ALKALINE SULFIDE LEACH OF CINNABAR ORE
AND
ELECTROLYTIC DEPOSITION OF MERCURY
FROM THE LEACH SOLUTION

by

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TABLE OF CONTENTS

INDEX OF TABLES AND CURVES

ALKALINE SULFIDE LEACH OF CINNABAR ORE
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INTRODUCTION

In historical writings, dating back even before 400 B.C., the
element mercury is referred to as Hydrargyrum (liquid silver) or as
quicksilver. One of the earliest recorded reports of this element
was made by Aristotle, who called it fluidsilver. Other early authors
to mention mercury were Agricola in his "De Re Metallica" and Deoscor-
ides, who was the first to describe the distillation method for recov-
ery of mercury from cinnabar. Pliny and Theophrastus experimented
with this metal. In all the early alchemical writings the metal is
referred to by the symbol of the speedy messenger of the gods, the
caduceus or wand. Use of this symbol of Mercury the messenger (☿)
shows a recognition of the speed at which the metal vanished when
heated, and of its fluidity of motion when under stress.

Due to its physical and chemical properties the metalurgy of
mercury is much simpler than that of most metals. Thus, from the
days of Deoscorides to the present time, mercury has been obtained
from its ores by the vaporization and condensation method. The very
simplicity of its metalurgy has caused a lack of careful study into
the problems of the industry. In later years, however, there has

been a marked change in this attitude, and modern producers are keenly aware of the problems that face them.

In all industries the producer is chiefly interested in the most economical and most complete utilization of his raw materials. One of the big problems of the mercury producer is that of using low grade ores and getting almost complete removal of mercury contained in it.

Other problems face the prospector who is developing a newly discovered mercury mineral deposit or the owner of a small mercury mine. The cost of installation of a furnace for treatment is usually more than a new and unproved property can stand. It is, then, desirable to establish or develop new ways of mercury recovery from low grade ores or at a property that does not yet merit or afford an expensive furnace installation. The essential features of these new developments should be low initial cost of equipment, ease of installation, and simplicity of recovery of the mercury. The furnace plants are expensive and usually must be run several weeks in order to saturate them before metallic mercury can be obtained from the stills. The furnace must be run 24 hours per day with labor on a 3-4 shift basis. Small mines, with no proven reserves, need some less costly method of recovering the mercury, so that with a smaller capital outlay they can be placed on a paying basis.

Numerous schemes have been used to concentrate mercury ores; gravity concentration being the first one tried. Due to the high density of cinnabar, simple devices readily produced high grade concentrates. With development of flotation methods, this principle has also been applied. Flotation methods also produced high grade concentrates because the cinnabar responds readily to flotation

reagents. Both of these fundamental methods, while successful as a means of producing a concentrate, have the handicap of producing a very finely divided concentrate which can not be readily handled in the stills and furnaces.

In   In order to get away from these difficulties in treatment, leaching methods have been suggested. Leaching of ores to extract the desired metal content is not new; the cyanide leaching of gold ores is one of the most widely used leaching processes. Technique developed in gold cyaniding might be applied to more ores.

Various types of leach solutions have been tried experimentally on mercury ores. Among the methods discovered by Schnable and Louis (3) is that devised by Sieveking (5,6) which involves treatment with cuprous chloride in the presence of an alloy of copper and zinc. The reaction which takes place is

$$Cu_2Cl_2 \neq HgS = CuCl_2 \neq CuS \neq Hg$$
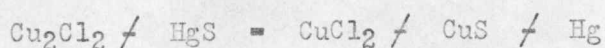
The mercury amalgamates with the alloy and is later distilled. The chemistry of this method seems vague since cuprous chloride is water insdlulbe. It also seems to be an indirect method since retorting of the mass for mercury recovery is required anyway. The method proposed by R. Wagner (8) uses as the leaching agent, solutions of concentrated Hydrochloric acid and Bromine water to obtain the mercury as a soluble halide. A third method that is mentioned by Schnable and Louis (3) uses alkali sulfide solutions for the leaching agent.

The solubility of mercuric sulfide in alkali sulfide solutions has been known for more than a century. In 1799 Kirchoff (2) described a wet method for the preparation of vermillion which was based on this fact. Several of the classical methods for the quantitative estimation

of mercury depend upon the separation of mercury sulfide from other
group II sulfides by its solution in a solvent of sodium sulfide.
The solubility is due to the formation of soluble complex double salts;
much in the same way soluble gold cyanide complex is formed. Ground
red cinnabar or pure black mercury powder when dissolved with sodium
sulfide yields a water clear solution.

The reactions which take place are as follows:

$$Na_2S \, + \, HgS = HgS:Na_2S$$
$$2 \, Na \, S \, + \, HgS = HgS:2Na_2S$$
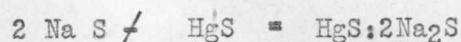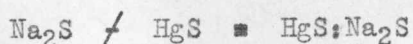
The two complex salts are soluble and stable in the presence of al-
kali, but in acid solutions are decomposed giving insoluble mercuric
sulfide. It is necessary, therefore, that the leaching solutions
have an excess of free alkali present at all times.

In 1917-1918 Walter W. Bradley (1) of the "State Mining Bureau
of California" experimented with California cinnabar ores using an
alkali sulfide leach. In his work he found that ocher and other iron
compounds caused trouble in the leaching process by using up sulfide
in forming colloidal suspensions of iron sulfide. In ores containing
little iron this problem is not important.

The recovery of the mercury from the leach solutions is another
problem which needs considerable study. The mercuric sulfide can be
precipitated by lowering the pH of the solution, but once again a
high grade concentrate is obtained. However, such a concentrate
could be placed in a retort and the mercury distilled therefrom. Such
treatment with strong acid would entail complete loss of the leach
chemicals and hence might not be practical.

One method proposed and patented for lowering the pH of the sulfide leach liquors uses sulfur dioxide gas. The gas is forced through the solution forming sulfurous acid and thus neutralizing the excess base by formation of Na_2SO_3. This causes the mercuric sulfide to be precipitated from solution, and it is separated by filtration for further treatment.

