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08/15/86

ARIZONA DEPARTMENT OF MINES AND MINERAL RESOURCES FILE DATA

PRIMARY NAME: CYMET PLANT

ALTERNATE NAMES:

PIMA COUNTY MILS NUMBER: 1144

LOCATION: TOWNSHIP 16 S RANGE 13 E SECTION 36 QUARTER NE4  
LATITUDE: N DEG MIN SEC LONGITUDE: W DEG MIN SEC  
TOPO MAP NAME: SAHUARITA - 7.5 MIN

CURRENT STATUS: OTHER

COMMODITY:

BIBLIOGRAPHY:

ADMMR CYMET PLANT FILE  
E&MJ 4/73, P UU,VV,WW; 7/74, P 27  
MNG ENGIN. 5/73, P 61  
MNG CNGRS JNL 5/73, P 14; 2/73, P 8,50; 9/74,  
22,23 (ABOUT PROCESS & PERSONNEL)  
MNG MAGAZINE 6/73, P 471  
MNG ANL RVW 7/73, P 247



CYMET

Field interview with D. L. Sawyer, Cymet, who is manager of the construction for the new cymet plant south of Tucson. He had a meeting with these men about some of the problems they will have in the area regarding pollution we discussed. GWI WR 10/31/72

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CYMET ELECTROMETALLURGICAL PROCESSES FOR TREATING  
BASE METAL SULFIDE CONCENTRATES

P. R. Kruesi  
E. S. Allen  
J. L. Lake

Abstract

An electrochemical process is described which converts concentrates of base metal sulfides such as chalcopyrite, sphalerite and galena to the corresponding pure metals and recovers the sulfur from these minerals quantitatively in the elemental form. In processing chalcopyrite or concentrates containing pyrrhotite, pure iron is a by-product. The application to standard-quality and low-quality concentrates is described. A brief summary of the economics of the process in comparison to traditional smelting practices is made. The process is such that it involves neither air nor water pollution.

347

# CYMET ELECTROMETALLURGICAL PROCESSES FOR TREATING BASE METAL SULFIDE CONCENTRATES

## Introduction

Hydrometallurgical processing of base metal ores and concentrates has received much attention since the gold miner learned how to extract his metal in a very pure form by cyanidation at the mine site, but because of the technical problems and much lower unit values of the base metals the hydrometallurgical processes were not usually economically successful except for the oxide ores of the base metals and some unusual specific concentrates containing relatively large quantities of nickel and/or cobalt.

Zinc sulfide concentrates might be considered another exception to this general statement; however, the electrolytic zinc plants usually roast the zinc sulfide materials to produce zinc oxide before commencing the hydrometallurgical processing.

During the early 1950's the demand for uranium resulted in a surge of hydrometallurgical-chemical processing research and development and erection of commercial plants. The uranium processing united the chemical and metallurgical engineers to handle abrasive and corrosive slurries and to effect complex solvent extractions for uranium and for certain deleterious impurities. This same period brought the chemical industry salesmen to the mining processing plants, resulting in mutual economic benefits to mining and chemical industries.

Recently the public and the politicians have become very aware of the activities of all industry, and the mining industry in particular, and their effects on the environment. This has resulted in some very adverse public relations, not without some cause, for the industries of mining, manufacturing, pulp and paper, power production, automobiles, and to some extent farming because of its use of fertilizers and pesticides.

It appears, as a result of the present awareness of our environment, that these industries have been adversely showcased and thus we can anticipate some radical deviations from past process practices to correct the most objectionable processes. Smokestacks of almost any kind are now industrial badges calling for public contempt. In the mining industry the mine dumps, the concentrator tailings and the smelter fumes are all looked upon with scorn. Worldwide, the federal and local governments are promulgating laws and regulations for control of the mining activities.

Pyrometallurgical smelting processes are being subjected to very restrictive legislation and regulatory actions, with particular reference to the plume rising from the smelter stack which, in the past, consisted of sulfur dioxide that polluted the atmosphere with gases that have a pungent odor and kill vegetation in the surrounding area.

Cyprus Metallurgical Processes Corporation commenced research in 1970 under a joint venture consisting of Cyprus Mines Corporation, a Los Angeles-based international resources company; Hazen Research, Inc., a Colorado commercial research firm; and Paul R. Kruesi, a self-employed individual, with the objective of developing processes for recovery of base metals from their oxide and sulfide ores and concentrates. The objectives of the R & D processes included commercial potential and a less adverse impact on the environment. The concepts for the initial process research, through elimination of processes not meeting the objectives of the joint venture, pointed to hydrometallurgy using electrical energy and chlorides.

The Cymet processes for base metal sulfides all depend upon disintegration of the sulfides, hydrometallurgically, in hot acidic environment, using electrons to assist in the dissolution of the sulfides and for recovery of the sulfur and base metals all in the elemental form. The optimistic results, after approximately seven months of progressive testing, were consummated in a patent application filed with the United States Patent Office, outlining some 20 claims. The U.S. patent has subsequently been awarded to the inventor and assigned to Cyprus Metallurgical Processes Corporation. During the processing period for the U.S. patent application, the research and development work program was continued at an accelerated rate consistent with the optimistic and gratifying laboratory findings, which showed that the basic chemistry of the base metal sulfides was applicable to most base metals, although the rates of dissolution of the base metal sulfides varied. The sequence of base metal dissolution rates for minerals tested, from the most difficult to the least difficult to "burn down" is listed in descending order as follows:



### Process Description and Chemistry

Figure 1 is a block unit operation flowsheet of the Cymet process and also indicates the location of the samples which are shown in the Typical Product Analyses section of this paper.

#### Feed Preparation

The base metal sulfide concentrates should contain not more than approximately 5 percent moisture so that the lixiviant will not be diluted during the grinding and leaching operations. If the moisture content of the feed materials is greater than the desired content the concentrates would be partially dried.

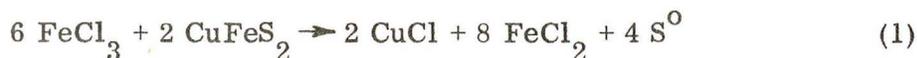
The chemical dissolution rates in the leaching operations are substantially increased on finely ground concentrates. Also, the material handling characteristics of finely ground feed materials are more advantageous to the processing operations. Test results have indicated that the feed material should be ground to a fineness of at least 95 percent minus 200 mesh.

The grinding circuit consists of corrosion-proof lined ball mill using ceramic balls as grinding media. The feed material is ground in the lixiviant and classification is effected in rubber-lined hydroclones closed-circuited with the mill. The ball mill shell is rubber covered with chlorobutyl rubber and the mill lining is also chlorobutyl to resist both abrasive and corrosive action of the slurry.

#### Leaching

Leaching of the ground slurry is performed in counter-current leaching employing cyclones between leaching stages to provide maximum efficiency of the lixiviant. A thickener is provided between the first and second leaching stages to provide a clear solution for feeding the cathode compartments of the electro-dissolution cell. The lixiviant for the leaching operations is the ferric chloride anolyte solution from the iron electrolytic cells. The chemical reactions during leaching are as follows:

Chalcopyrite:



Sphalerite:



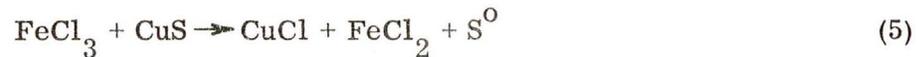
Galena:



Chalcocite:



Covellite:



Pentlandite:



All of the above chemical reactions are exothermic.

