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Recovery of Mercury From Cinnabar Ores by Electrooxidation

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Recovery of Mercury From Cinnabar Ores by Electrooxidation

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RECOVERY OF MERCURY FROM CINNABAR ORES BY ELECTROOXIDATION

by

B. J. Scheiner,[1] R. E. Lindstrom,[2] and D. E. Shanks[1]

ABSTRACT

The Bureau of Mines investigated an electrolytic technique for oxidizing ore slurried with brine to determine its effectiveness in extracting mercury from ores. Optimization experiments conducted on a 2.5-pound-mercury-per-ton ore resulted in 95 percent mercury extraction with operating conditions of 30° C, a current density of 0.5 ampere per square inch, and a treatment time of 3.5 hours. Corresponding power consumption amounted to 38 kilowatt-hours per ton of ore treated.

Amenability experiments conducted on 62 different mercury ores resulted in 90 to 99 percent mercury dissolution from ores containing 0.6 to 20 pounds of mercury per ton of ore. Treatment time ranged from 1 to 7 hours in 4- to 20-percent sodium chloride solutions, and power consumption was in the range of 10 to 50 kilowatt-hours per ton of ore.

Pilot mill experiments in a 100- to 200-pound-per-hour extraction plant have been in progress to quantify power and reagent requirements. These data will be reported in a subsequent publication.

INTRODUCTION

Mercury is classically recovered from ores by roasting sulfide minerals and condensing the vapors to obtain the metal. The process is efficient from the standpoint of the degree of mercury recovery from the calcine; however, vapor and particulate losses in the condensing system, as well as losses owing to recombination of the mercury with sulfur, can be substantial. These losses are usually aggravated by the use of low-grade or wet ores, as vapor and particulate losses are directly proportional to the flue gas volume.

A hydrometallurgical approach to mercury recovery from cinnabar and materials containing native mercury offers several benefits: (1) Environmental pollution in the form of SO_2 and mercury vapor in the flue gas is eliminated; (2) the hazard of salivation to plant employees by accidental exposure to

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mercury vapors is minimized; (3) mercury recovery from low-grade ores is more efficient; and (4) the method is simple and suitable for various sizes of operation.

Hydrometallurgical treatment of mercury ores has been considered by several investigators. The dissolution of cinnabar by basic sodium sulfide and hypochlorite solutions is well known (1, 4, 13-14),[3] and attempts have been made in the past (3, 5-6, 8) to exploit procedures based on this chemistry to develop commercially acceptable processes for mercury recovery. More recently, G. A. Parks (10) and R. S. Olson (9) were issued patents for a process employing the leaching of cinnabar with sodium hypochlorite-chlorine.

An electrooxidation process, originally developed by the Bureau of Mines for pretreatment of carbonaceous gold ores (11), was observed to be effective in dissolving small amounts of mercury in the ore. Subsequent investigations have shown that the electrooxidation procedure is capable of effecting nearly complete extraction of mercury from a variety of ores and concentrates (12). The chemistry involved in electrolytically oxidizing the cinnabar is similar to that encountered in adding sodium hypochlorite to the pulp; however, it was determined that 1 pound of chlorine equivalent could be produced electrolytically for about 2 kilowatt-hours of power, thus giving a substantial economic advantage over direct addition of reagents.

MATERIALS AND APPARATUS

Baseline laboratory studies reported in this paper were conducted on an ore from the Goldbanks district, near Winnemucca, Nev. The ore occurs in volcanic rock and is opalitic in nature. The cinnabar is disseminated through the opalite rock and coats fragments and line fractures in the brecciated chalcedonic rock. The ore sample contained 2.5 pounds of mercury per ton. Subsequent experiments were conducted on a variety of ores from California, Utah, Nevada, Peru, and Mexico to evaluate the oxidation system. In all, 62 different ores were tested in the laboratory. These ores represented a wide range of host rock, varying from clay to hard opalite. The grade of the ore ranged from 0.6 to 20 pounds of mercury per ton.

Laboratory electrooxidation experiments were conducted in the following manner: (1) 1,362 grams of ore, 300 grams of NaCl, and 2,500 milliliters of water were slurried together in a 4-liter beaker; (2) the temperature was held constant; (3) the electrodes were immersed in the ore slurry; and (4) the direct current was adjusted to the desired amperage. Figure 1 shows the reaction system. The size of the electrodes were 1/4 inch by 1-3/8 inches by 12 inches and the current density was controlled by the depth of immersion. The following conditions were chosen for initial runs, based on preliminary experiments and experience gained from development of the carbonaceous gold process: ore size, 100 percent minus 35 mesh; treatment rate, 5 amperes; current density, 0.3 ampere per square inch; pulp density, ~35 percent; salt concentration, 10 weight-percent; reaction temperature, 30° C; and