A method of mercury recovery from sulfide solutions with a partial regeneration of the chemicals has been used at the Buffalo Mines, Cobalt Ontario, and described by Thornhill (7) in 1915. The process developed for the precipitation of mercury from the caustic alkaline sulfide solutions consisted of treatment with metallic aluminum. The equations for the precipitation and regeneration are:

$$3\ HgS \cdot Na_2S\ +\ 8\ NaOH\ +\ 2\ Al\ =\ 3\ Hg\ +\ 6\ Na_2S\ +\ NaAlO_2 +\ 4\ H_2O$$
$$Ca(OH)_2\ +\ 2\ NaAlO_2\ =\ 2\ NaOH\ +\ Ca(AlO_2)_2$$
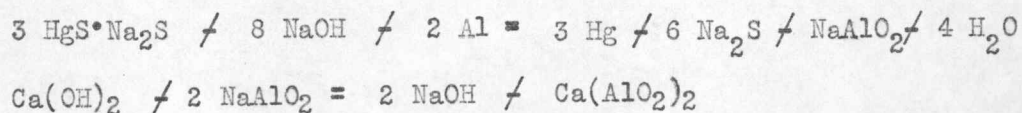
This process will regenerate the sodium sulfide but part of the alkali must be replaced. The use of aluminum is also apt to be expensive. However, scrap metal and turnings are comparatively inexpensive and can be employed. In the west, a long way from the source of the cheap waste metal, its cost might be excessive. Other metals have been suggested as replacement for aluminum in this process, among these mentioned are chromium and zinc. The use of these metals would also be expensive and it is probable that cheaper methods of recovery are possible.

The electrodeposition of mercury from the leach solution has also been proposed but as yet very little work has been done on this phase of the problem. Schnable and Louis (4) in their handbook sug-

gest such treatment. The fact that such solutions can be electrolyzed is well known, and a number of quantitative methods for estimation of mercury use deposition of the mercury electrolytically on platinum cathodes.

Recovery of the mercury with simultaneous regeneration of the chemicals is the ideal of any recovery process.

This research work has been directed toward adapting the sulfide leach method to Oregon cinnabar ores and the recovery of the mercury from the leach solution with concomitant regeneration of the chemicals used in the leach solutions.

EXPERIMENTAL LEACHING OF CINNABAR ORES

In any leaching process the effectiveness depends upon contact between the solution and the material to be extracted. In large particles there is always the possibility that isolated pockets of the desired material are surrounded by the country rock. Such pockets are rarely reached by the chemical solutions, since diffusion of the liquor throughout the rock particle is extremely slow. Such penetration that does take place is along the small cracks or planes of weakness that have been filled with the mineral.

Crushing and grinding the ore in preparation for leaching is apt to be expensive, especially when the ore has to be ground to a very fine powder. Therefore, the first problem studied was that dealing with the fineness of particle size required for adequate extraction of the mercury sulfide.

A fifty pound sample of cinnabar ore was prepared for use in the leaching experiments by crushing and rolling to pass all particles through a four mesh screen. The material was then well mixed and quartered. One quarter was selected for further work. This sample was screened and separated into three different fractions; plus ten mesh, minus ten mesh, plus twenty mesh, and minus twenty mesh. The three fractions and the feed ore were analysed for mercury content.

The ore was analysed by the Whitton (9) method which depends upon the conversion of mercuric sulfide to mercury in the presence of iron powder. The reaction upon which this method is based is:

$$HgS + Fe + heat = Hg + FeS$$
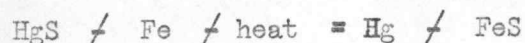
The mercury vapor is caught on a water cooled silver plate. The increase in weight of the silver plate gives the weight of mercury vaporized from the ore sample.

The analyses of feed rock and the three fractions obtained on screening are given in the table below. In this table is also included a column showing the weight percent of each of the three fractions.

Table I

	% Hg	Weight percent of each fraction
Feed	1.96	100.
plus 10 mesh	1.62	38.5
minus 10 plus 20	1.67	23.8
minus 20 mesh	2.65	37.7

The above table shows that the cinnabar is more concentrated in the fines produced by crushing than in the original ore. This would tend to indicate that the cinnabar is more friable than the gangue rock, thus more readily pulverized, and the breaking occurs along the planes of deposition. Since deposition of mineral usually takes place in cracks and pockets of the country rock as mineral bearing waters seep through, leach solutions should in this case more readily penetrate the rock and extract the values. To test this theory, leaching experiments were tried on particles usually considered too coarse for leaching purposes.

In these studies the leaching efficiendy was calculated by the amount of HgS extracted from the ore. The amount extracted was found by either of two methods, by analysis of the leached ore residue or analysis of the leach solution. The ore residue was analysed by the Whitton (9) method while the solutions were analysed by precipitating

the mercuric sulfide from the solution by addition of Hydrochloric acid. The metal sulfide usually was contaminated with sulfur which was extracted with carbon disulfide. The purified precipitate was dried and weighed in a previously prepared Gooch crucible.

A. Particle Size and Leaching Efficiency

Leaching experiments were started with the material of plus ten mesh material. Ore particles of this size can be leached and a reasonable amount of extraction obtained in one hour. The initial rapid rate of extraction is probably due to solution of the surface material. The slowly increasing percent extraction, which is still increasing after one hour, indicates that the more remote particles are being reached. It is apparent from these experiments that a longer period of time is required for material of this size. This is not altogether disadvantageous since a batch of material could be started and left to set over night. See Table II and figure I for summarized results of these runs.

The material of minus ten - plus twenty mesh material was treated in the same manner. The results on this material were not as satisfactory as with the coarser material. In most all cases curves showing the amount of mercuric sulfide extracted have flattened out and in some even have dropped off with less extracted in one hour than in thirty minutes. There seems to be no ready explanation of this fact. Table III and Curve II summarize these experiments.

