

POTENTIAL ECONOMIC BENEFIT FROM INNOVATIVE MERCURY SEPARATION TECHNOLOGY

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ABSTRACT

The U.S. Department of Energy teamed with the National Mining Association to select research projects that could significantly benefit the mining industry. This paper describes one such project—By-Product Recovery from Mining Process Residue. The Oak Ridge National Laboratory is researching and developing the SepraDyne[®] system—a high-vacuum, indirectly heated rotary kiln that operates at temperatures of up to 750EC.

The U.S. mining industry produces over 7,000,000 ton/yr of process residue that may contain hazardous species as well as valuable by-products. Process residues are generated by (a) smelter off-gas cleaning—5,500,000 tons/yr and (b) bag house dust and wastewater treatment—2,100,000 tons/yr (U.S. Environmental Protection Agency, 1995). New approaches may be able to recover marketable by-products from this process residue to generate revenue and reduce disposal costs for the mining industry. For example, a rotary vacuum kiln was invented by a small U.S. business, SepraDyne[®]. This technology operates commercially at a copper mine separating mercury from sulfuric acid plant blowdown sludge, which also contains lead, copper, gold, and silver. Two materials result: (1) concentrated mercury and (2) process residue with extremely low concentrations of mercury. The concentrated mercury is either sold or treated and disposed. The “mercury-free” residue can be either recycled to recover additional copper or sold to recover lead, bismuth, and trace gold and silver (U.S. Environmental Protection Agency, 1991).

The paper summarizes this research and development project: (1) SepraDyne’s[®] process is being developed and improved by modeling and evaluating process and thermodynamic variables, (2) key factors in the economics of by-product recovery are the value of acid plant sludge before separating mercury, after separating mercury, and the \$500/ton treatment cost, and (3) kinetics and thermodynamic experimental results from investigations of two mixtures—mercury, sulfur and oxygen, and mercury and selenium—confirm that the presence of oxygen affects separation of mercury compounds and the recovery of elemental mercury.

INTRODUCTION

The U.S. Department of Energy (DOE) Office of Industrial Technologies, Mining Industry of the Future Program, is working with the mining industry to help promote the industry’s advances toward

environmental and economic goals. Two of these goals are (1) responsible emission and by-product management and (2) low-cost and efficient production (U.S. Department of Energy, 1998). The Oak Ridge National Laboratory (ORNL) is working with the mining industry and the separation-process industry to develop a process that achieves these goals by separating mercury from process residue allowing valuable lead and metals to be economically recovered. The results of this project will contribute to sustainable production in the mining industry.

By-product recovery provides an opportunity for the mining industry to make environmentally-sound process improvements while generating revenue for the industry. SepraDyne[®], a small U.S. business, has patented a technological breakthrough that uses an improved separation process to recover metals from mining process residue. The technology provides a processing environment for separating metals (primarily mercury) and destroying organic chemicals (e.g., dioxins, furans) that contaminate valuable products, such as copper and lead and traces of gold and silver.

To realize the potential of this technology, DOE and SepraDyne[®] co-funded work at ORNL, in collaboration with the Colorado School of Mines. This paper summarizes this research and development project including (1) process descriptions of mercury separation from acid plant sludge including baseline and vacuum rotary kiln mercury separation techniques, (2) process modeling of the SepraDyne[®] operations, (3) factors that influence the economics of by-product recovery; and (4) results of process chemistry kinetic and thermodynamic experiments on two mixtures—mercury, sulfur and oxygen, and mercury and selenium.

PROCESS DESCRIPTIONS OF MERCURY SEPARATION FROM ACID PLANT SLUDGE

Baseline Mercury Separation Technique

ORNL searched the literature, and interviewed mine and SepraDyne[®] personnel to determine the composition of the acid plant sludge and assess mercury separation techniques. This information indicates that acid plant sludge contains lead, copper, and bismuth, as well as trace quantities of gold, silver, and mercury sulfide (U.S. Environmental Protection Agency, 1991; Jeanette B. Berry and H. Patton, 2000). The mine used a traditional baking method to reduce the concentration of mercury to acceptable disposal levels for Resource Conservation and Recovery Act-regulated waste. The acid plant sludge was loaded into “baking trays” that were exposed to direct heat. Since the material was not mixed as it was heated, heating was not uniform. Consequently, the effectiveness of mercury removal varied. Since the process residue contained relatively high concentrations of mercury, the valuable lead and copper were not cost-effectively recovered (Jeanette B. Berry and J. Talburt, 1999).

Rotary Vacuum Kiln Mercury Separation Technique

ORNL analyzed the SepraDyne[®] technology by visiting the operating site and evaluating the process. Initial evaluation indicates that this process has advanced by-product recovery by more effectively separating mercury on site with compact processing equipment. Mercury is removed to <10 ppm so that valuable metals, such as lead, can be economically recovered from acid plant sludge—the mine can market the lead bearing process residue to a lead smelter.