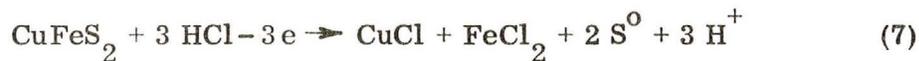
### Electrolytic Dissolution

The leached slurry discharge is pumped and distributed to the anode compartment of the electrolytic dissolution cells which are diaphragm-fitted cells to separate the anode compartment from the cathode compartment. The diaphragms are permeable woven synthetic material to form a barrier to the anode slurry. The anodes in the electrolytic dissolution cell are titanium coated with conducting oxides. The anodes are proprietary patented items.

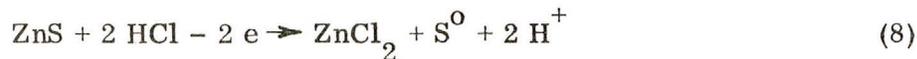
The voltage drop in the electrodisolution cell is dependent upon numerous factors such as diaphragm material, the spacing between the anodes and cathodes, the temperature of the anolyte and catholyte, composition of the lixiviant.

Temperature of the anolyte is maintained above 50°C. The electrodisolution cell produces heat as well as escalating the dissolution of the solids contained in the anolyte slurry. The temperature of the anolyte slurry is controlled through regulation of the temperature of the feed to the anode compartment and through regulation of the flow rate through the anode compartment. Typical chemical reactions in the anode compartment are as follows.

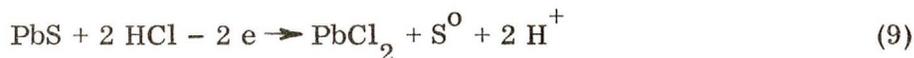
Chalcopyrite:



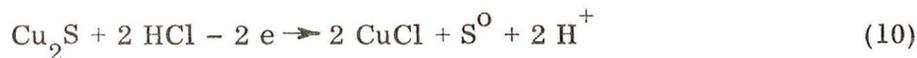
Sphalerite:



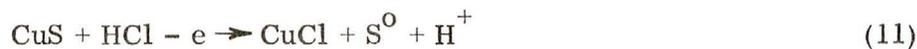
Galena:



Chalcocite:



Covellite:



Pentlandite:



The anolyte compartment slurry discharge goes to the final leach stage discharge for counter-current flow.

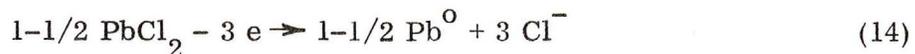
Some of the diaphragm materials permit rather high flows of catholyte to the anode compartment which results in considerable dilution of the anolyte. It is for this reason and to recover the dissolution products (solubilized base metals and the elemental sulfur) that the anolyte slurry discharge from the electro-dissolution cell is returned to the leach counter-current operations.

Throughout the electrolytic dissolution operation the anolyte pH is maintained at less than 4.0.

### Copper Recovery

The copper is recovered from the leach and anolytic solutions by electro-winning in the cathode compartments of the electro-dissolution cell. The catholyte solution is prepared in the following manner.

- Subsequent to the first-stage leach the slurry is pumped through hydrocyclones to effect a partial liquid-solid separation. The unreacted base metal sulfide materials largely report in the hydrocyclone underflow product for further leaching, whereas the majority of the lixiviant, together with the elemental sulfur and some slime materials, reports in the hydroclone overflow product which goes to a thickener for further liquid-solid separation by free settling.
- The thickener underflow product contains the settled elemental sulfur and other solids in slurry form at approximately 40 percent solids. This underflow product is filtered, repulped, and filtered for a minimum of three filtration steps. These washed solids are the feed to the sulfur recovery operations which will be described in more detail in another section of the process description.
- The thickener overflow solution is subjected to a polishing filter to remove any remaining suspended solids in preparation for electroprecipitation (partially) of the copper, gold, silver, lead and bismuth contents in the cathode compartments of the electrodisolution cell. The cathodes of the cell are round copper rods uniformly spaced and oriented parallel to the anodes in the anode compartments. The ratio of cathode surface area to anode surface area is maintained at approximately 1:1.
- At the high current density maintained in the electrodisolution cell, the metals are precipitated, in elemental state, as powders to form a metallic slurry which, through controlled discharge rates, is pumped to a thickener for partial liquid-solid separation. The chemical reactions at the electrodisolution cell cathode bars are as follows:



- A side reaction at the cathode results from the cathode efficiency loss. This reaction is very minor and is as follows:



- The chlorine ( $\text{Cl}^-$ ) ions from the chemical reactions (13), (14), (15), and (16) migrate through the electrodisolution cell diaphragm to the anode compartment where there is a reaction with the hydrogen ( $\text{H}^+$ ) ions from the chemical reactions (7), (8), (9), (10), (11), and (12) in the anode compartment as follows:



### Sulfur Recovery

In the above description for copper recovery the hydrocyclone overflow product from the first-stage leaching operation is thickened to obtain the catholyte feed solution for the copper recovery operations. The thickener underflow product contains relatively high content of finely disseminated elemental sulfur and some slime products such as clays and finely ground insoluble materials. These thickened solids are filtered and washed, as stated above, and become the feed to the sulfur recovery section.

The feed material to the sulfur section in the form of filter cake is treated by a proprietary process (patent applied for) briefly described as follows:

- The material must be well washed.
- The material is reslurried to approximately 25 percent solids.
- The elemental sulfur content of the feed should be above approximately 20 percent for efficient sulfur recovery operations.
- The elemental sulfur-bearing slurry is charged into an autoclave where the slurry is agitated and heated to approximately  $135^\circ \pm 5^\circ\text{C}$ .
- The slurry is maintained at the above stated temperature for approximately two hours under constant agitation that maintains all of the solids in uniform suspension. Under these conditions the elemental sulfur agglomerates into globules.
- At the conclusion of the sulfur agglomeration period the slurry is cooled, in approximately 15 minutes, from  $135^\circ\text{C}$  to  $120^\circ\text{C}$  to solidify the sulfur globules into beads. The autoclave is then further cooled below the flash point before discharge.

- The autoclave is discharged at controlled rates by pumping to a screen fitted with woven wire mesh cloth with approximately 80 mesh openings. The screen oversize product is the sulfur beads containing elemental sulfur usually at 96+ percent and normally assaying less than 0.50 percent copper.
- Impurities contained with the elemental sulfur beads are usually iron oxide and fine pyrite for total iron content of approximately 1.4 percent. Selenium contained in the plant feed reports with the elemental sulfur and if it is of sufficient quantity it may be recovered as the residue after sulfur distillation.
- The elemental sulfur beads may be further refined to 99+ percent by re-melting and filtering operations to obtain a "bright" sulfur product.
- The screen underflow product resulting from the sulfur agglomeration and screening operations is thickened for further treatment to recover its residual elemental sulfur, copper and molybdenite.

The Cymet process to treat base metal sulfide materials is built on operating conditions which will recover the sulfur in elemental form and will prohibit the reactions of oxidizing the sulfide sulfur beyond its elemental state. The oxidation of sulfide sulfur to the sulfate sulfur state is represented as follows:



Instead, in the Cymet process, oxidizing sulfide sulfur to elemental sulfur, the electrical power requirements are 1.5 electrons per mole of sulfur rather than 8 electrons per mole as required in equation (18) above.