The ore of minus twenty mesh particle size most readily leached. The initial rate of extraction is quite rapid. This is probably due to ready solution of surface material and very small particles of

Table II

Extraction Results on Plus Ten Mesh Ore

No.	Wt. gms.	Pulp ratio	% Na$_2$S	Time	% ext. Calc. from sol.
1	100	1:1	1%	15 min.	4.4 %
2	"	"	2%	"	6.5 %
3	"	"	3%	"	8.2 %
4	"	"	4%	"	10.68%
5	"	"	5%	"	12.85%
6	"	"	6%	"	13.00%
7	100	1:1	1%	30 min.	3.82%
8	"	"	2%	"	5.37%
9	"	"	3%	"	9.04%
10	"	"	4%	"	10.84%
11	"	"	5%	"	13.02%
12	"	"	6%	"	15.75%
13	100	1:1	1%	60 min.	3.19%
14	"	"	2%	"	7.45%
15	"	"	3%	"	13.73%
16	"	"	4%	"	16.82%
17	"	"	5%	"	19.00%
18	"	"	6%	"	23.53%

Curve I

Graphical Summarization of Extraction Results

using plus 10 mesh ore

percent HgS extracted

20

10

6% Na$_2$S
5% Na$_2$S
4% Na$_2$S
3% Na$_2$S
2% Na$_2$S
1% Na$_2$S

0   10   20   30   40   50   60

Time Minutes
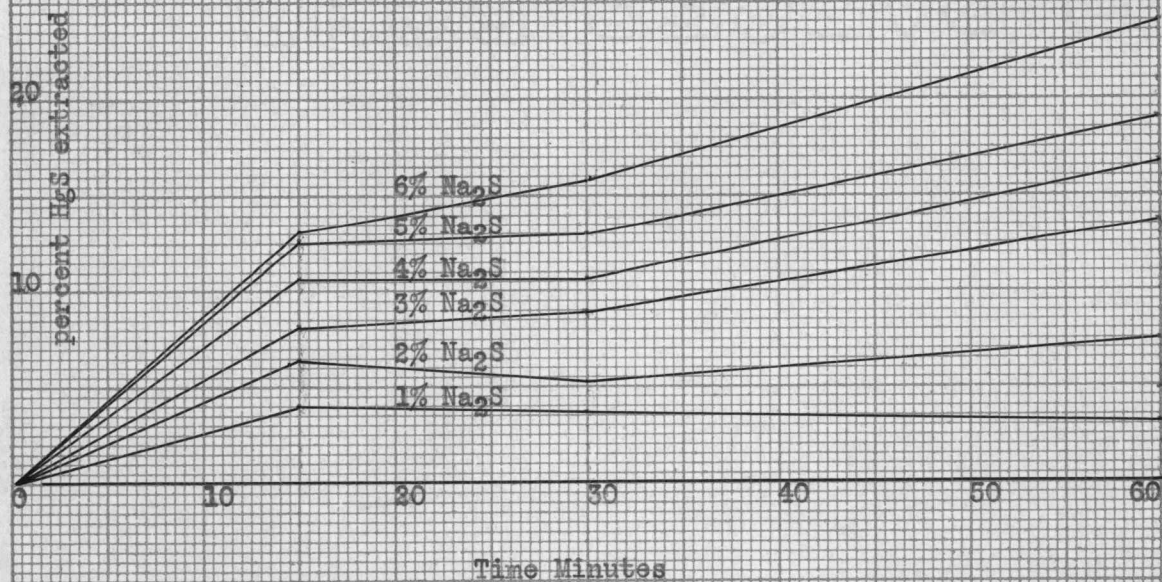
Table III

Extraction Results on Minus 10 Plus 20 Mesh Ore

No.	Wt. gms.	Pulp ratio	% Na$_2$S	Time	% ext. Calc. from sol.
1	50	1:1	1%	15 min.	5.58%
2	"	"	2%	"	10.74%
3	"	"	3%	"	10.33%
4	"	"	4%	"	12.70%
5	"	"	5%	"	15.34%
6	"	"	6%	"	19.20%
7	50	1:1	1%	30 min.	6.17%
8	"	"	2%	"	9.58%
9	"	"	3%	"	11.50%
10	"	"	4%	"	16.61%
11	"	"	5%	"	18.20%
12	"	"	6%	"	22.89%
13	50	1:1	1%	60 min.	3.62%
14	"	"	2%	"	6.81%
15	"	"	3%	"	10.22%
16	"	"	4%	"	14.26%
17	"	"	5%	"	18.01%
18	"	"	6%	"	23.95%

