOLUTION TO PURIFICATION																							
	Cleaner Strip	0.0	0.0	0.0	0.0	#DIV/0!		#DIV/0!					0.0		0.0									

GALLIUM RECOVERY FROM ZINC RESIDUES
MATERIAL BALANCE

REV. 5/8/2013

PLANT CAPACITY TPY	4201
OPERATING DAYS/YEAR	175
OPERATING HOURS/DAY	16
% OPERATING UPTIME	0.85
H2SO4 STRENGTH	93%

CaO REQUIREMENT

CaO (50%)	0.043

Filter Cake Moisture

Ga Cake	50.0%
Gyp Cake	50.0%

NaOH REQUIREMENT

Na(OH) (50%	2
Kg/Kg Ga	
NaOH	50%

GA/CA PRECIP

Ratio	2.27

Filtrate Loss

Solid Loss	0.50%

Redisolution Recovery

GA	99.50%
FE	0.01%

STREAM	DESCRIPTION	MTPD SOLIDS	MTPD LIQUID	ORGANIC	MTPD TOTAL	Ga PPM	Ge PPM	Fe PPM	Zn PPM	Cu PPM	Pb PPM	% SOLIDS	KG Ga	KG Ge	KG Fe	KG Zn	KG Cu	KG Pb	GPD	GPM	KG H2SO4	NaNO3 kg/tn	G/L H2SO4	% H2SO4
41	Ga Strip Solution	0.0	7.0	0.00	7.0	5934.3		3056.4					41.3		21.3									
	Ga Precipitation																							
130	CaO Addition		0.15																					
50	Precip #1	0.34	6.77	0.00	7.1	2904.7		1496.1					20.6		10.6									
130	CaO Addition		0.15																					
50	Precip #2	0.68	6.58	0.00	7.3	5689.6		2930.4					41.3		21.3									
50	To Filter	0.68	6.58	0.00	7.3	5689.6		2930.4					41.3		21.3									
52	Filtrate	0.00	5.90	0.00	5.9	35.0		18.0					0.2		0.1									
	Filter Solids	0.68	0.68	0.00	1.4	30550.6		15735.0				50.0%	41.3		21.3									
	Ga ReDissolution																							
	Filter Solids	0.68	0.68	-	1.4	30550.6		15735.0					41.3		21.3									
131	NaOH Addition		0.17									50.0%												
55	To Electrorefinning	0.68	0.84	-	1.5	27087.6		1.4				44.6%	41.07		0.002126									
	Water		18.92																					
56	**Ga Metal**	0.041			0.04								41.07		0.002126									
57	**Zn Metal**																							
87	Low GA Residue	0.63	0.84	-	1.48	139.9		14410.5					0.2		21.3									
	Low GA Filter																							
87	Filter Solids	0.63	0.63		1.27	162.6		16751.9				50.0%	0.2		21.3									
84	Acid Wash		3.17																					
83	**Filtrate**		22.09	-	22.09	0.0		962.4							21.3									
54	**Gypsum**	0.63	0.63	-	1.27	162.6		0.0				50.0%	0.2		0.0									

SIGNATURE PAGE

This is to certify that the project prepared by Todd S. Fayram entitled "The Development and Implementation of Industrial Hydrometallurgical Gallium Recovery of the Clarksville Refinery Waste Residue" has been examined and approved for acceptance by the Department of Metallurgical and Materials Engineering, Montana Tech of The University of Montana, on this 16th day of August, 2013.

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