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

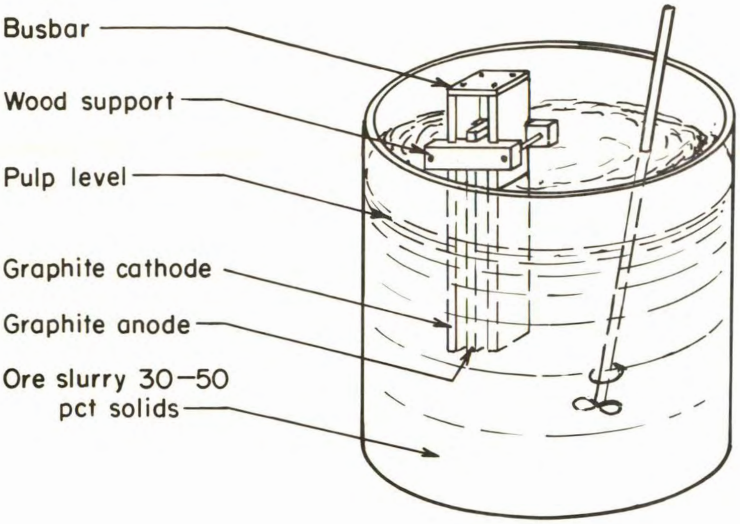


FIGURE 1. - Plate-type laboratory-scale electrooxidation cell and agitation vessel.

graphite-graphite electrodes. The effect of the agitation rate on extraction was not studied in this report; however, the pulp was stirred vigorously to maintain solids suspended in solution and to result in favorable pulp flow between the electrodes.

Solid samples containing mercury were analyzed by the combustion-atomic absorption method developed by the Bureau of Mines (7) utilizing the Lemaire mercury sniffer. Solutions containing mercury were analyzed by standard atomic absorption methods.

THEORY

The oxidizing media for dissolution of mercury are generated by electrolysis ore pulped in brine solutions. The chloride ion is converted to chlorine at the anode, as shown in equation 1:

$$2Cl^- \rightarrow Cl_2 + 2e^-. \qquad (1)$$

At the cathode, water is hydrolyzed to produce hydroxyl ion and hydrogen, according to equation 2:

$$2H_2O + 2e \rightarrow H_2 + 2OH^-. \qquad (2)$$

Equation 3 shows the reaction between the chlorine and the hydroxyl ion, which produces hypochlorite and chloride ions and water:

$$Cl_2 + 2OH^- \rightarrow OCl^- + H_2O + Cl^-. \qquad (3)$$

The dissolution of the cinnabar may be visualized as a two-step process involving oxidation of the sulfide followed by dissolution of the sulfate by chloride ion, as shown in equations 4 and 5, in which the mercury is carried in solution as a stable tetrachloride complex:

$$HgS + 4OCl^- \rightarrow HgSO_4 + 4Cl^-, \tag{4}$$

$$HgSO_4 + \text{excess } Cl^- \rightarrow HgCl_4^{2-} + SO_4^{=}. \tag{5}$$

Also, some direct oxidation of the cinnabar apparently occurs at the anode to produce mercuric sulfate. This reaction is shown in equation 6:

$$HgS + 4O^{=} \xrightarrow{8e} HgSO_4. \tag{6}$$

RESULTS AND DISCUSSION

The important parameters in the electrooxidation process include temperature, salt concentration, current density, type of electrodes, electrode spacing, treatment rate (ampere per ton of ore), particle size of the ore, pH, and pulp density.

The effect of salt concentration on power consumption required to attain 90- to 95-percent mercury extraction from the Goldbanks ore was investigated in a series of experiments. Figure 2 shows a sharp decrease in the power required for 90- to 95-percent extraction on increasing the salt concentration from 5 to 10 percent; the curve levels off between 10 and 20 percent salt concentration. The data indicate that 10 percent salt is an adequate concentration to obtain high conductivity with the graphite-graphite electrode system.

Experiments were conducted using a lead dioxide anode-iron cathode electrode assemblage in place of the previously used graphite-graphite system. The lead dioxide anode is commercially available and consists of a 1/8-inch-thick titanium plate coated with lead dioxide. Electrolysis with this electrode system using the same reaction condition as those used in previous

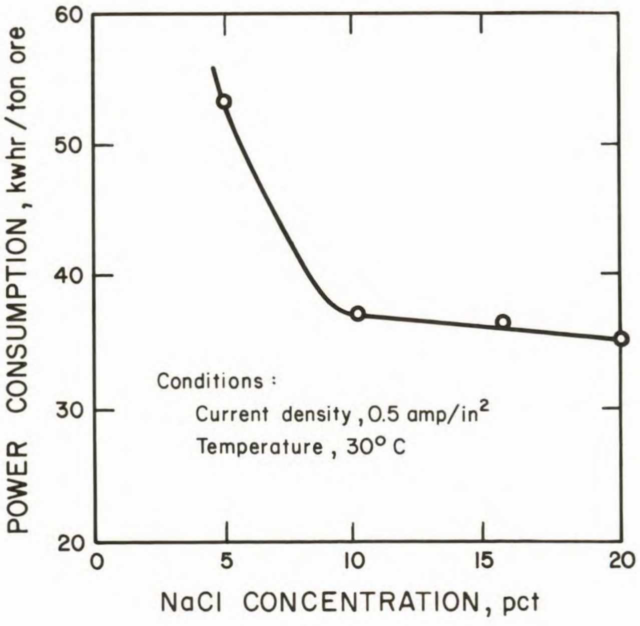


FIGURE 2.-Effect of NaCl concentration on power consumption required to attain 90- to 95-percent mercury extraction.

experiments with the graphite electrode system, resulted in mercury extractions of 90 to 95 percent with sodium chloride concentrations as low as 4 percent. Corresponding power consumption was 42 kilowatt-hours per ton of ore, which was a power increase of 20 percent over that required for the graphite-graphite system. The capital cost of lead dioxide-coated titanium anodes is much higher than that for graphite anodes; therefore, the cost of salt and power would have to be considered before deciding which electrode system to use in an operating process plant. The graphite-graphite electrode system was used for all subsequent experiments.