Curve II

Graphical Summarisation of Extraction Results

using minus 10 plus 20 mesh ore

6% Na₂S
5% Na₂S
4% Na₂S
3% Na₂S
2% Na₂S
1% Na₂S

percent HgS extracted

Time Minutes
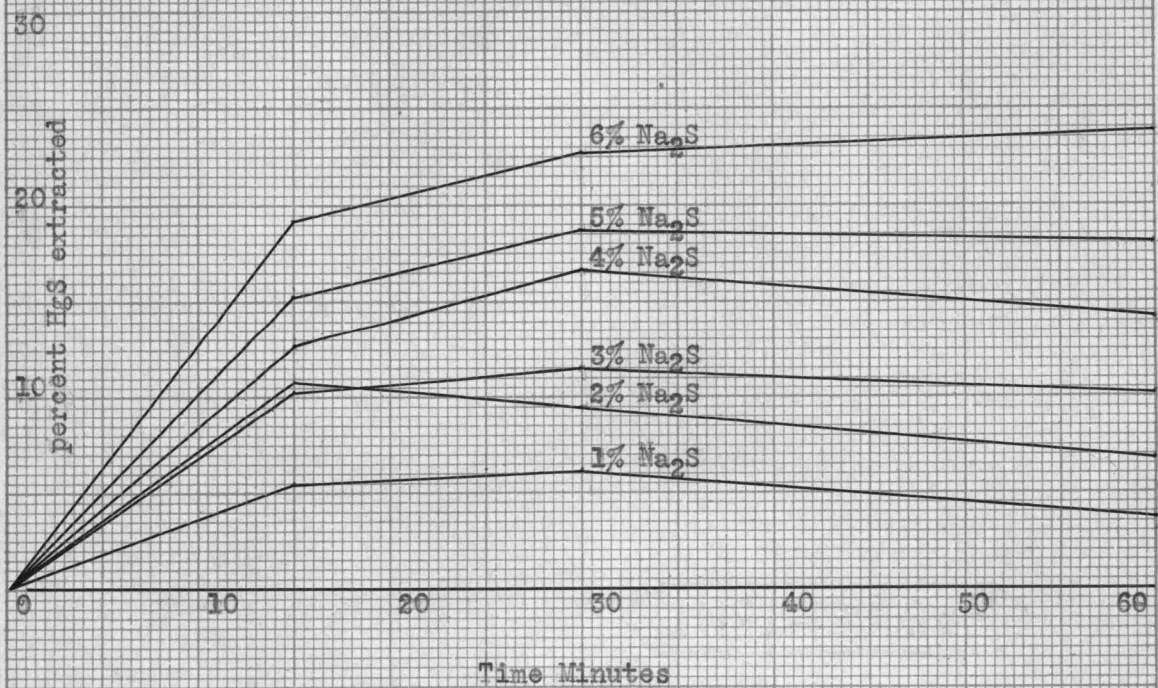
Table IV

Extraction Results on Minus 20 Mesh Ore

No.	Wt. gms.	Pulp ratio	% Na_2S	Time	% ext. Calc. from sol.
1	50	1:2	1%	15 min.	7.94%
2	"	"	2%	"	8.66%
3	"	"	3%	"	11.24%
4	"	"	4%	"	18.35%
5	"	"	5%	"	19.00%
6	"	"	6%	"	27.66%
7	50	1:2	1%	30 min.	6.37%
8	"	"	2%	"	10.02%
9	"	"	3%	"	16.01%
10	"	"	4%	"	20.57%
11	"	"	5%	"	27.20%
12	"	"	6%	"	32.92%
13	50	1:2	1%	60 min.	14.96%
14	"	"	2%	"	39.04%
15	"	"	3%	"	59.22%
16	"	"	4%	"	74.05%
17	"	"	5%	"	89.40%
18	"	"	6%	"	99.69%

