

REMOVAL OF MERCURY ENABLES RECYCLE OF COPPER SMELTER ACID PLANT SLUDGE

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Abstract

Oak Ridge National Laboratory and Colorado School of Mines are developing a process, which separates mercury from sulfuric acid plant **blowdown** sludge. This process operates commercially at a **copper** mine and includes a rotary vacuum kiln, invented by a small U.S. business, SepraDyne®. Two materials result: (1) mercury and (2) a recyclable process stream with 5-20% copper and extremely low concentrations of mercury. The mercury is sold or treated and disposed. If the “mercury-free” stream contains >7% copper, it is recycled to recover copper, if not, it is sold to recover lead, and trace gold and silver.

The paper summarizes the results of interactive modeling of process and thermodynamic variables including: (1) process analysis indicating that the SepraDyne process achieves an 80% reduction in mercury with low rates of air in-leakage, (2) evaluation of the effect of air in-leakage on mercury separation indicating that a reducing environment could lower the temperature at which mercury separates from 600 to 225°C and improving product purity.



Introduction

The U.S. copper, lead, and zinc commodity sectors generate between 23,300,000 and 24,000,000 metric tons per year of process residue and waste that may contain hazardous species as well as valuable by-products [1]. Because mining extracts complex mixtures of elements, process residues typically contain metals with different economic value. Some process residues contain valuable and less valuable metals, which can be separated to allow recovery of the valuable metals [2].

The U.S. Department of Energy (DOE) Office of Industrial Technologies, Mining Industry of the Future Program, and the mining industry collaborate to further environmental and economic goals. Two of these goals are (1) responsible emission and by-product management and (2) low-cost and efficient production [3]. To achieve these goals, DOE formed an alliance with the National Mining Association (NMA) to strengthen the basis for research projects conducted to benefit the mining industry. NMA and industry representatives actively participate in this alliance by evaluating project proposals and by recommending research project selection to DOE. Oak Ridge National Laboratory (ORNL) and Colorado School of Mines (CSM) engineers conducted one such project to research and develop a process that separates mercury from copper acid plant blowdown.

This team of researchers collaborated with a small U.S. business, **SepraDyne**[®], to optimize their metal separation process that operates at an Arizona mining site. The heart of the process is a patented rotary kiln that operates at a high vacuum and temperature. These operating conditions separate metals such as mercury and selenium from valuable products such as copper, lead, silver and gold. The **SepraDyne** process increases the amount of products generated per ton of ore, making it possible to “find constructive use for . . . material removed in the mining process” [4].

Process description

The U.S. copper sector generates 10,500,000–11,000,000 metric tons per year of process residues. Fully 80% of the primary copper in the world comes from low-grade or poor sulfide ores. These ores are treated by pyrometallurgical methods that generate major process residue streams. The smelting process concentrates copper to matte and produces a sulfur-bearing gas that is converted to sulfuric acid. Acid production and gas cleaning generates sludge.

Acid plant process residue

Waste gases from the smelting operation are separated from flue dust at 1250°C in the off-take shaft and pass through a waste boiler that generates steam, and subsequently to an electrostatic precipitator to separate the bulk of the flue dust, which is recycled to the feed. The sulfur dioxide gas contains >8% SO₂, trace quantities of hydrocarbons, and precious metals. The gas stream is treated to remove coarse entrained particulate matter (i.e., bag-house dust) and processed to make commercial grade sulfuric acid. The gas cleaning section of the acid plant uses dilute sulfuric acid to scrub these gases. The process re-circulates the scrubber water; however, some of the stream must be purged (i.e., blown down) periodically to prevent buildup of solids and minimize corrosion of the scrubber.

The wet solids are filtered with the liquid pumped to a holding pond and solids, termed acid plant blow down, are stored on a solar pad. The composition of this material remains



relatively stable because the composition depends on a process that is not changed. The process residue contains 5-20 wt % Cu that can be recovered **after** SepraDyne separates the mercury. When the concentration of Cu in residues is less than 7%, residues are sold to a lead smelter to recover the -45 wt % lead, and trace amounts of gold and silver (Figure 1).