### Tailings

In order to eliminate the waste materials such as gangue minerals and pyrite contained in the plant feed, the sulfur recovery screen undersize product is thickened and combined with a predetermined and metered flow from the electro-dissolution cell anode compartment discharge, which has been separately filtered and washed, as feed to a flotation circuit. The flotation feed is diluted to approximately 25 percent solids, conditioned for a short period (approximately 5 minutes) with a promoter (AC 238) and lime (pH about 9.5 to 10.0) and floated for approximately 15 minutes.

The flotation concentrate product is cleaned once, thickened and filtered for return to the plant feed. Typical analysis of the cleaned flotation recycle concentrate is as follows:

Copper	17.5 percent
Molybdenum	0.7 percent
Sulfur (total)	43.5 percent
Sulfur (elemental)	15.6 percent

The flotation tailings product is the total plant tailings which is discarded. The composition of the tailings is dependent to a large extent upon the plant feed composition, particularly with reference to pyrite and insoluble gangue mineral contents. Typical analysis of a chalcopyrite feed material and the tailings product resulting therefrom are as follows:

	Assay in Percent	
	Feed	Tailings
Copper	27.1	0.8
Sulfur	32.1	20.0
Iron	27.5	19.0
Zinc	0.265	trace
Molybdenum	0.221	0.55 ?
Lead	0.074	trace
Antimony	0.047	trace
Arsenic	0.033	trace
Bismuth	0.022	trace
Selenium	0.009	trace
Insol.	12.24	60.1
Silver	2.4 oz./ton	0.3 oz./ton
Gold	0.04 oz./ton	0.08 oz./ton

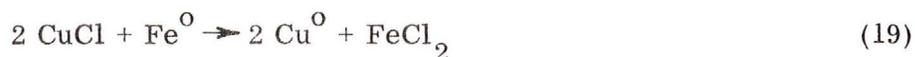
Under the above specified conditions, the Cymet process copper recovery was in excess of 99 percent, silver recovery was approximately 97 percent, and approximately 60 percent of the gold was recovered. The tailings product was approximately 20 percent of the plant feed, by weight.

### Solution Purification for Zinc and Iron Recovery

The spent catholyte from the copper recovery contains soluble metal chlorides such as residual copper, residual lead, cadmium, arsenic, antimony, zinc and that iron contained with the iron-bearing base metal sulfide minerals such as chalcopyrite, marmatite and pyrrhotite. To recover the soluble iron by electrolysis in a pure and salable form requires that all of the above-mentioned impurities, except some soluble zinc, be removed from the solution. Likewise, the recovery of zinc in a pure and salable form requires the removal from solution of all of the residual copper, lead and bismuth and the elimination of arsenic, antimony and cadmium.

To precipitate these undesirable impurities, two steps of precipitation are required. These are briefly described as follows:

- Residual copper, lead and bismuth are precipitated using metallic iron in the form of shredded iron or iron powder. In this precipitation the iron replaces the copper, lead and bismuth in solution and a mixed precipitate of metallic copper, lead and bismuth is formed. These reactions are illustrated chemically as follows:



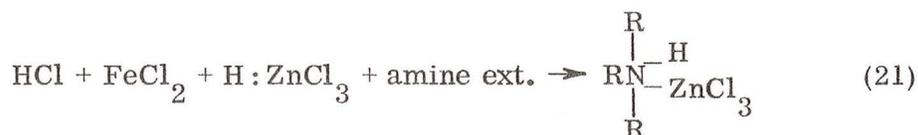
- The second-stage precipitation step is similar to the first step except that metallic zinc, in the form of powder or slurry, is added to complete the elimination of residual copper, lead, bismuth, antimony, arsenic, and mercury. The zinc replaces these impurities in solution, thus precipitating these impurities in elemental form or, in the case of mercury, as an amalgam (alloy). The chemistry of these precipitations is similar to that shown in (19) and (20) above.
- Subsequent to each of the precipitation steps the solution is filtered to recover the impurities in elemental form for further treatment and separations, if economic. The resultant filtrate is now ready for zinc and/or iron recovery steps.

### Zinc Recovery

Iron electrolysis may be performed in the presence of soluble zinc at a concentration of at least 2 grams per liter without any adverse effects upon the quality of the iron or upon the electrolytic efficiencies. It is not required, therefore, that the soluble zinc be completely eliminated from the ferrous chloride catholyte for iron electrolysis.

The zinc removal, therefore, is dependent upon the zinc content in the copper concentrate and the quantity of the iron catholyte going to zinc recovery operations is adjusted to maintain the zinc content within the desired concentrations.

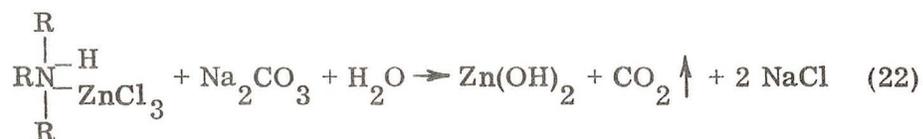
Zinc is removed from the solution by solvent extraction with a tertiary amine. The tertiary amine solvent extraction of zinc will not tolerate any ferric iron ions. It is imperative, therefore, that the soluble iron be in the ferrous state at all times to preserve the tertiary amine's efficiency to extract zinc. This is controlled largely by maintaining a low pH (approximately 1.5) of the aqueous solution by the addition of HCl during the solvent extraction. The elimination and removal of oxygen in the extraction units is advantageous. The solvent extraction reaction is illustrated by the following chemical formula:



The tertiary amine is dissolved in an organic carrier similar to kerosene. The organic solvent is normally approximately 7-1/2 percent tertiary amine and 92-1/2 percent solvent (kerosene) resulting in a density of less than 1.0 and it has a very low solubility in the aqueous solution. The zinc loading of the organic is normally performed in five counter-current contacting stages of the aqueous and organic phases with hydrochloric acid addition in each extraction stage.

The organic solution prior to stripping is washed in two stages using water to remove any ferrous chloride solution entrainment.

The washed organic is then stripped with sodium carbonate solution in a single stage. This chemical reaction illustrating the organic solvent stripping is as follows:



The resulting zinc hydroxide may be dried and sold in the form of zinc oxide or it may be redissolved in acid and recovered in pure metallic form as electrolytic zinc.

### Iron Recovery

Electrolysis of the ferrous chloride solution serves two useful purposes to the Cymet process as follows:

- It removes most of the iron that dissolved from the copper and/or zinc minerals containing iron, such as chalcopyrite and marmatite, and
- It regenerates the remaining ferrous chloride in the anode compartment to ferric chloride for recycle to the leaching circuit for dissolving and disintegrating the base metal sulfide minerals as shown in the chemical equations (1), (2), (3), (4), (5), and (6) contained in the Leaching section herein.

The electroplated iron product is of very high purity, is very ductile, and contains very low quantities of phosphorus, carbon, hydrogen, nitrogen, aluminum, chromium, silicon and titanium. The high quality of the electrolytic iron should find many uses where high-quality product is required for such applications as electrical transformer cores, electric motor laminations, special alloys such as for ball and roller bearings, aluminum-iron alloys for heat exchangers in desalinization of sea water, etc.