Curve III

Graphical Summarization of Extraction Results

using minus 20 mesh ore

percent HgS extracted

100
90
80
70
60
50
40
30
20
10

6% Na₂S
5% Na₂S
4% Na₂S
3% Na₂S
2% Na₂S
1% Na₂S

0   10   20   30   40   50   60

Time Minutes
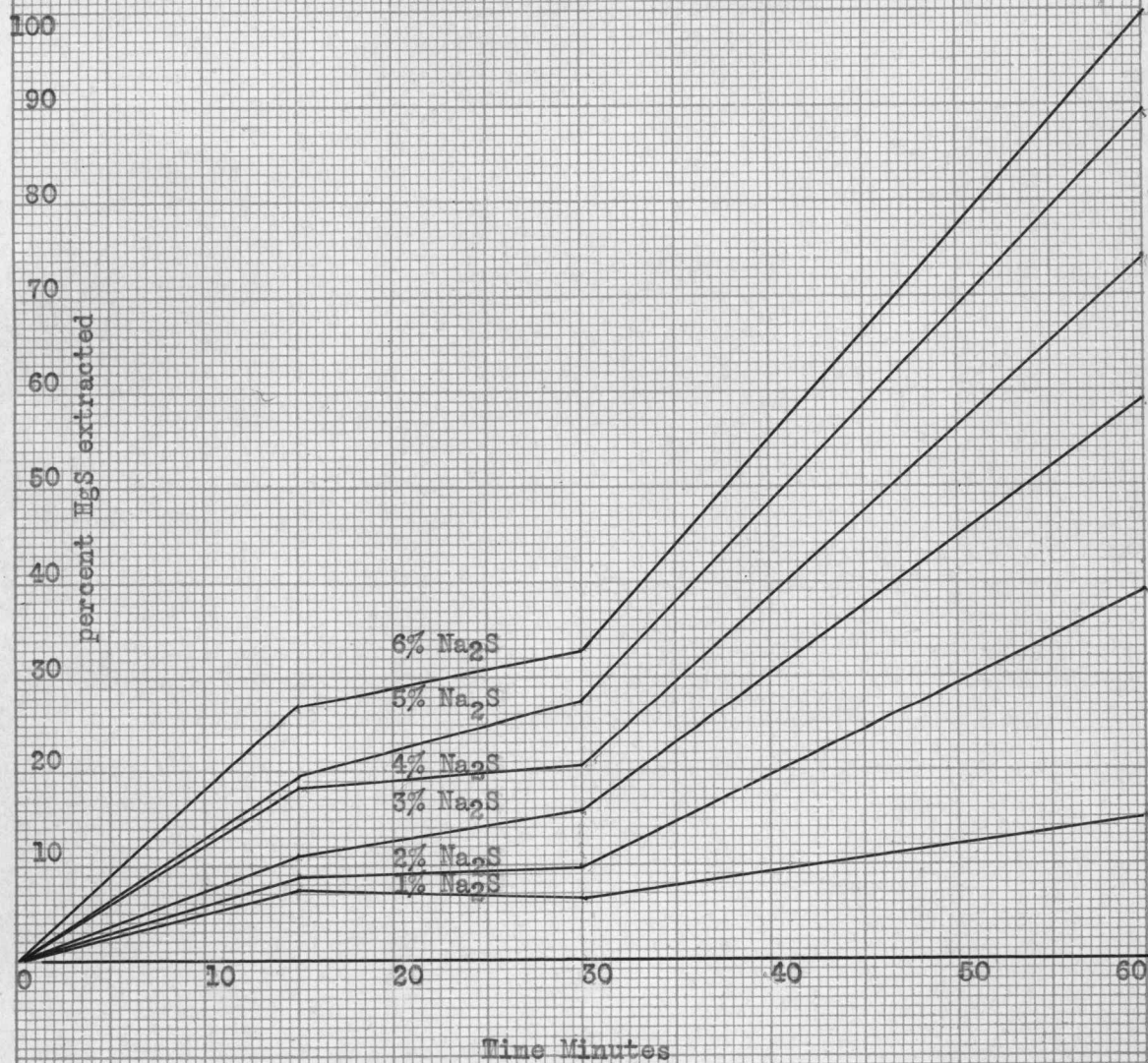
Table V

Extraction Results on Minus 20 Mesh Ore

No.	Wt. gms.	Pulp ratio	% Na$_2$S	Time hours	% Ext.
1	50	1:1	2%	2	26.41%
2	"	1:2	2%	2	61.73%
3	"	1:1	2%	3	28.98%
4	"	1:2	2%	3	64.62%
5	"	1:1	2%	5	32.01%
6	"	1:2	2%	5	63.56%
7	"	1:1	2%	6	33.28%
8	"	1:2	2%	6	66.13%
9	50	1:1	3%	2	52.29%
10	"	1:2	3%	2	99.88%
11	"	1:1	3%	4	51.10%
12	"	1:2	3%	4	99.70%
13*	50	1:1	2%	21	21.22%
14*	"	1:2	2%	21	51.63%
15*	"	1:1	3%	21	44.67%
16*	"	1:2	3%	21	83.82%

* not agitated while being leached.

cinnabar. The curves show a lower rate of solution in the second fifteen minutes. This dropping off is probably due to the fact that the easily soluble material has been removed and the material less readily accessible has not yet been extracted. The sharp increase in the amount of dissolved cinnabar in the leach solutions after the fifteen minute period is probably due to the diffusion of the liquor into the small cracks and pores of the rock. Material of this smaller size also has a greater proportion of surface than the larger pieces; thus the cinnabar is more apt to be exposed on the surface of the particles and diffusion of solvent into cracks is not such an important factor.

From these studies it is apparent that the rate of extraction is dependent upon the size of the ore particles being treated. If time is an important factor it is evident that small size particles should be treated. If time is not so important larger sized material can be used. Refer to Table IV and Curve III for results of these runs.

B. Strength of Leach Solutions and Leaching Efficiency.

The cost of chemicals used in a leaching treatment of ore is one of the more important of the expense items. In order to compare the relative leaching ability of solutions of different strength a series of runs was made using solutions with varying sodium sulfide content.

The leach solutions were made up from a ten percent stock solution of $Na_2S \cdot 9 H_2O$. This solution was diluted to the desired concentration for the leach trials. Alkali was introduced by addition of sodium hydroxide solution. The leach solutions were made to contain

from one to six percent sodium sulfide and one percent sodium hydroxide.

Weighed samples of ore for leaching were placed in beakers and a measured volume of leach solution was added. During the leaching period the samples were agitated by a stirring device. The liquid was removed by filtration and the residue well washed. The filtrate was made up to a definite volume and analysed for mercury content.

In most cases the percent efficiency of mercury extraction was calculated from the amount of mercuric sulfide contained in the leach solution. The percent extraction can also be determined by analysis of the residues. This method requires more attention than does analysis of the solution so was not used as much as the first method. However, it was necessary to make some comparative analyses to see if analysis of the solution gave a true measure of the percent mercury sulfide extracted from the ore. When percent extraction was calculated from solution analyses and compared to percent extraction calculated from residue analyses, close agreement was found.

From these studies it is quite noticeable that the more concentrated solutions dissolve the cinnabar more rapidly than the weaker solutions. This is, of course, to be expected since the speed of a reaction, or the completeness of a chemical reaction, is dependant upon concentration of substances involved. A six percent sodium sulfide will extract practically all of the cinnabar in minus twenty mesh ore in about half the time required for complete extraction by means of three percent sodium sulfide solution.

C. Discussion of Leaching Results

All three factors, size of particle, concentration of solution and contact time, influence the leaching efficiency of the leach solutions. It seems that for each particle size and each leach solution a certain minimum time is required for extraction of the cinnabar. The time of contact allowed depends, therefore, upon the solving of a problem of economic balances.

Because of the fact that time may be less costly than chemicals, it seems that the most economical solution of the problem would be the use of the most dilute leach solution which gives efficient extraction in a reasonable length of time.

From the data obtained from these experiments it seems that the minimum concentration of sodium sulfide is about three percent if a 1:2 pulp ratio is used. The two percent solutions, when used seem to reach a saturation point and even with considerable length of time dissolve only about sixty six percent of the mercury present in the minus twenty mesh material.

A calculation of the stochiometric requirements based on the equation $HgS \neq 2 Na_2S = 2 Na_2S:HgS$ gives the following results; 2.65 grams of mercury present as mercury sulfide requires 2.061 grams of sodium sulfide to form the soluble complex. Thus with a 1:1 pulp ratio complete extraction is theoretically impossible if the above equation is correct. Inasmuch as an excess of Na_2S should be present the three percent solution seems best. With ores containing a lower percent mercury more dilute leach solutions can be used.

Agitation of the solution has quite a marked effect upon the speed of extraction. The last four runs listed in table V show this to a startling degree. These runs are comparable to the other runs listed in the table with the exception that they were not stirred during the leaching period. In 21 hours the percent extraction is less than in 2 hours when the solutions were stirred. The most reasonable explanation is that some of the liquor becomes saturated with cinnabar and stagnates, thus preventing unsaturated liquor from contacting and diffusing throughout the ore particles.

D. Leaching in Ball Mill

It is common metallurgical practice to treat ores while being ground in a ball mill, either with a leach solution or with chemicals to condition the material for later steps in the recovery process. Runs were made to test the applicability of this kind of treatment to the problem being studied.

These runs were made by placing the ore in a pebble mill with leach solution and grinding in the sealed mill for the desired length of time. The material was removed from the mill and filtered. In all cases the period of contact was always longer than the grinding period by the length of time required for filtration. Since this period was about the same in all cases the results are comparable.

This method of treatment greatly speeded up the rate of solution of the mercuric sulfide. This is probably due not only to the effects of constant agitation but also to the exposure of fresh surface as the material is broken. The importance of agitation has already been demonstrated as illustrated by table V. The grinding in the ball mill

also develops new surfaces by reducing the size of particles, thus the diffusion of solution is not so important as in the larger pieces of ore. Table VI compares results of leaching with stirring and leaching during ball mill grinding.