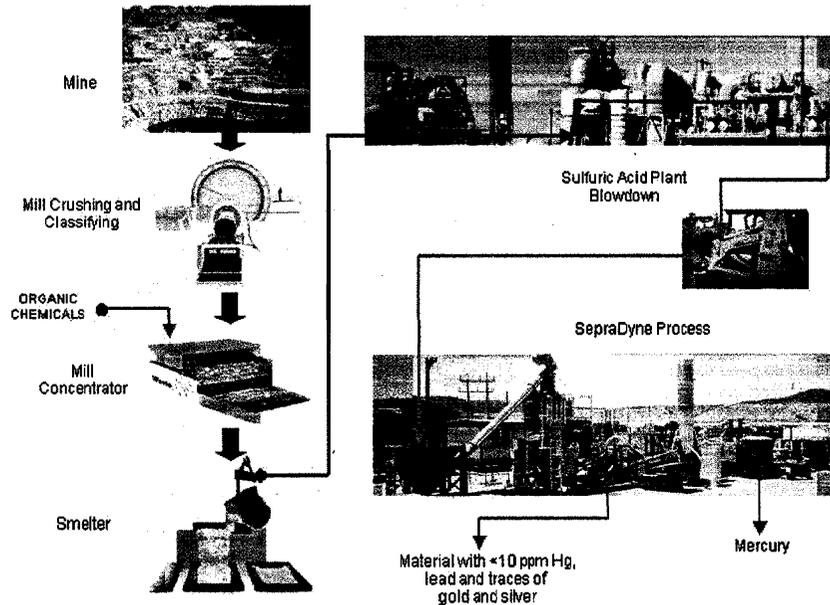


Figure 1. Copper mining and by-product recovery

Baseline mercury separation operation

Acid plant sludge contains lead, copper, and selenium, as well as trace quantities of gold, silver, and mercury sulfide [5],[6]. A traditional baking method was used to reduce the concentration of mercury to acceptable disposal levels. The acid plant sludge was loaded into “baking trays” that were exposed to direct heat; but the material was not mixed as it was heated, and heating was not uniform. Consequently, the effectiveness of mercury removal varied. Because the process residue contained relatively high concentrations of mercury (i.e., >60 mg/kg), the valuable lead and copper could not be recovered [7].

Vacuum retort mercury separation process

The Arizona mine assessed alternative mercury separation methods and selected the SepraDyne process [8]. The heart of the SepraDyne process is an indirectly heated rotary vacuum kiln (Figure 2). These conditions produce an environment that volatilizes water and low to moderate boiling point metals such as mercury, arsenic, selenium, and cadmium. Since air is eliminated from the kiln, combustion does not occur and complex off gas treatment systems are not needed making the process compact while reducing capital and maintenance costs. Mercury volatilizes at lower temperatures and forms **simple** compounds because of the reduced oxygen in the processing environment. Material that would have become air pollution is recovered. Dust and particulate formation is minimized.