The effect of temperature on power consumption was determined at 25°, 30°, 40°, and 50° C. Figure 3 shows a sharp increase in power consumption as the temperature increases above 30° C. The data show that the optimum operating temperature is in the 25° to 30° C range. Bench scale and pilot plant data indicate that heat losses in the system are sufficient to maintain a temperature of 30° C without external temperature control. Operation at temperatures much lower than 30° C would require cooling of the pulp. Because heat input to the system is a function of the conductivity of the electrolyte and of the power required to accomplish the oxidation, both the electrode spacing and salt concentration are critical in maintaining desired temperature. Generally speaking, electrode spacing should be as close as is consistent with good pulp flow between the electrodes. The effect of increasing electrode spacing on voltage-amperage relationships is shown in figure 4. Spacings of 3/8, 5/8, and 1-1/8 inches, pulp densities of 40 percent, and salt concentrations of 10 percent were used for the experiments. As expected, above 3 volts the resistance across the electrodes increased directly with increases in electrode spacing.

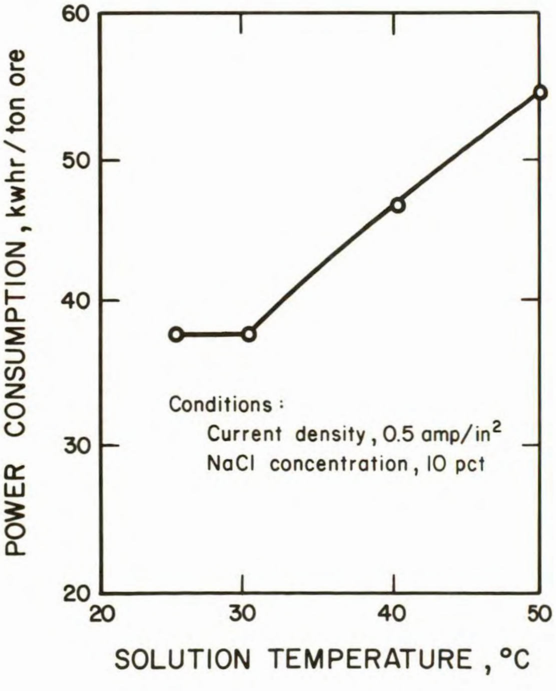


FIGURE 3.-Effect of temperature on power consumption required to attain 90- to 95-percent mercury extraction.