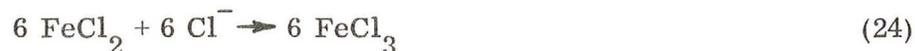
The electrical efficiencies in the iron electrolysis cells are very high. The chemical equations for the reactions in these cells are as follows:

- Electrowin Iron Cell Cathode:



- Electrowin Iron Cell Anode:

The six chloride ( $\text{Cl}^-$ ) ions from the cathode compartment migrate to the anode compartment, through the diaphragm, to react in that compartment with the ferrous chloride, at the anode, as follows:



It will be noted that equation (24) corresponds with the ferric chloride requirements in the leaching equations (1) through (6).

Typical Product Analyses

Typical product analyses from treating a copper concentrate containing largely chalcopyrite as the copper-bearing mineral:

① Plant Feed Materials:

	<u>Percent Weight</u>
Copper	27.1
Sulfur	32.1
Iron	27.5
Zinc	0.265
Molybdenum	0.221
Lead	0.074
Antimony	0.047
Arsenic	0.033
Bismuth	0.022
Selenium	0.009
Insol.	12.24
Silver	2.4 oz./ton
Gold	0.04 oz./ton

② Copper Powder Product:

	<u>Percent Weight</u>
Copper	90+
Iron	1.1
Lead	0.27
Bismuth	0.032
Silver	0.026
Antimony	0.013
Selenium	0.00007

② Copper Powder Product: (Cont.)

	<u>Percent Weight</u>
Zinc	0.10
Sulfur	0.35
Arsenic	< 0.005

③ Crude Sulfur Product - Plus 100 Mesh:

	<u>Percent Weight</u>
Sulfur (elemental)	96.1
Selenium	0.027
Copper	0.5
Molybdenum	0.05
Iron	1.39

④ Refined Sulfur Product - Filtered Crude:

	<u>Percent Weight</u>
Sulfur	99
Selenium	0.03

⑤ Zinc Oxide - Precipitated SX Product:

	<u>Percent Weight</u>
Zinc	61
Copper	1.7
Iron	0.12
Chromium	0.055
Nickel	0.024

⑥ Electrolytic Iron:

	<u>Analysis</u>
Iron	99.5 percent
Oxygen	0.035 percent
Phosphorus	20 ppm
Carbon	80 ppm
Hydrogen	50 ppm
Nitrogen	30 ppm
Aluminum	50 ppm
Chromium	< 1 ppm
Copper	500 ppm
Molybdenum	30 ppm
Nickel	150 ppm
Lead	100 ppm
Silicon	< 1 ppm
Titanium	< 1 ppm

② The following products were made by refining the Copper Powder Product above:

⑦ Electrorefined Cathode Copper:

	<u>Analysis</u>
Copper	99.95 percent
Aluminum	20 ppm
Bismuth	< 10 ppm
Iron	20 ppm
Magnesium	50 ppm
Nickel	< 10 ppm
Lead	< 10 ppm
Silicon	25 ppm

⑦ Electrorefined Cathode Copper: (Cont.)

	<u>Analysis</u>
Tin	< 10 ppm
Arsenic	< 25 ppm
Cobalt	< 10 ppm
Phosphorus	< 50 ppm

⑧ Electrowon Cathode - NH<sub>3</sub> Leach - SX with LIX 64:

	<u>Analysis</u>
Copper	99.95 percent
Silver	< 1 ppm
Aluminum	< 10 ppm
Chromium	< 10 ppm
Iron	150 ppm
Magnesium	< 100 ppm
Manganese	< 1 ppm
Molybdenum	< 10 ppm
Nickel	< 10 ppm
Lead	< 10 ppm
Tin	< 10 ppm
Zinc	< 25 ppm

⑨ Anode Sludge from Electrorefined Copper ⑦:

	<u>Percent Weight</u>
Copper	46
Silver	0.48
Zinc	0.75
Tin	1.3
Lead	12.0

⑨ Anode Sludge from Electrorefined Copper ⑦: (Cont.)

	<u>Percent Weight</u>
Iron	0.75
Chromium	0.023
Manganese	0.005

Economic Comparison

Cymet vs. Conventional Conversion

In the early part of 1972 economic studies were made to determine the economic potential of the Cymet process for chalcopyrite copper concentrates as compared to the conventional pyrometallurgical smelter to produce 80,000 tons of electrolytic copper of "wirebar" grade. Both facilities were assumed to be located in south-central Arizona.

Other premises used in these economic evaluations were as follows:

Table 1

Chemical Analysis of Chalcopyrite Feed

<u>Element</u>	<u>Assay</u>
Copper	27.70 percent
Iron	29.24 percent
Sulfur	33.70 percent
Zinc	0.25 percent
Lead	0.02 percent
Gold	0.04 oz./ton (ST)
Silver	2.40 oz./ton (ST)

Table 2

Mineral Composition of Feed

<u>Mineral</u>	<u>Approximate Percent</u>
Chalcopyrite	80.1
Pyrite	10.4
Sphalerite and galena	0.4
Quartz and insol.	<u>9.1</u>
Total	100.0

Table 3  
Costs of Utilities

<u>Utility</u>	<u>Cost per Unit</u>
Water from wells	\$0.03 per 1000 US gal.
Fuel oil	\$0.50 per million BTU's
Electricity including demand charge and energy charges	\$0.0105 per kwh

Table 4  
Hourly Wage Rates - Operating

<u>Classification</u>	<u>\$ per hour</u>
Operators	4.81
Operator Helpers	4.46
Laborers	3.89
Mobile Equipment Operators	5.04
Maintenance Men	5.04
Maintenance Helpers	4.24
Craftsmen (Specialists)	5.27

Table 5  
Fringe Wage Benefits

<u>Classification</u>	<u>Percent of Annual Wage</u>
Salaried Employees	30
Hourly Paid Employees	22

Preliminary capital cost estimates were made of the facilities required for the Cymet process and the conventional pyrometallurgical smelter. Also included in the capital cost for each facility was a copper electrorefining facility that would produce copper cathodes of wirebar grade for direct comparison of the two copper production facilities.

Table 6

Capital Cost Comparison for 80,000 TPY of Wirebar Copper

Pyro-smelter plus Electrorefinery	1.00 (Unity)
Cymet Process and Electrorefinery	0.83

Operating cost estimates were also prepared for the conventional pyro-process smelter plus electrorefining of copper as compared to the Cymet hydro-metallurgical process plus electrorefining of copper. These operating cost comparisons are summarized as follows:

Table 7

Comparison of Cu Production Costs, Conventional Smelter vs Cymet Processes

	<u>Cents per pound of Recovered Copper</u>	
	<u>Conventional Pyro-Smelter + Electrorefining</u>	<u>Cymet Process + Electrorefining</u>
Direct Operating Costs	10.103	9.568
Administrative and Indirects	<u>0.781</u>	<u>1.019</u>
Total Direct and Indirect	10.884	10.587
Fixed Costs (Depreciation)	<u>2.733</u>	<u>2.022</u>
Total Operating Costs	13.617	12.609
Credits:*		
Gold, silver, lead and zinc	0.790	0.790
Sulfur and iron	<u>0.535</u>	<u>4.361</u>
Total Credits	<u>1.325</u>	<u>5.151</u>
Conversion Cost per lb. of recovered copper	12.292	7.458
Conversion Cost per lb. of total contained copper	12.939	7.590

\*Credits were estimated using the following values:

Gold @ \$42.00 per Troy oz.	Zinc @ \$ 0.085 per pound
Silver @ 1.45 per Troy oz.	Iron (electrolytic) @ 0.05 per pound
Lead @ 0.06 per pound	Sulfur equivalent @ 10.00 per long ton

### Cymet Process Application to Other Base Metal Sulfide Concentrates

The majority of the laboratory and pilot plant work performed to date has been concentrated on copper concentrates, and largely on those containing chalcopyrite, because of the environmental problems resulting from conventional copper pyrometallurgical smelting throughout the world.