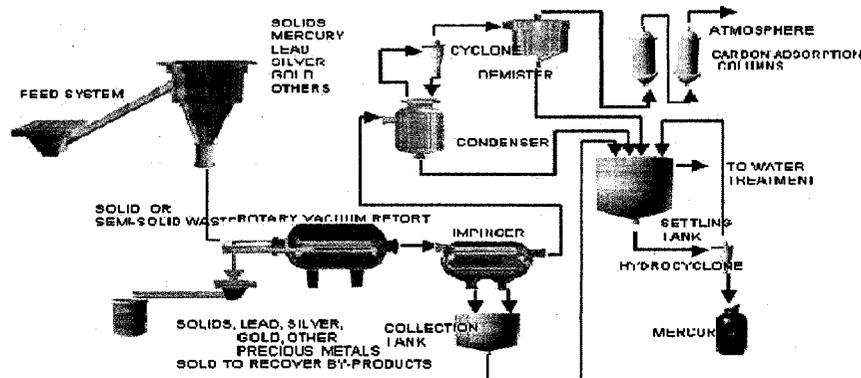


Figure 2. SepraDyne mercury separation process

Solid or semi-solid waste is fed into the retort through a hopper/auger assembly. Once the unit is loaded, a vacuum is established and the retort rotated, heat is indirectly applied using insulated **firebox** burners fueled with natural gas, diesel oil or propane. The acid plant **blowdown** 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. Once the material is dried, the temperature of the retort is raised to 600°C to 750°C , and it is held under a vacuum of greater than 0.7 atm for a set time. The SepraDyne retort maintains this vacuum—the only possible point for air in-leakage is a mechanical seal that wraps around a 4-inch axle. Chemicals are separated from the condensed water and the water is discharged to on-site wastewater treatment systems or the sanitary sewer. Waste heat from the process is exhausted to the atmosphere. Trace hazardous vapors are removed with carbon absorption. Mercury is recovered from the settling tank.

The material in the retort is maintained at the target temperature until system monitoring indicates that 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. Mercury is volatilized, condensed, and sold to a mercury vendor or disposed of. Materials containing by-products are collected in separate containers for shipment to an off-site smelter for recovery of lead and trace quantities of gold and silver or returned to the smelter if the concentration of copper is high enough to warrant additional smelting. As of April 1999, SepraDyne Corporation treated 880 tons of **acid** plant solids on site with all processed batches containing <280 mg/kg total mercury [7].



Process analysis

Researchers analyzed the SepraDyne process by reviewing operational procedures, inspecting process operations, and sampling specific points in the process. Sampling points were selected to support process modeling, including thermodynamic and mass balance calculations, required to model system performance. Ten duplicate samples were collected in two different

batch-operating modes. Chemical compositions were calculated at each processing step stage using these data (e.g., Table 1), providing sufficient data for researchers to model thermodynamic behavior and close the material balance. Analytical data on the feed composition (e.g., 1,300 mg/kg mercury) were used to establish initial conditions for modeling; the data showed that the product contained approximately 280 mg/kg of mercury. The SepraDyne process reduces the concentration of mercury in the product by 80%.

Table 1. Compounds present in the feed

Element	Likely compound	Normalized mole fractions	Wt %	Element	Likely compound	Normalized mole fractions	Wt %
H ₂ O	H ₂ O	0.36041	5.57	K ₂ O	K ₂ SO ₄	0.00248	0.37
Ag	Ag ₂ SO ₄	0.000527	0.14	MgO	MgSO ₄	0.08508	8.79
Al ₂ O ₃	Al ₂ (SO ₄) ₃ •6H ₂ O	0.00667	2.58	Na	Na ₂ SO ₄	0.00574	0.29
Au	Au	0.0000015	0.00	Na ₂ O	Na ₂ SO ₄ •7H ₂ O	0.00836	1.92
Ba	BaSO ₄	0.01772	3.55	Pb	PbSO ₄	0.02373	6.18
CaO	CaSO ₄ •5H ₂ O	0.01248	2.42	Se	SeO ₂	0.00680	0.90
Cu	CuSO ₄ •5H ₂ O	0.13621	18.66	SiO ₂	PbSiO ₄	0.14436	37.08
Fe ₂ O ₃	FeSO ₄	0.02408	3.14		H ₂ SO ₄	0.16471	13.86
Hg	HgSO ₄	0.00066	0.13	Solids		0.63959	100

Modeling methodology

The mercury separation process occurs primarily in the retort process where chemical compounds are volatilized by raising the temperature while a vacuum is applied to the system. Complex chemical reactions occur within the retort chamber, yielding a combination of solid and gas compounds. Formation of some compounds assists mercury volatilization, while other compounds impede mercury separation.