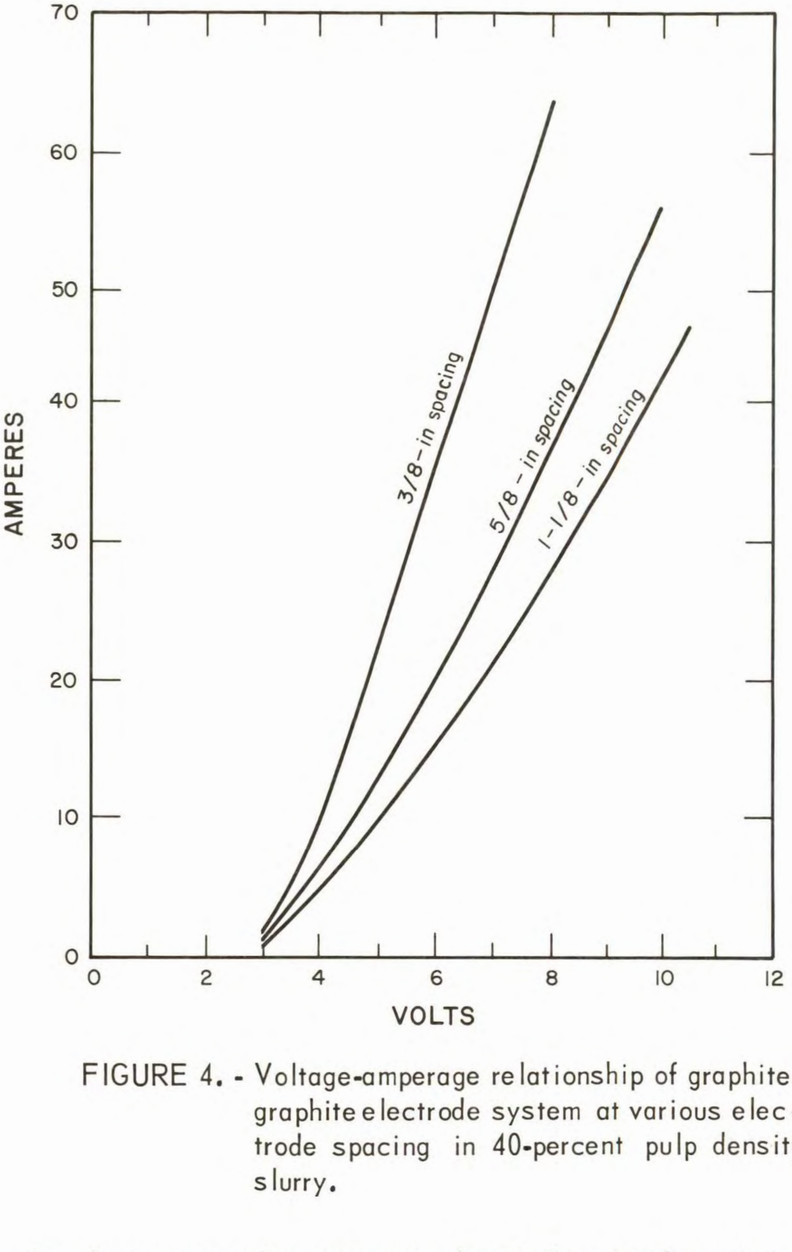


FIGURE 4. - Voltage-amperage relationship of graphite-graphite electrode system at various electrode spacing in 40-percent pulp density slurry.

The effect of treatment rate (amperes) on mercury extraction was determined in a series of experiments in which the ore was electrolyzed at 2.5, 5, and 10 amperes for a total of 17.5 amperes per hour, which corresponds to 7, 3.5, and 1.75 hours of treatment, respectively (fig. 5). The data indicate that a favorable treatment rate for this particular ore is 5 amperes, which corresponds to 3.5 hours of treatment time. At a treatment rate of 2.5 amperes, a slight decrease in power consumption per ton is observed; but at a treatment rate of 10 amperes, the power required for 90- to 95-percent extraction is increased nearly 20 percent. Because the treatment rate affects the sizing and capital cost of almost all the plant equipment, the increased cost of rectification and operation for higher treatment rates should be carefully balanced against the cost of smaller agitators and supplemental equipment.

Current density is a critical operating parameter in that excessive current densities tend to increase the temperature and decrease the efficiency of the desired chemical reactions at the electrode-electrolyte interface. The effect of increasing current density from 0.15 to 1.0 ampere per square inch on the power required to give 90- to 95-percent mercury extraction at a constant temperature of 30° C is shown in figure 6. The data show that current densities of less than 0.40 ampere per square inch should be used for maximum efficiency; however, the number and size of the agitators required to accommodate the electrode for a milling operation may limit the practical electrode area employed.

Grinding is an important part of any hydrometallurgical process because the mineral must be released from the host rock so that it can come in contact with the reactants. The effect of particle size on mercury extraction by

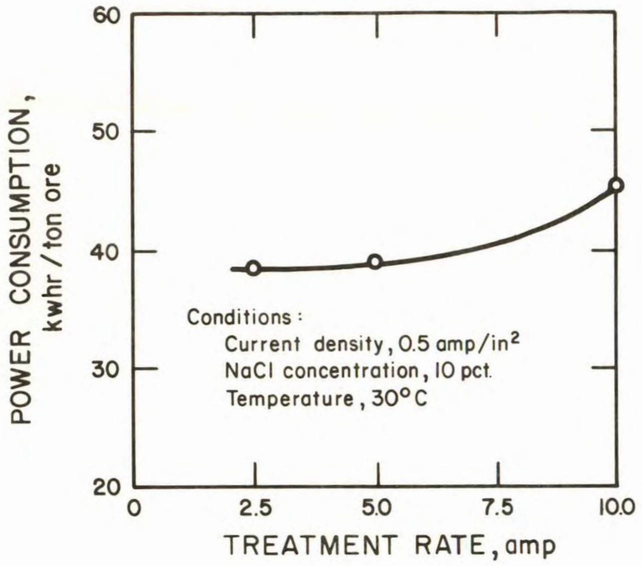


FIGURE 5. - Effect of treatment rate on power consumption required to attain 90- to 95-percent mercury extraction.

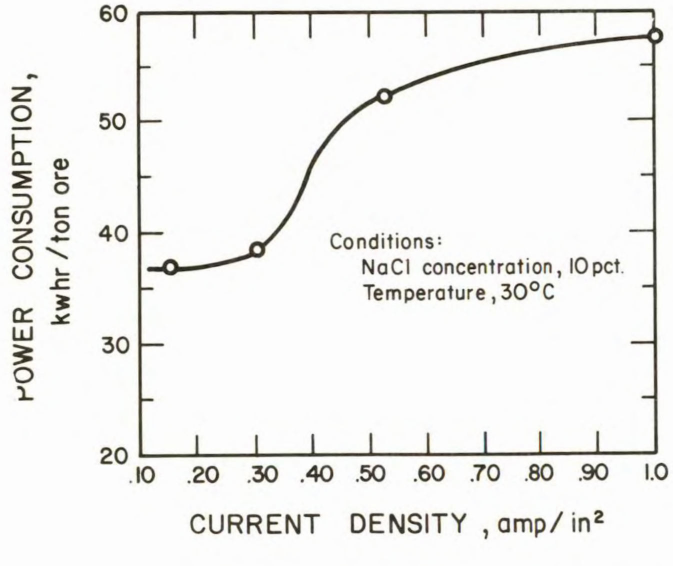


FIGURE 6. - Effect of current density on power consumption required to attain 90- to 95-percent mercury extraction.