This series of runs indicates that grinding while leaching markedly increases the speed of solution and efficiency of extraction. Grinding and leaching trials suggest that more dilute solutions can be used to get a high degree of extraction in short periods of time. In cases where the time is important this treatment can readily be applied. In those plants where time is not so vital, but cost of machinery is a definite factor, ore can be leached even if the rock is of considerable size.

In many cases this flexibility of treatment is very desireable. One disadvantage of the furnace treatment is the fact that continuous operation is necessary. This means that three or four complete shifts of workers are required to operate the plant. With the more flexible leaching process, a batch of material can be set and left for any desireable period of time with only a minimum of supervision.
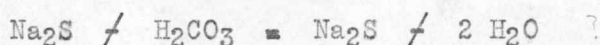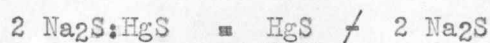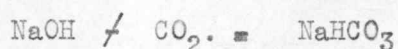
Table VI

| % Na$_2$S	Time hours	Leach & Stirring % ext.	Grind & Leach % ext.
1%	.5	6.35%	30.25%
2%	.5	10.02%	36.10%
3%	.5	16.01%	50.24%
4%	.5	20.57%	69.07%
5%	.5	27.20%	92.53%
6%	.5	32.92%	99.9 %
1%	1.0	14.96%	50.05%
2%	1.0	39.04%	60.21%
3%	1.0	59.22%	82.81%
4%	1.0	74.05%	90.98%
5%	1.0	89.39%	99.9 %
6%	1.0	99.69%	----

RECOVERY OF MERCURY FROM LEACH SOLUTIONS

A. Precipitation of Mercuric Sulfide by means of CO_2.

The second phase of this research problem dealt with the recovery of mercury from the leach solutions. The use of strong acids for lowering pH of the leach solutions causes almost complete loss of the leach chemicals. Weaker acids may be used with less loss of chemicals and greater recovery possibilities. Since sulfur dioxide has been used for this purpose it seemed possible that CO_2 could also serve as precipitating reagent. The reactions taking place are

$$NaOH + CO_2. = NaHCO_3$$

$$2\ NaOH + CO_2 = Na_2CO_3 + H_2O$$

$$2\ Na_2S:HgS = \underline{HgS} + 2\ Na_2S$$

$$Na_2S + H_2CO_3 = Na_2S + 2\ H_2O\quad ?$$

The precipitated mercuric sulfide can then be removed by filtration and the NaOH or Na_2S regenerated by addition of lime

$$Na_2CO_3 + CaO + H_2O = 2\ NaOH + \underline{CaCO_3}$$

$$2\ NaOH + H_2S = Na_2S + 2\ H_2O$$
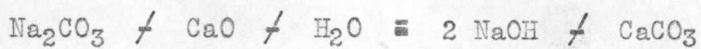
Calcium carbonate is removed by filtration and then the leach solution is ready for reuse. Carbon dioxide could be supplied from flue gas which contains CO_2 in moderate concentrations.

This method of precipitation was tested and will cause precipitation of mercuric sulfide. The precipitation is not complete at ordinary pressures because the carbon dioxide is not sufficiently soluble to lower the pH below 7. The sodium carbonate or bicarbonate

have considerable buffer action and thus maintain a basic solution.
Increasing pressure on the system causes more complete precipitation.

This method also has the disadvantage of producing an almost
colloidal precipitate of mercuric sulfide that is hard to catch on a
filter and needs to be retorted for the final step in mercury recovery.

B. Electrolytic Deposition

The disadvantages of the carbon dioxide precipitation method suggested that other methods of mercury recovery might well be tried.

In several analytical methods mercury is deposited on platinum
cathodes from alkali sulfide solutions. This electrolytic deposition
seemed at once to be the most desireable recovery process. The use
of precious metal electrodes, however, should not be necessary for a
successful commercial method. Mercury cathodes have been used in
other electrolytic depositions so it was decided to try such a setup.

The high hydrogen overvoltage of a mercury cathode enables sodium to be deposited. The formation of sodium amalgams would in this
case be undesireable. It was necessary therefore to run the decomposition potential of several solutions to determine if mercury deposited before the sodium. The curves obtained showed two rather
distinct breaks. The first break was at about 2 volts with the
amperage at one tenth. This break indicated the deposition of mercury. The second break was at about 4 volts and one ampere, indicating the deposition of sodium.

Some sodium can be deposited at lower potentials as indicated
by the behavior of the cathode surface. If the voltage was raised