Laboratory bench scale testing of other base metal sulfide concentrates using the basic Cymet process principles has indicated some extremely attractive potentials, especially for converting the mixed and complex bulk concentrates to high-purity metals recovered electrolytically. Some of the materials tested include the following mixed and complex bulk concentrates:

- Copper-nickel sulfide concentrates.
- Lead-zinc bulk concentrates from which it has been difficult to make adequate selective flotation concentrate products.
- Copper-zinc bulk concentrates.
- Copper-cobalt bulk concentrates.
- Mixed copper oxide and sulfide bulk concentrates of low copper content.
- Refractory flotation concentrates containing arsenic and/or mercury minerals.

The test work on these materials has indicated process flowsheets that provide some very exciting potentials of the Cymet processes for production of high-purity metals and elemental sulfur, resulting in high recoveries at low conversion costs.

### Pollution Control

The Cymet electrometallurgical process conversion of base metal sulfides to the separate components in the elemental state reduces the hazards of pollution. The major waste product from the Cymet process is the tailings product consisting mainly of the gangue minerals and pyrite that were contained in the feed materials. This tailings product can be impounded in the normal manner, similar to flotation plant tailings.

The soluble chlorides contained in the lixiviant are recycled within the circuit. Some "salting out" of these chlorides will result in minor quantities and may be disposed of in one of several alternate means.

The nature of the chemistry and the electrometallurgical processes results in the generation of heat which may be dissipated by cooling water or by evaporation by air.

Any solutions leaving the process may be neutralized, clarified and discharged into sewers.

Dust presents no problems except in receiving and storage ahead of processing. This minor potential dust hazard can be handled by either wet or dry dust collectors of very limited capacity requirements.

There are minor gas emissions from the electrolytic cells, of which chlorine has been detected only in extreme process upset conditions, oxygen emission in very minor amounts, and hydrogen gas emission in limited amounts arising from the powder copper and electrolytic iron cells. Good building ventilation will adequately control the disposal of the gas emissions.

Acknowledgements

It has been a pleasure to have the opportunity to present this paper to this distinguished audience of engineers and scientists from around the world.

It is fitting and proper that credit be given to the numerous engineers, scientists and technicians who have worked so relentlessly in helping to develop the Cymet processes as described. Particular credit and encouragement have been provided by Hazen Research, Inc. management and personnel, and by Cyprus Mines Corporation management and engineers. Without the assistance and guidance from these organizations, the progress on this work would not have been possible.



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CYMET PROCESS  
HYDROMETALLURGICAL CONVERSION  
OF BASE METAL SULFIDES TO PURE METALS

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CYMET PROCESS  
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OF BASE METAL SULFIDES TO PURE METALS

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Abstract

An electrochemical process is described which converts concentrates of the base metal sulfides to the corresponding pure metals and elemental sulphur. The application of the process to chalcopyrite is discussed, as well as the application of the process to zinc-lead concentrates. Indications of process economics are given. The process is such that it creates neither air nor water pollution.

## Introduction

Hydrometallurgical processing of base metal concentrates has been long discussed, but little acted upon. As early as the 1890's, a substantial patent literature developed and various attempts were made at commercial application. With the exception of gold cyanidation, however, very little has resulted. Recently we see the development of hybrid processing such as International Nickel's matte process, the Falconbridge matte process, and, of course, in zinc, the rapid replacement of the zinc retorts with the electrolytic process.

The further step to total hydrometallurgical processing may soon be made. Pressures from the adverse problems associated with gas discharges from pyrometallurgical processing, coupled with advancement in the equipment and techniques for hydrometallurgy, lead to the expectation that purely aqueous processes will now become competitive. The "Cymet" process is such a development.

In 1970 a joint venture was formed between Cyprus Mines Corporation, Hazen Research, Inc., and Paul R. Kruesi to develop processes for the recovery of base metals from their sulphide and oxide concentrates. The objective was to develop processes which would be economically competitive and yet free from adverse impact on the environment.

A process did evolve on which a series of patent applications have been filed around the world. The first U.S. Patent has been issued (U. S.

Patent 3,673,061). The basic approach was the electrochemical conversion of the sulphides to elemental sulphur and a solution of the desired metal ions at the cathode. The process involves a simple concept. Its development into workable techniques has involved substantial research and development efforts. These efforts have resulted in continuous operation of a 1200-pound (concentrate) feed per day pilot plant for processing chalcopyrite, and Cyprus Mines Corporation has announced that a demonstration plant will be built. This is now in final engineering for construction. It is anticipated that it will be in operation in mid-1973.

#### Basic Chemistry of the Process

Slide I illustrates the basic chemical reactions which occur with chalcopyrite feed. As illustrated, ferric chloride generated at the anode of a cell reacts with chalcopyrite to produce cuprous chloride, ferrous chloride, and elemental sulphur. Additional chalcopyrite is reacted directly at the anode to produce additional cuprous chloride, ferrous chloride, and sulphur. This anode balances the current requirement necessary to reduce the cuprous chloride to elemental copper. Ferrous chloride is reduced to elemental high purity iron and the cycle is completed by the oxidation of residual ferrous chloride to ferric chloride.

Slide II illustrates the basic chemical reactions which occur with certain other metallic sulphides. Similar reactions could, of course, be written for the various other sulphide minerals.

There are substantial differences, however, in the ease with which the various sulphides are attacked. Slide III illustrates in descending order of difficulty the ease of conversion of various sulphides. Under the conditions Cymet employs, pyrite and molybdenite are essentially inert. Cobaltite, pentlandite, and chalcopyrite fall in a group in which reaction at high efficiency requires controlled conditions, and sphalerite, chalcocite, pyrrhotite, and galena are readily attacked.

The Cymet process can perhaps be illustrated best by more detailed reference to its application to specific concentrates.

#### Chalcopyrite

Slide IV presents the flowsheet developed and pilot plant tested for chalcopyrite. The features of the flowsheet are as follows:

1. Feed Preparation: Reactivity is increased by surface area so that the flotation concentrate is ground in a rubber-lined mill using ceramic balls as media to 95% minus 200-mesh. Classification is effected by rubber-lined hydroclones in closed circuit with the mill.
2. Leaching: Leaching of the ground slurry is performed counter-currently. A thickener is provided between Stage 1 and Stage 2 leaching to provide clear solution for feeding the cathodes of the electrodisolution cells. The lixiviant is

ferric chloride recycled from the iron cells. The reaction is exothermic but provisions are made to control temperature at about 75-80°C.