electrooxidation was investigated using several ores with different host rocks. A coarse grind of 100 percent minus 35 mesh was adequate for all ores tested. Additional grinding to a particle size of 80 percent minus 200-mesh pulp decreased the extraction of mercury by approximately 5 percent. This decline in mercury extraction was attributed to a loss in oxidizing efficiency caused by consumption of the oxidant by other minerals in the gangue material. However, a grind of 100 percent minus 35 mesh should not be construed as a standard grind required for the process, because each ore must be tested individually to determine the optimum particle size for reaction. Pulp density affects the conductivity and handling characteristics of the slurry, but these effects were shown to be minimal in the 30- to 50-percent pulp density range.

Effect of Time on Electrolyte Composition

The effect of electrolysis time on the pH and the composition of mercury, sodium hypochlorite, and sodium chlorate of the electrolyte is summarized in figure 7. The data show that as the reaction proceeds, mercury in the tails drops from 2.4 to 0.5 pound per ton during the first hour, and by the end of the third hour, mercury remaining in the tails is in the 0.10- to 0.20-pound-per-ton range. The corresponding mercury concentration in the electrolyte builds up rapidly, reaching a maximum at the end of the first hour. The mercury in solution decreases slightly during electrolysis owing to plating at the cathode. This behavior is typical for clean electrodes; however, if a set of electrodes is used several times, the cathode appears to become passivated, and the plating phenomenon ceases. Sodium hypochlorite concentration in solution increases slowly during initial stages of the oxidation reaction and then increases linearly with electrolysis time after about 80 percent of the cinnabar has been extracted.

The sodium chlorate concentration in solution is dependent on sodium hypochlorite concentration; as the hypochlorite ion concentration builds up, the hypochlorite ion reacts with itself to form chlorate. This is shown in equation 7:

$$3ClO^- \rightarrow ClO_3^- + 2Cl^- \qquad (7)$$

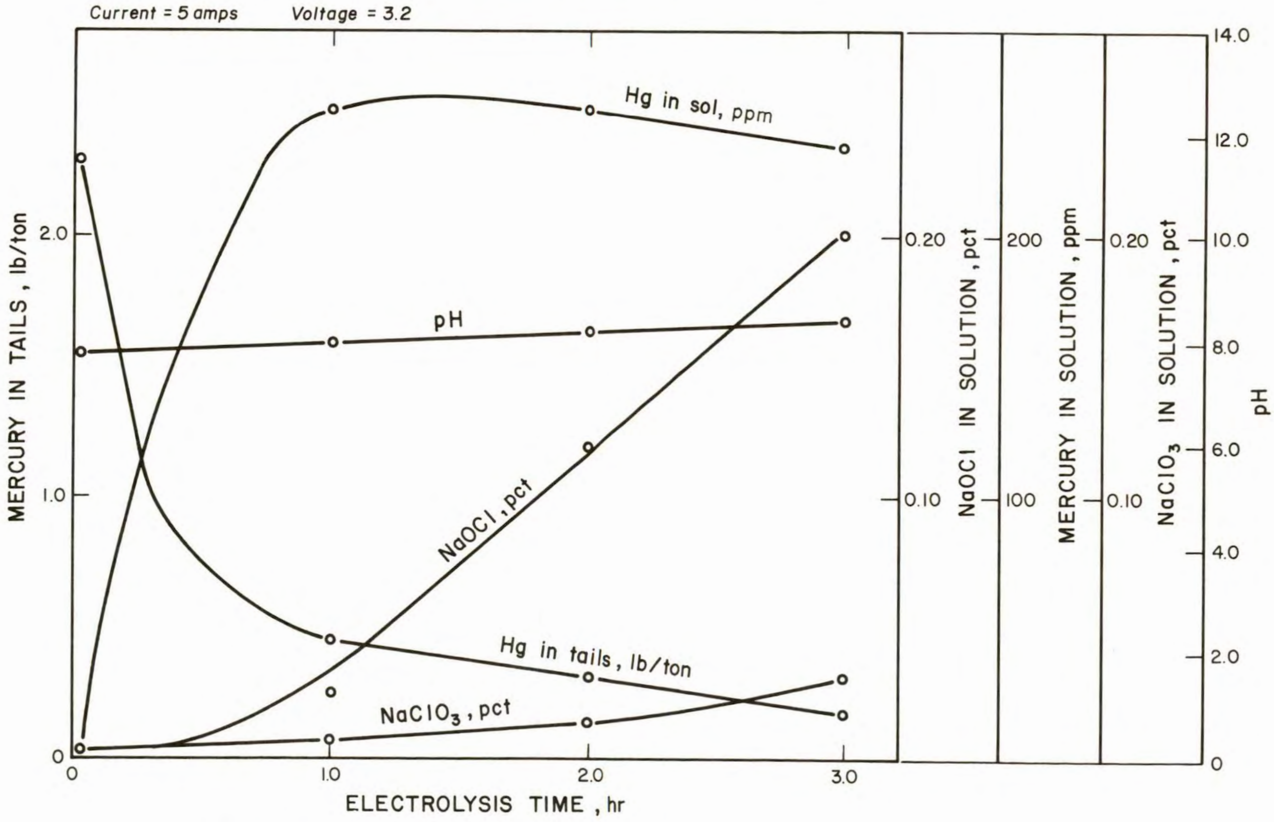


FIGURE 7. - A typical reaction profile of an electrooxidation extraction.

In an operating plant, this reaction is an inefficient use of power and should be avoided by slowing the rate of current flow toward the end of the oxidation reaction.

The pH of the system is very important since the equilibrium between soluble tetrachloromercurate ion and insoluble HgO is pH-dependent. This can be seen from the predominance-area diagram constructed in figure 8 (2). Figure 8 indicates that at a pH of 10 the chloride ion concentration must be maintained at 100 molar to prevent mercury from precipitating. Laboratory data indicate that electrooxidation at a pH above 9 causes precipitation of a large amount of the mercury oxide. Normally, this is not a problem, as the gangue minerals tend to buffer the pH to a value of near neutrality when electrolyzing most low-grade mercury ores. This pH is near the optimum pH value for hypochlorite production and utilization. Pilot scale experiments on 1 to 4 pounds of mercury per ton of ore showed that sulfate generated during oxidation of cinnabar reacted with gangue components of the ore; however, the treatment of cinnabar concentrates and ores high in sulfur or pyrite can pose a problem. Oxidation of large amounts of sulfide causes formation of H_2SO_4, which results in a sharp drop in pH value. Below a pH of about 4, chlorine is regenerated from