The heart of the SepraDyne[®] process is an indirectly heated rotary kiln that operates at a high vacuum and high temperature. These conditions produce an environment that volatilizes liquid and low- to

moderate boiling-point metals such as mercury, arsenic, selenium, and cadmium. The process has also been shown to destroy organic compounds. Since air is eliminated from the kiln, combustion does not occur; and off-gas treatment equipment is minimized. The vacuum system has the following advantages over traditional thermal processes:

- Reduced oxidation of mercury and formation of mercury compounds because of the reduced oxygen in the processing environment.
- Reduced formation of organic products of incomplete combustion because of the reduced oxygen in the processing environment.
- Reduced capital, and maintenance costs because complex off-gas treatment systems are not needed.
- Reduced particulate formation and dust.

The operating parameters and processing sequence of the rotary vacuum retort (illustrated in Fig. 1) are as follows. Solid or semi-solid process residue is fed into the retort through a feeding system (a hopper/ auger assembly). Once the unit is loaded, a vacuum is established and the retort is set into rotation. Heat is indirectly applied within an insulated firebox through burners fueled by natural gas, diesel oil, or propane. As an alternative, electric heating can be employed in sensitive environmental settings, or on sites with low-cost electric

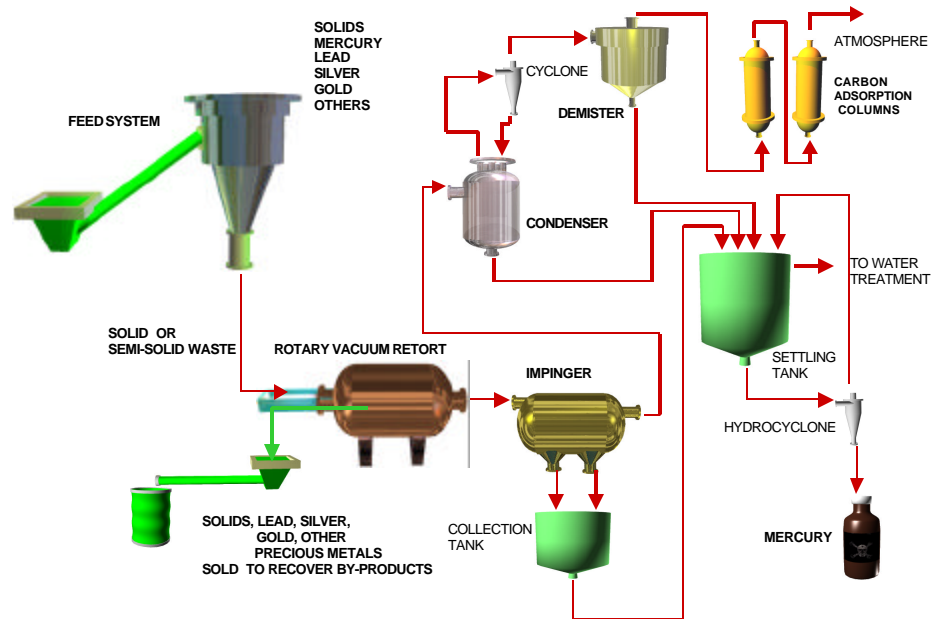


Figure 1. Vacuum Rotary Kiln Mercury Separation Process.

power. Residue is initially heated to remove the moisture. The water vapor and other low-boiling-point gaseous compounds are normally condensed in the off-gas treatment train, passing initially through an impinger system. If very-low-boiling-point organic chemicals are present, cryogenic cooling can be employed to condense these chemicals.

Once the material is dried, the retort temperature is raised to a target value, up to 600EC to 750EC, under a vacuum of greater than 0.7 atm (20 inches of Hg), and held at the target temperature for a set time. Organic compounds, including heavy tars and compounds of mercury volatilize under these conditions. Non-volatile chemicals and residual metals are separated from the condensed liquid, and the liquid is discharged to on-site wastewater treatment systems or the sanitary sewer. Waste heat from the process is exhausted to the atmosphere. Any trace hazardous vapors that have passed through the off-gas system are removed in the carbon absorption section. Mercury is recovered from the solids collected in the

settling tank using a hydrocyclone. The material within the retort is maintained at the target temperature until system monitoring indicates that all of the contaminants of concern have been removed. After processing, the burners are turned off and the vacuum is released. The processed material is then conveyed via a screw feeder into a receiving vessel fitted with particulate air control equipment. Materials containing by-products are collected in separate containers for shipment. The mine sells the material to an off-site smelter for recovery of lead and trace quantities of gold and silver. Alternately, if the concentration of copper is high enough (e.g., >7 %), the mine returns the material to the onsite smelter for additional processing (J. B. Berry and J. Talburt, 1999).