Decomposition Curve
of
$2Na_2S:HgS$ Solutions

Amps

3.5
3.0
2.5
2.0
1.5
1.0
.5

0   1   2   3   4   5   6   7   8
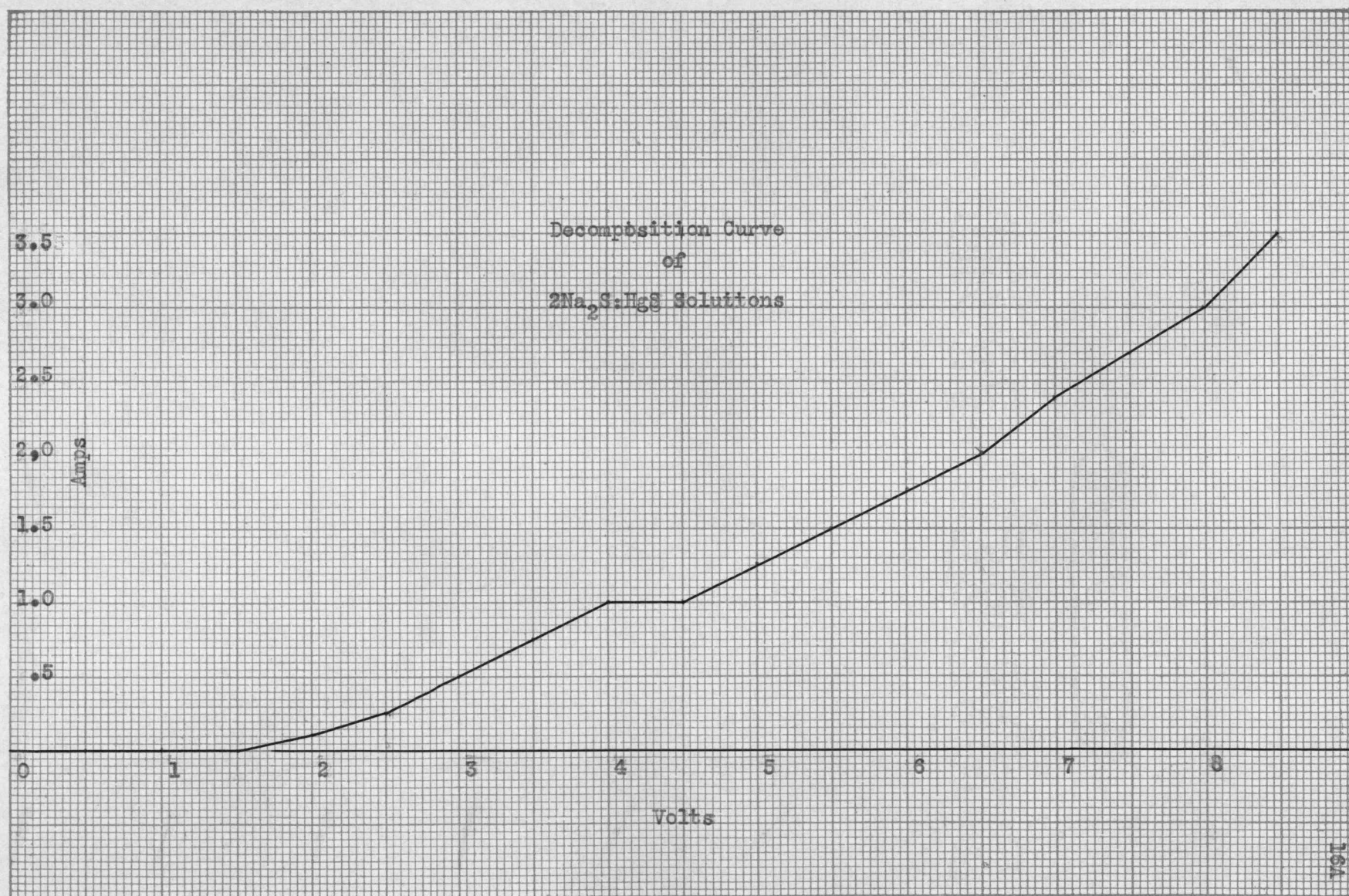
Volts

above three volts and the amperage more than .75, gas bubbles were discharged from the mercury surface. That this gas probably resulted from reaction of sodium amalgam with water seemed evident since gas continued to be evolved even after the current was shut off. This means then that conditions for deposition of mercury alone must fall within rather narrow limits.

To determine conditions of most efficient deposition, current efficiency was determined using several different potentials.

The efficiency at 2 volts and .15 amps was 51.8%. At 2.5 volts and .25 amps the efficiency was 71.3%. At 3 volts and .75 amps the efficiency was 40.1%. The equipment used in the experiments did not allow the amperage to be increased without increasing the voltage. It may be therefore that even more efficient conditions can be had if voltage is kept down and amperage is increased.

The current efficiency was calculated from analysis of the solutions for mercury content as has previously been discussed. The decrease in mercury content of the solution gave the weight of mercury deposited in the given length of time. These efficiencies are only approximate since the amount of current was determined only by maintaining the same voltage and amperage, as close as possible, during the test period. Some fluctuations in the current were unavoidable. For more correct results a coulometer should be included in the electrical circuit.

C. Regeneration of Chemicals During Electrodeposition.

Because the chemicals used in the leaching process do cost money, it is desireable to regenerate as much of the chemicals as possible

during or after the recovery of the mercury. In order for the electro-
lytic deposition method to be a commercial success this regeneration
must be accomplished. Although the anode and cathode reactions are not
definitely known it is possible to experimentally determine the reuse
value of the spent electrolyte and determine its leaching efficiency.

Runs were made using and reusing spent electrolyte to determine
its efficiency as a solvent for mercuric sulfide. The original sol-
utions were three and six percent sodium sulfide. These solutions were
used to leach an ore sample, and then the mercury deposited by means
of electric current. The spent electrolyte was then used for a second
extraction. This process was repeated with each solution five times
and the leaching efficiency calculated from the mercury sulfide dis-
solved by the solution during each leach period. The sodium sulfide
content was evaluated by titration with zinc chloride. This gave an
approximation of the sulfide content of the solution as it was put on
the ore to be leached. Table VII gives results of these runs.

The loss of leaching efficiency is due to the loss of free avail-
able sodium sulfide. The loss of sulfide is due to deposition of some
material on the anode as free sulfur and probably due to conversion of
some material to partially oxidized sulfur compounds. Some compounds
of this nature must be formed since no gas is observed at the anode
and the fresh solution from electrolytic cell reacted with iodine sol-
utions. These oxy-compounds are apparently unstable for in a few hours
the spent electrolyte no longer reacts with dilute iodine solutions.

From these experiments it is seen that mercury can be deposited
electrolytically from the leach solutions and that by this process the

Table VII

Table Showing Loss of Na_2S and Leaching Efficiency of Reused Electrolyte

Current used 2.5 volts .25 amps.

Run No.	Time-hrs.	wt. ore -gms.	% HgS ext.	% eff.	Approx % Na_2S
1	1	250	99.9 %	100. %	6 %
2	1	250	90.32%	90.41%	4 %
3	1	250	84.44%	84.52%	3.5%
4	1	250	64.92%	64.98%	2.5%
5	1	250	58.10%	58.15%	2.0%
1	2	50	99.88%	100. %	3 %
2	2	50	91.04%	91.14%	2.6%
3	2	50	79.35%	79.44%	2.0%
4	2	50	58.17%	58.23%	1.0%
5	2	50	35.61%	35.65%	0.5%

loss of free sulfide is not excessive. Replacement of lost sodium sulfide after each deposition of mercury will maintain efficiency of the leach solutions.