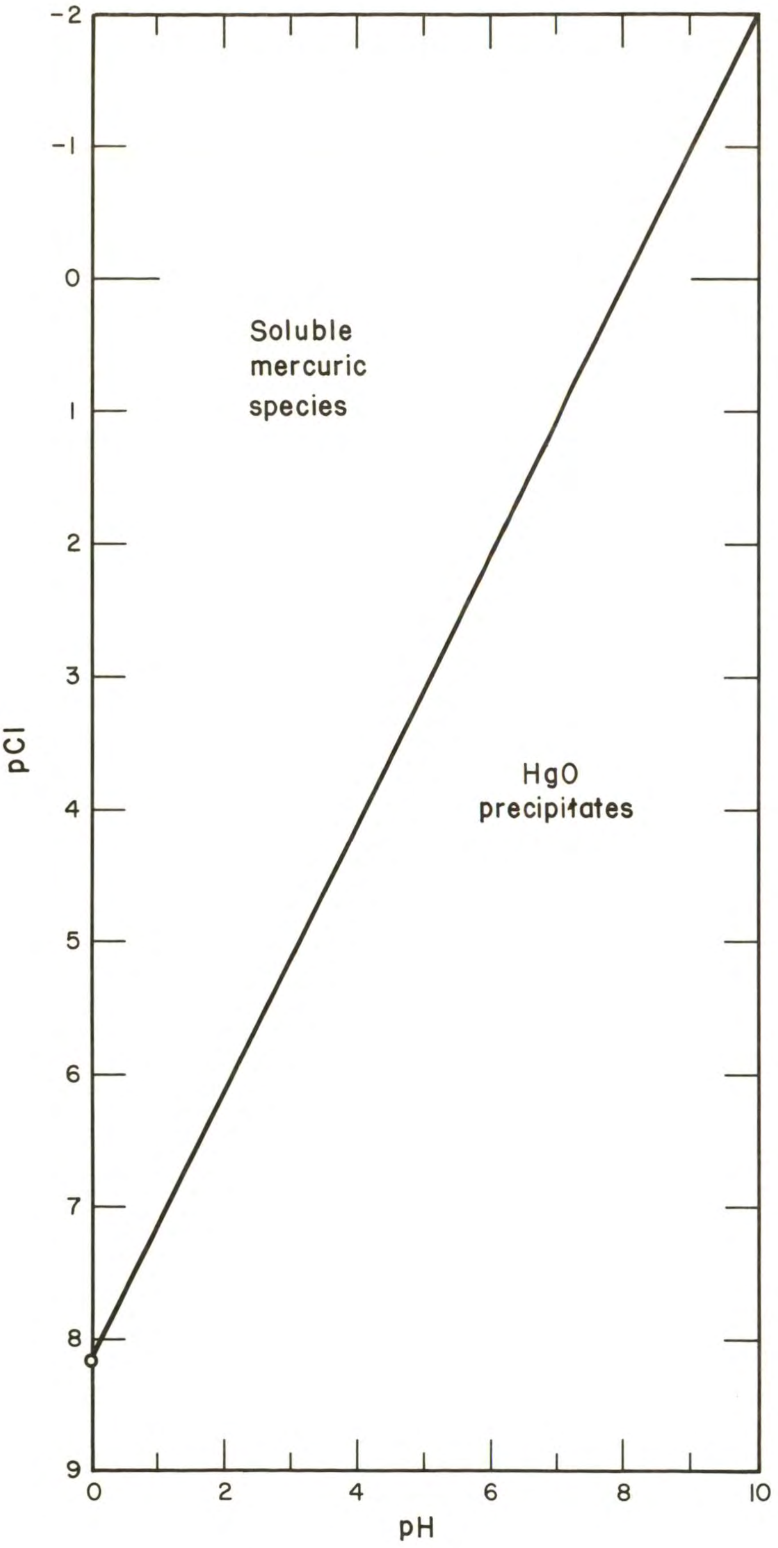


FIGURE 8. - The effect of pH and chloride ion concentration on HgO precipitation.

hypochlorite (equation 3), which increases the power consumption somewhat owing to the inefficiency of chlorine as an oxidant.

Recovery of Mercury From Solution

Mercury was recovered from process solutions by precipitation with an active metal powder, such as zinc or iron. Recovery of mercury from the resulting precipitate was accomplished by heating to 500° to 600° C and condensing the mercury vapors. Any silver or gold solubilized during electro-oxidation would be in the residue after distillation of the mercury and could be recovered by standard fire refining techniques.

Both zinc and iron powder proved to be effective reducing agents for the aqueous mercury tetrachloride complex. The use of zinc as the reductant was found to be highly dependent on the pH. The data in table 1 indicate that near optimum pH for precipitation is close to 3 with a ratio of 1.5 pound of zinc per pound of mercury in contact with the pregnant solution. Mercury recovery was 99.9 percent under these conditions, and zinc consumption per pound of mercury recovered was 0.5 pound. Because amalgamation with zinc starts immediately on contact with the pregnant solution, vigorous stirring is important.

TABLE 1. - Effect of pH on mercury precipitation with zinc powder

pH[1]	Zinc powder in contact with Hg, lb Zn/lb Hg	Barrens, ppm Hg	Precipitation, pct
5.0	1.30	530	3.7
4.0	1.30	260	52.8
3.0	1.30	5	99.1
2.5	1.30	21	96.2
3.0	1.06	78	98.6
3.0	.80	31	94.4
3.0	1.5	1	99.9

[1] pH adjusted with H_2SO_4.

The data in table 2 indicate that the precipitation of mercury with iron powder is independent of pH over the range of pH values studied. At a ratio of 2.0 pounds of iron to 1.0 pound of mercury in contact with the pregnant solution, 99.9 percent of the mercury was precipitated at all pH values investigated. During precipitation at pH 7, the iron salts are immediately hydrolyzed to an iron hydroxide that coprecipitates with the mercury; for this reason vigorous stirring of the solution during precipitation is important.

TABLE 2. - Effect of pH on mercury precipitation with iron powder

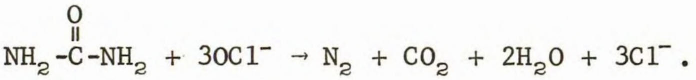
pH^1	Iron powder in contact with Hg, lb Fe/lb Hg	Barrens, ppm Hg	Precipitation, pct
3.5	2.00	0.4	99.9
4.5	2.00	.4	99.9
5.5	2.00	.46	99.9
6.5	2.00	.4	99.9
7.0	2.00	.4	99.9
7.0	.54	95	78.5
7.0	1.08	11	97.5
7.0	1.62	1.4	99.7

[1] pH adjusted with H_2SO_4.

The concentration of hypochlorite ion in the pregnant solution affects the precipitation of mercury by both iron and zinc powder. The data in table 3 indicate that as the hypochlorite level increases from 0 to 0.2 percent, corresponding precipitation decreases from 99.9 to 11 percent. This difficulty in precipitation by iron and zinc powders may be overcome by controlling the electrooxidation and subsequent digestion so that only a trace of hypochlorite is present at the end of the experiment. However, several procedures can be followed to remove hypochlorite from solution: (1) lower the pH to the 3.0 range, which shifts the chlorine-hypochlorite equilibrium towards the production of chlorine, thereby driving the gas from the solution:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl; \tag{8}$$

or (2) add a reductant such as urea or sulfur dioxide to react with the hypochlorite ion:



$$NH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH_2 + 3OCl^- \rightarrow N_2 + CO_2 + 2H_2O + 3Cl^-. \tag{9}$$

TABLE 3. - Effect of sodium hypochlorite on the precipitation of mercury by iron[1]

NaOCl, pct	Precipitation, pct
0	99.9
.05	84
.10	58
.20	11

[1] All experiments conducted at pH of 7 and a Fe to Hg weight ratio of 2.0.

Zinc and iron taken into solution during the cementation or precipitation of the mercury, convert to the hydroxide in the neutral solution, thus circumventing any buildup of these metals in recycle solutions.