PROCESS MODELING

ORNL researchers modeled the SepraDyne[®] system using process modeling software, FLOW[™], to analyze the effect of changing process equipment (e.g., improved materials of construction) and operating parameters (e.g., feed stream composition) (see Fig. 1). FLOW[™] is a modular computer simulation program that models and analyzes emerging chemical and physical processes. Process analysis starts with a simple material balance, using available data. Process developers use an icon-based, user-friendly interface to model material balances around each unit operation. These unit-operation material balances are then combined to calculate a material balance around the entire process. Analysis can be extended to evaluate process effectiveness, efficiency, and operability. ORNL modeled and evaluated the SepraDyne[®] system resulting in a basic understanding of process variables and their influence on the effectiveness of mercury separation. Continued process analysis is planned to better understand unit-operation alternatives, efficiency, operability, cost, risk and uncertainty.

ORNL and the Colorado School of Mines used thermodynamic models to predict compounds likely to result from critical processing steps. Feed stream data were provided by SepraDyne[®]. Version 4.1 HSC Chemistry for Windows Chemical Reaction and Equilibrium Software (by Outokumpu) was revised to reflect experimental results obtained by the participating researchers at the Colorado School of Mines (G. L. Fredrickson and John P. Hager, 1996). Equilibrium species were estimated by minimizing the collective Gibbs free energies for temperatures between 30E and 600EC (86E to 1112EF). ORNL developed a procedure to simulate a reaction path under vacuum by removing all of the gaseous species after each time-temperature-equilibrium step. This procedure recalculates the equilibrium composition of each subsequent reaction step using only the residual solids from the previous step. Along with an allowance for particulate carry-over, the collective gaseous species from all of the reaction steps were modeled to simulate the composition of the sludge that condenses from the off-gas.

Analysis of experimental data and model results led to a better understanding of the importance of oxygen in the oxidation rates of the metals present in the process feed and the importance of air in-leakage in the volatilization and separation of elemental mercury.

PROCESS CHEMISTRY EXPERIMENTAL RESULTS

Since acid plant sludge contains high concentrations of sulfur and selenium, it is important to understand interactions between these elements and mercury in the presence of oxygen to better control the process and optimize the removal of mercury. The Colorado School of Mines conducted experiments on the chemistry of the Hg-S-O and Hg-Se systems specific to removal of mercury from acid plant sludge. Experiments to date have shown that operating conditions can dramatically influence process effectiveness (John P. Hager, Antonio E. Blandon, and Jeanette B. Berry, 2000).

The results show that there are significant differences in the temperatures required to achieve rapid rates of volatilization. The most difficult compounds to volatilize are HgSO_4 , Hg_2SO_4 , and $\text{HgSO}_4 \cdot 2\text{HgO}$. These three compounds all have volatilization temperatures in excess of 600EC for 100% volatilization in 60 minutes. The next most difficult compounds to volatilize are HgO and HgSe with minimum temperatures of 557E and 451EC, respectively. The least difficult compound to volatilize is HgS with a required temperature of 382EC. This highlights the importance of having accurate information on the speciation of the mercury in the acid plant sludge to correctly design operating temperatures for the retort. These results provide data necessary to calculate the required process temperatures over differing process periods. Also, the results obtained for HgS , for the two different reactor pressures, suggest that an increase in the reactor pressure from 0.07 to 0.13 atm (2.0 - 3.9 inches of Hg) could result in an increase in the required operating temperature of 40EC or more. In the case of mercury sulfates being the predominant species, it is possible that a required process temperature in excess of 700EC could be required for 100% volatilization with short residence time (e.g., 60 minutes).

Back-reactions of the mercury vapor, as it is transported from the experimental reactor to the condenser, were observed to be very rapid. This is a significant factor in considering the use of a vacuum retort/condenser system to recover elemental mercury from smelter acid plant sludges. It is clear from the modeling studies that primarily mercury vapor is generated during the volatilization of the compounds investigated in this study. The extent to which mercury is transported as HgS(g) , HgO(g) , or HgSe(g) is insignificant. Mercury collected on the experimental condenser (i.e., a water-cooled cold finger) was generally in compound form, rather than as elemental mercury—confirmation under controlled, experimental conditions that recovery of a liquid mercury product is difficult from such a complex mixture. Excess oxygen in the system would increase the production of SO_2 , increase the concentration of SO_2 in the off-gas stream to the condenser, and further increase the rate of the back-reaction of the gaseous mercury. Key factors for the successful separation of elemental mercury include (1) limited presence of oxygen and (2) the rate of condensation and quenching of the mercury vapor to prevent back-reaction to non-elemental forms (e.g., HgSO_2 , HgSe).