3. Electrolytic Dissolution: Second stage thickener underflow is distributed to the cell anodes where the attack of chalcopryrite is continued. The anode compartments of the cells are isolated from the cathode compartments by diaphragms.

Cells I operate at high current density (up to 200 amperes per square foot) and substantial amounts of heat are generated. The cells are evaporatively cooled to maintain temperature above 50°C but below incipient boiling.

Cells II operate at lower current density and complete the dissolution of chalcopryrite to the predetermined level of recirculating load. The cells anode compartments discharge to a thickener with overflow returning to first stage leach and the underflow going to filtration and washing in preparation for sulphur removal.

4. Sulphur Recovery: The filtered and washed solids are slurried in autoclave thickener recycle and autoclaved at about 135°C under conditions which cause the sulphur to agglomerate into plus 80-mesh beads. These beads assay 90-96% sulphur and

Slide I

Chemistry of the Process

Chalcopyrite:

Leach Step:



Cell Anodes:



Cell Cathodes:



Fe Cells:

Cathodes:



Anodes:



Summary:



Theoretical current = 573.8 ampere hours per pound Cu

Slide II

Chemistry of the Process

Sphalerite:

Anode Reaction:



Cathode Reaction:



Theoretical current = 371.95 ampere hours per pound.

Galena:

Anode Reaction:



Cathode Reaction:



Theoretical current = 117.4 ampere hours per pound.

Chalcocite:

Anode Reaction:



Cathode Reaction:



Theoretical current = 191.3 ampere hours per pound.

Slide III

Reactivity of Various Sulphides

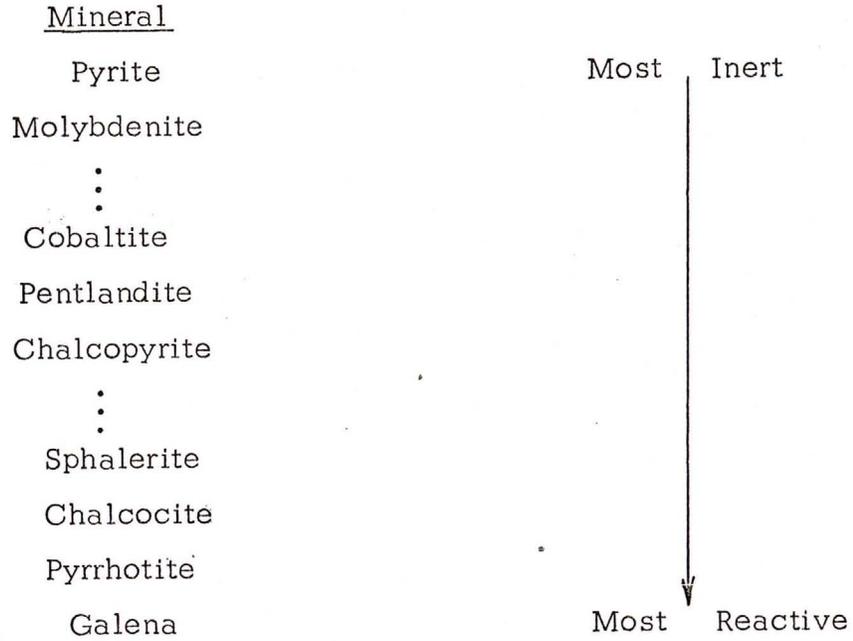
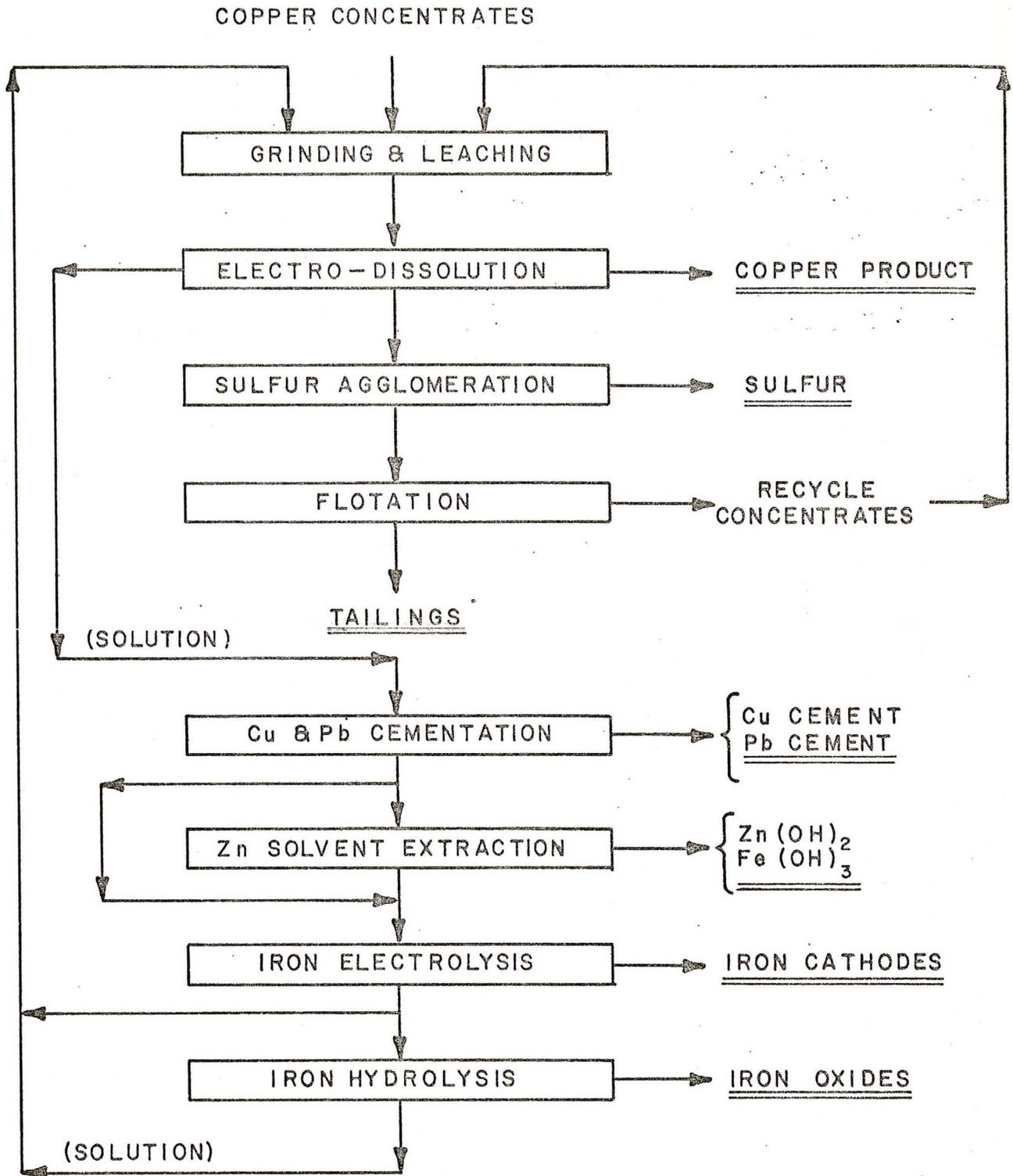


DIAGRAM OF CHALCOPYRITE PROCESS



represent about 85% of the elemental sulphur fed to the autoclaves. The beads are removed by screening. Melting and filtering the beds produces high purity bright yellow sulphur.