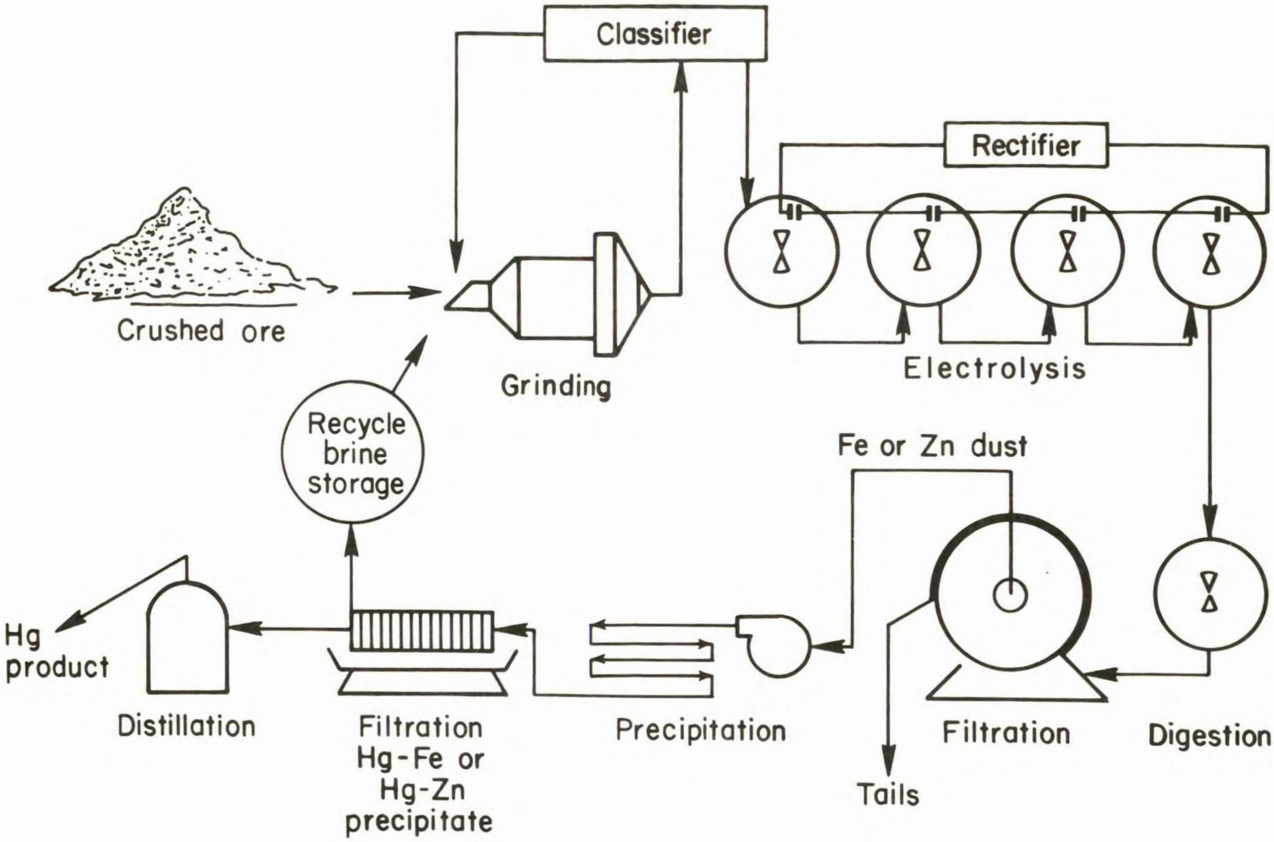


FIGURE 9. - Conceptual plant layout and flow diagram based on laboratory data.

The data indicate that iron and zinc are nearly equally effective in precipitating mercury; however, iron is preferred since the overall cost would be approximately one-eighth that of zinc.

Proposed Flowsheet for Electrooxidation of Cinnabar Ores

A process flow diagram, based on laboratory data, is shown in figure 9. The conceptual plant would consist of a crusher, a ball mill, four agitation tanks for electrolytic oxidation, a digestion tank, provision for solid-liquid separation (such as a filter, centrifuge, or thickeners), a clarifier, and a mercury precipitator. This general flow scheme was utilized for further research conducted in a 100- to 200-pound-per-hour pilot mill.[4]

CONCLUSIONS

The Bureau of Mines has shown that an electrooxidation process for extraction of mercury from cinnabar ore is feasible on a laboratory scale. Mercury extractions of 90 to 99 percent were obtained in laboratory experiments on

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[4] Pilot plant data will appear in a subsequent Bureau of Mines publication.

62 different ores by electrooxidation of cinnabar ore pulps at 30° C with a 10-percent salt solution as the electrolyte. Power consumption ranged from 10 to 50 kilowatt-hours per ton of ore. Precipitation of the mercury from solution with iron or zinc powder was demonstrated to be feasible, resulting in barren solutions containing 1 part per million or less Hg. Mercury recovery from solution was 99.9 percent using 1.5 and 2.0 pounds of zinc and iron, respectively, per pound of mercury contained in solution.

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