ECONOMIC ASPECTS

A. Cost of Replacement Chemicals.

In order for a new process to replace an established method of
treatment, the new method must be able to copete with the old one
on a favorable cost basis. Enough data has been collected in this
work to enable an approximate cost analysis to be made. It must be
understood, however, that the costs of chemicals will vary with the
ore being treated. A high grade ore will require more sodium sulfide
than a low grade ore, because an excess of sodium sulfide over the
stochiometric minimum required must be present in the leach solutions.

The fact that most of the chemicals can be regenerated means
that replacement costs are the chief costs.

The cost analysis made here is based on an ore containing about
forty pounds mercury per ton of ore.

The data on regeneration of chemicals indicates that about one
third of the sulfide is lost when using a six percent leach solution.
This means that the replacement of Na_2S would be 80 pounds per ton of
ore when a 1:2 pulp ratio is being used. At three cents a pound for
Na_2S this would be $2.40 per ton of ore. If the ore contains 40
pounds of mercury per ton the cost reduces to six cents per pound of
mercury extracted. This cost is probably more than most ores can
stand and still compete with the furnace recovery process where heating
cost is usually under one dollar per ton or on a 40 pound ore less
than 2.5 cents per pound of mercury recovered.

The data shows however that efficient extraction may be had using

a three percent leach solution in a 1:2 pulp ratio. The loss of sulfide for such a solution was found to be about sixteen pounds per ton of ore. The cost of replacement in this case comes to 48 cents per ton of ore leached, or on a 40 pound ore is 1.2 cents per pound of mercury extracted. Since a three percent solution can efficiently extract the cinnabar from ores containing up to and perhaps more than 50 pounds of mercury per ton, the more concentrated solutions need not be used for most mercury ores as few are as rich as this. This means, then, that a three percent solution is the maximum concentration needed for most cases and can compete with the furnace method in cost.

In addition to sodium sulfide some caustic soda must be added. The cost of NaOH is about 2.3 cents per pound, with a 1% caustic solution and assuming the same percentage loss of NaOH as Na_2S, the replacement cost would be about 12.5 cents per ton of ore. On the 40 pound per ton ore this would be about 0.3 cents per pound of mercury extracted.

The total replacement chemical cost, using a three percent Na_2S and 1% NaOH leach solution, would be therefore, 48 cents for Na_2S and 12.5 cents for NaOH and total 60.5 cents per ton of ore treated. On the basis of a 40 pound per ton ore it amounts to about 1.5 cents per pound of mercury extracted.

The cost of chemicals has been calculated from the losses found in very small scale operations. Expansion of operations to a full size plant may make it possible to affect even more complete recovery of the chemicals from the leach solutions. If more efficient operations follow expansion in this case, the new method will have an even more favorable cost balance in its favor.

B. Power Costs.

By experiment it was found that the most efficient deposition occurred with a current of 2.5 volts and .25 amperes. Under these conditions 16.66 grams of mercury will be deposited in one hour. From this data it is possible to calculate the weight of mercury deposited in one watt hour, or kilowatt hour, thus getting a measure of the power costs.

$E I$ = watts and watts = Joules/sec

then $E I T$ = Joules = Power if T = time in sec.

then 2.5 x .25 x 3600 = 2250 Joules for deposition of 16.66 grams of Hg in an hour. 1 watt hour = 3600 Joules, thus the weight of mercury deposited in 1 watt hour is $\dfrac{3600}{2250}$ x 16.66 = 26.656 grams.

Therefore, 1 kilowatt hour of power will deposit 26.656 kilograms or 58.776 pounds of mercury.

With a relatively high power cost of four cents per kilowatt hour this will reduce to a cost of about 0.07 cents per pound of mercury deposited. This is a high estimate of power cost since consumers of large amounts of power can obtain much lower rates.

The advent of power from Bonneville Dam and the low rates at which this power may be obtained should make such a recovery process even more economical.

C. Incidental Costs.

Some of the other factors less readily analysed as to cost should also be mentioned. This method eliminates the hazards of mercury vapor poisoning always present at a furnace for distillation of mercury from

the ore.

A furnace plant has considerable labor overhead since it must operate on a 24 hour schedule. The flexibility of the proposed method should make it possible to lower labor costs by arranging to leach at night, thus having a minimum of laborers to supervise operations.

Fines, which cause trouble in furnaces by creating serious dust problems in the stills, are most readily treated by a leaching treatment. As has been pointed out in Table I these fines produced by crushing are very apt to be richer in mercury than the original ore. Thus, a liability of the furnace method becomes an asset of the leach method.

Another factor which should be taken into consideration is the fact that furnaces must be operated for some time before mercury can be removed from the stills, since the plant must be saturated with mercury vapor. A plant using the leach method and electrolytic deposition method would not need to be saturated with mercury vapor and recovery would be had a short time after operation begins.

From this brief analysis it seems that this method of extraction and recovery of mercury should be able to compete economically with the furnace method of obtaining mercury from its ores.

SUMMARY

Data collected in this research work lead to the following
conclusions:

Cinnabar can be leached from cinnabar ores by means of alkaline
sodium sulfide solutions.

The speed of extraction depends upon the size of ore particles
and the concentration of sodium sulfide in the leach solutions.

Grinding the ore in a ball mill with the leach liquor shortens
the extraction time.

Mercury can be recovered from leach solutions by electrode-
position in a mercury cathode.

Chemicals used in leaching can be largely regenerated during the
electrodeposition process.

Calculations based on the data collected indicate that cost of
chemicals and electricity required are nominal.

Other conclusions which may be drawn from these studies are:

Flexibility of treatment will enable certain labor savings to
be made.

Cost of equipment should be less than cost of furnaces used in
the older method.

Danger of mercury poisoning is eliminated by this method of
treatment.

No mercury is lost as in the furnace method in saturating the
equipment with mercury.

Small plants can be established at new mines which cannot afford expensive equipment.

Fine ores or concentrates which cause trouble in furnaces and stills are very readily leached; thus this method might be used to supplement a furnace plant already in operation.

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