5. Flotation: The thickened autoclave discharge is diluted, conditioned with reagents, and rougher floated using standard chalcopryrite flotation conditions including one-stage cleaning for recycle to plant feed. The flotation concentrate contains about 18% Cu and about 5.6% elemental sulphur. The flotation tailings are the throw-away plant tailings.
  
5. Cathodic Precipitation of Copper: The first stage leach thickener overflow solution is clarified and sent to Cathode I where copper is electroprecipitated as copper powder. Cells II, in cascade with Cells I but at a lower current density, deplete the catholyte of copper to an acceptable residual concentration. The copper powder is thickened, filtered, washed, and dried and is then briquetted or melted and sent to electrorefining.
  
7. Solution Purification: The spent copper catholyte is further depleted in copper by cementation with metallic iron. The

solution is further purified by zinc cementation to remove residual traces of copper and to remove other impurities such as lead, antimony, bismuth, and arsenic. Zinc occurring in the feed and added for purification is removed by solvent extraction with a tertiary amine. The amine is stripped with an alkaline aqueous solution and zinc hydroxide is precipitated.

8. Iron Electrolysis: The purified ferrous chloride solution is sent to electrolytic iron cells which plate massive high purity iron on iron starter sheet cathodes, and ferric chloride is regenerated at the anodes. These cells operate at about 95% cathode efficiency. While in theory the iron electrolysis perfectly balances the copper circuit, in practice, provision is made to remove a small quantity of iron oxide by hydrolysis to balance the iron content in the circuit.

Slide V

Chalcopyrite Flowsheet  
Chemical Analysis of Feed and Products

Elements	Chalcopyrite Feed %	Tailings %	Copper Powder %	Refinery Anode Sludge, %	Sulphur Product %
Cu	27.1	0.8	90+	46	
S	32.1	20.0	0.35	0.48	99
Fe	27.5	19.0	1.1	0.75	
Zn	0.26	Trace	0.1	-	
Mo	0.22	0.56	-	-	
Pb	0.07	Trace	0.27	12.0	
Sb	0.04	Trace	0.01		
As	0.03	Trace	<0.005		
Bi	0.02	Trace	0.032		
Se	0.009	Trace	0.0007		0.03
Insoluble	12.24	60.1	-		
Ag	2.4 oz/ton	0.3 oz/ton	0.02	0.48	
Au	0.04 oz/ton	0.0 oz/ton	-		

Electrorefined Copper

Cu 99.95%  
Following Trace  
Elements Detected:

Al 20 ppm  
Fe 20 ppm  
Mg 50 ppm  
Si 25 ppm  
Pb <10 ppm

Electrolytic Iron Product

Fe 99.5%  
Following Trace  
Elements Detected:

Cu 500 ppm    C 80 ppm  
S 3 ppm    H<sub>2</sub> 50 ppm  
Mo 30 ppm    N<sub>2</sub> 30 ppm  
Pb 100 ppm    Al 50 ppm  
O<sub>2</sub> 350 ppm    Ni 150 ppm  
P 20 ppm

Cu Recovery 99%  
Ag Recovery 97%  
Au Recovery 60%

Slide VI

Comparison of Estimated Production Costs

Scale: 80,000 Ton/year Cu (Wirebar Grade)

Location: Arizona (Power, \$.0105 per kwhr; Fuel, \$0.80 per 10<sup>6</sup> Btu)

	Cents per Pound Copper Recovered	
	<u>Smelter</u>	<u>Cymet</u>
Direct Operating Costs	10.103	9.568
Administrative and Indirect	0.781	1.019
Fixed Costs (Depreciation)	<u>2.733</u>	<u>2.022</u>
Total Operating Costs	13.617	12.609
Credits:		
Au, Ag, Pb, and Zn	0.790	0.790
S <sup>o</sup> and Fe	<u>0.535</u>	<u>4.361</u>
Total Credits	<u>1.325</u>	<u>5.151</u>
Conversion cost per lb of recovered Cu	<u>12.292</u>	<u>7.458</u>
Conversion cost per lb of contained Cu	12.939	7.590

Credits were estimated using the following sales price for by-product elements:

Au \$42 per troy oz.	Zn \$0.085 per lb.
Ag \$ 1.45 per troy oz.	Fe \$0.05 per lb.
Pb \$ 0.06 per lb	S (or S equivalent) \$10 per long ton

The economics of the Cymet process, compared to a conventional smelter with a sulphuric acid plant, are presented in Slide 6. As may be noted, Cymet economics before credits are comparable to those of a pollution equipped smelter. Including the credits for electrolytic iron at \$100 per ton, Cymet shows a substantial economic advantage.

A scale of 80,000 tons/year was chosen because engineering studies on both approaches were available at that scale. Because of return on investment versus capital considerations, pyrometallurgical copper smelters usually have a capacity of more than 150,000 tons of copper per year. Similarly, a Cymet plant would benefit economically by being larger; however, the process is less capital intensive and can be economic at a substantially smaller scale.

### Zinc-Lead Concentrates

The Cymet process also can be applied to the processing of zinc and lead concentrates. A number of laboratory studies have been made to demonstrate the application of the process to:

1. Lead concentrates (high silver)
2. Copper-zinc bulk concentrates
3. Zinc concentrates (with substantial lead and iron)
4. Lead concentrates (high zinc)
5. Zinc-lead bulk concentrates

Each concentrate, of course, requires flowsheet modifications to accommodate the particular values and impurities contained. The general approach, however, can be illustrated by the flowsheet developed for a zinc-lead bulk concentrate. Indeed, one of the potential advantages of the hydrometallurgical processing approach is that concentrates normally considered "off-grade" to a pyrometallurgical smelter can be easily accommodated.

Slide 7 presents the analysis of a bulk zinc-lead concentrate that has been studied extensively in the laboratory. As may be noted, the concentrate is of commercial quality but has a relatively high iron content of which about 70% is pyrrhotite and marmatitic sphalerite.