ECONOMICS OF BY-PRODUCT RECOVERY

Acid plant sludge contains lead and copper, as well as trace quantities of mercury sulfide. It is difficult to recover the economic value of this acid plant sludge because it is contaminated with mercury. When the concentration of lead and copper exceeds a certain value, brokers may purchase this contaminated process residue and aggressively treat it to recover the value of the remaining metals (e.g., lead). If the value of the acid plant sludge is more than the cost of mercury removal, by-product recovery generates net revenue for acid plant operations.

ORNL reviewed the economics of this process as background for collecting relevant data from the mining industry. To gain an understanding of the process economics, information is needed at various mercury concentrations. Interviews with mining companies indicate that the concentration of mercury influences the value of the process residue, because the ability for down-stream processes to recover valuable by-products is significantly influenced by mercury concentration.

Economic values of each process residue are used to determine the cost-effectiveness of separating mercury—two processing stages and various final concentrations of mercury. The required information includes (1) value of a process residue before separating mercury (may be a negative value equal to the cost of disposal), (2) value of a process residue after separating mercury, and (3) value of a residue that

cannot be sold (may be negative because of its disposal cost). The value of a process residue varies with mercury concentrations—for instance, data at <100 ppm, <50 ppm, and <10 ppm mercury would provide a basis for this economic analysis.

To evaluate the value of improved mercury separation techniques, the baseline processing cost of mercury separation should also be considered. For example, baking acid plant sludge in open trays may result in a relatively high final concentration of mercury, but may also be relatively inexpensive. While aggressive chemical extraction may result in low mercury concentrations, this process may be relatively expensive. Using this information, the economic analysis can ascertain the following variables:

(1) processing cost saved, (2) the value of separating mercury, and (3) the final concentration of mercury that results in the highest net benefit for the mining industry.

This logic can be applied to other process residues to determine whether separating mercury would be cost effective. For example, smelter operations managers could use this analysis to determine whether their operation could generate revenue by receiving residue which is mercury-contaminated, and separating the mercury prior to smelting the metal-bearing process residue. A summary of the on-going economic analysis is shown in Table 1.

Table 1. Mercury Separation Economic Variables

A	Value of process residue before separating mercury	<i>need data – may be negative</i>		
	Concentration of mercury	<100 ppm	<50 ppm	<10 ppm
Value of process residue after separating mercury				
B	Acid plant sludge	<i>need data</i>	<i>need data</i>	<i>need data</i>
C	Other mercury contaminated residue	<i>need data</i>	<i>need data</i>	<i>need data</i>
Gross value after separating mercury				
D	Acid plant sludge (B - A)	calculate	calculate	calculate
E	Other mercury contaminated residue (C - A)	calculate	calculate	calculate
F	New technology mercury separation cost per ton	\$500/ton	~\$500/ton	~\$500/ton
G	Processing cost per ton for next best technology	<i>need data</i>	<i>need data</i>	<i>need data</i>
H	Processing cost per ton saved by new technology (G - F)	calculate	calculate	calculate
Net value of separating mercury				
I	Acid plant sludge (D - H)	calculate	calculate	calculate
J	Other mercury contaminated residue (E - H)	calculate	calculate	calculate
Mercury removal level for highest net benefit based on highest value for each process residue				
	Acid plant sludge	Highest value in row I		
	Other mercury contaminated residue	Highest value in row J		

A preliminary assessment of available data indicates that if marketable by-products could be recovered from 30% of the U.S. mining industry's annual 7 million tons of process residue, because mercury was removed, the industry could generate \$400 million in revenue from the recovered metals each year and could avoid disposal costs. This potential for economic gain motivates further study of more cost-effective separation of mercury to allow by-product recovery from mining process residues (Juan J. Ferrada, et al., 1999).

CONCLUSIONS

The SepraDyne® process, which uses an indirectly heated rotary kiln that operates at a high vacuum and high temperature, shows promise as a mining by-product recovery system. The system is being operated commercially at a mining complex to separate mercury from acid plant sludge solids. DOE and the National Mining Association selected this process for a research and development project for the purpose of benefitting the mining industry.

ORNL and Colorado School of Mines are collaborating to develop this rotary vacuum kiln process by evaluating the process using engineering and economic assessments, by developing process and chemistry models, and conducting experiments on the fundamentals of the complex chemistry of acid plant sludge.

Both process modeling and experimental results indicate that oxidation of mercury controls separation of elemental mercury from this acid plant sludge, especially in the presence of selenium and sulfur: separation of mercury under vacuum increases the amount of elemental mercury recovered. This developmental work also indicates that back-reaction of mercury with excess oxygen is very rapid—control of conditions under which mercury condenses influences the amount of elemental mercury recovered.

Data indicate that the SepraDyne® process is an effective process for separating mercury from acid plant sludge. The remaining sludge, which contains lead, and other valuable metals, is sold to a lead smelter for by-product recovery—the research team is verifying the economics of this by-product recovery operation.

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