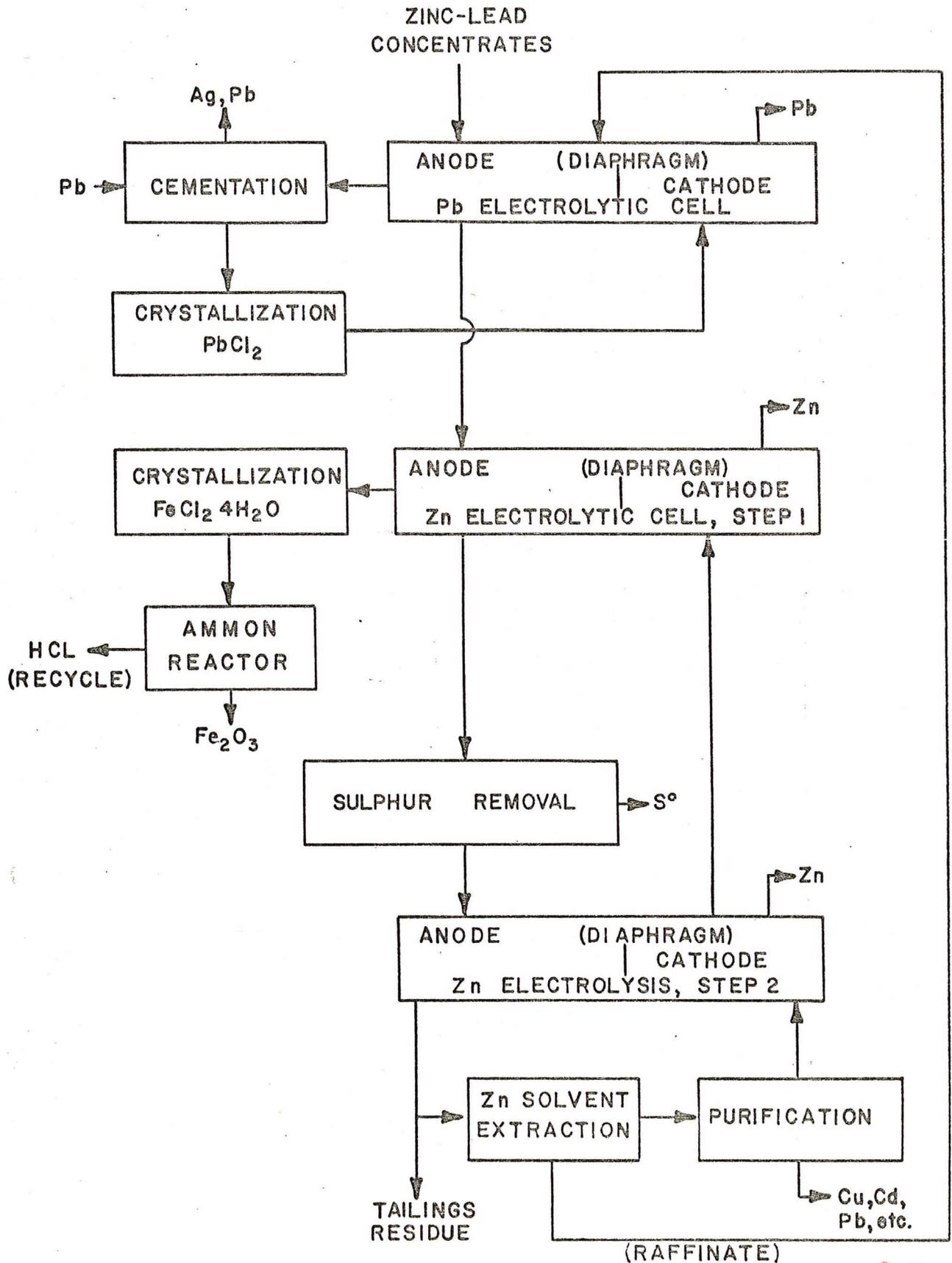
Slide 8 presents a conceptual flowsheet for the processing of this concentrate.

Slide VII

Galena-Sphalerite Bulk Concentrate  
(Typical Analysis)

Element	Percent
Zn	34.8
Pb	19.3
Fe	12.6
Cu	0.30
S	29.45
Insoluble	3.53
Ag	5.8 oz/ton

GALENA SPHALERITE BULK CONCENTRATE  
CONCEPTUAL FLOWSHEET



B6

1. Lead Cells: Ferric chloride from zinc chloride purification is recycled and selectively attacks galena in the concentrate. The attack is continued at the anode of the lead cells. The lead is substantially all dissolved together with about 22% of the zinc, 50% of the iron, and about 90% of the silver. After solid-liquid separation, the anolyte is purified by removing silver using lead for silver cementation, cooled, and lead chloride crystals removed. These crystals are redissolved in catholyte. Lead is plated on lead starter sheets in the cathode compartments. The lead chloride crystals are quite pure and the purity of the cathode lead is maintained by using an ion exchange membrane to isolate the cathode and anode compartments. Spent catholyte is bled for continuous purification and returned to the system. Cathode efficiency usually approximates 90%.

2. First Zinc Cells: The lead depleted concentrate solids are transferred to the first zinc cells where dissolution continues. An additional 67% of the zinc and 18% of the iron are dissolved. The solution is saturated with respect to ferrous chloride and by evaporative cooling, ferrous chloride tetrahydrate crystals are removed. These are burned with air and water to produce iron oxide and hydrochloric acid for recycling.

3. Sulfur Removal: Solids from the first zinc anodes are filtered and washed and sent to autoclave for sulfur removal and recovery. The dry solids assay about 50% sulfur, by weight. The autoclaves produce sulfur beads which are screened off, melted, and filtered to form bright sulfur product. About 85% of the total sulfur is recovered.

4. Stage II Zinc Cells: In these remaining cells, zinc is dissolved and ferrous chloride is oxidized to ferric chloride. The residual solids, representing about 18% of incoming feed weight, are filtered, washed, and discarded as tailings.

5. Purification: The zinc chloride anolyte is sent to purification which consists first of removal of ferric chloride using tributylphosphate reagent in solvent extraction. In order to assure complete iron removal, some zinc is coextracted and recycled back to the head of the processing. The iron free solution is further purified by zinc dust cementation of copper, lead, cadmium, etc., and subsequently sent to the zinc cathodes for electroplating of zinc on aluminum starting sheets. Catholyte recycles through the purification system to maintain its purity for electroplating. About 90% cathode current efficiency has been obtained.

Slide 9 presents preliminary or "ball park" economics for the processing of the zinc-lead concentrate described. It should be emphasized

that the figures shown are not supported to date by either pilot plant operation or by engineering estimates, and should therefore be considered only as an order-of-magnitude approximation.

The Cymet process offers the advantage of higher yield, particularly on zinc, when compared to conventional processing. Costs of processing are comparable if a reasonable return on investment were included in Cymet costs. As an approximation then, one can state that the Cymet process appears to be at least competitive in economics, and because of higher yield, may be advantageous when compared to the conventional processing of zinc-lead concentrates.

#### Conclusion

Hydrometallurgical processes have been developed for base metal sulphides. The advantages for the processes are:

1. Neither air nor water pollution problems are created.
2. The processes appear to be economically competitive.
3. Low grade and/or off-grade concentrates are amenable.
4. The final products are of high purity.

The processes will require additional development before achieving commercial recognition. The major step in this development, the operation of a demonstration production plant, is scheduled.

As in any new process, however, perhaps the greatest challenge is that of determining how it may be adapted to the industry it is designed

to serve. Perhaps, the greatest economic benefits will come, not from the processing of concentrates now well suited to existing conversion techniques but from the processing of those concentrates which are currently penalized or in which mines are forced into excessive yield losses in order to meet "smelter grades". We are actively seeking these opportunities.

Slide IX

Galena-Sphalerite Bulk Concentrate Economics  
Comparison of Estimated Net Profit

The following cost estimate is based on an operation treating 1,250 tons of concentrate per day with electric power cost of \$0.01 per kilowatt hour and fuel cost of \$0.80 per million Btu.

<u>Sales Value, \$/ton</u>	<u>Conventional Smelter</u>	<u>Cymet Refinery</u>
Zinc @ \$0.18	\$106.49	\$121.52
Lead @ \$0.145	50.37	55.12
Silver @ \$1.70	8.21	9.61
Copper @ \$0.40	<u>2.16</u>	<u>2.16</u>
	\$167.23	\$188.41
Less Freight	20.00	20.00
Smelter Conversion Charge or Cost	<u>58.00</u>	<u>43.31</u>
	\$ 78.00	\$ 63.31
Net Profit before Tax*	89.23	\$125.10

\* Does not include return on investment.