Two computational tools were used to model the SepraDyne process, (1) HSC™ Version 4.1, an equilibrium simulation program developed by Outokumpu and (2) FLOW®, an ORNL process simulation tool. HSC4 predicts multi-component equilibrium reactions based on thermodynamic principles while FLOW works with any heuristic or thermodynamically produced information. In addition to these computational tools, the modeling effort included experimental thermodynamic and kinetic data needed to model the process chemistry. Data from CSM experiments were used to amend the HSC V4.1 database for heats and entropies of formation and heat capacities of key compounds over the operating temperature range [9],[10],[11],[12]. Physical property data were amended for compounds of mercury, oxygen, sulfur and selenium allowing accurate predictions of equilibrium compositions of the complex mixture of sulfates and metals in the acid **blowdown** sludge.

ORNL researchers modeled the metal recovery system using object-oriented software, FLOW. Interfaces were developed to link FLOW with HSC to predict equilibrium outcomes of complex reaction systems. By linking these models, we predicted the effect of operational changes on improving mercury separation and reducing corrosive conditions of retort operations. The vacuum retort was modeled as two chemical reactors operating in series (Figure 3). Input data include the composition of the feed, amount of inlet air, temperature, and residence time of the reactor. Given these operating parameters, the model maintains both reactors under the specified vacuum and continuously extracts gases produced during the

reaction period. Chemical reactions are calculated by the HSC database that is linked to the FLOW reactor, allowing thermodynamics to dictate the composition of material exiting the reactor. Extracted gases consist of non-reacted chemicals and products of chemical reactions.

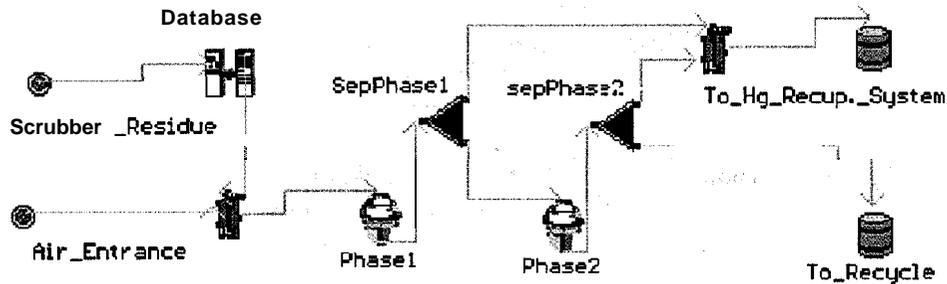


Figure 3. FLOW representation of the retort system

Chemical reactions are modeled in phases: reactions occurring at temperatures below 150°C (Phase 1) and above 150 °C (Phase 2) are modeled including the expected percent conversion (Table 2). Since the retort is connected to a vacuum system, gaseous streams continuously exit the reactor. FLOW models this continuous extraction of gases and phase separation with an object called “SepPhase.” Small solid particles, or carryover, exit the reactor with the gases. To model the process we assumed carryover of 2 wt % (Figure 3) [13].

Table 2. Chemical reactions modeled by process temperature

Chemical reactions in Phase 1 (<150°C)		Chemical reactions in Phase 2 (>150°C)	
Chemical reaction	Percent conversion	Chemical reaction	Percent conversion
$\text{HgO} \rightarrow \text{Hg} + \text{O}_2$	90	$\text{Hg} \rightarrow \text{Hg}$	100
$\text{HgSO}_4 \rightarrow \text{HgO} + \text{SO}_3$	100	$\text{HgSO}_4 \rightarrow \text{HgO} + \text{SO}_3$	100
$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$	100	$\text{AlBr} \rightarrow \text{AlBr}_3$	90
$\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$	80	$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$	100
		$\text{AlI} \rightarrow \text{AlI}_3$	90
		$\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$	80
		$\text{AlCl} \rightarrow \text{AlCl}_3$	90
		$\text{HgO} \rightarrow \text{Hg} + \text{O}_2$	90
		$\text{Fe} + \text{Cl} \rightarrow \text{FeCl}_3$	90
		$\text{Ni} + \text{Cl} \rightarrow \text{NiCl}_2$	90

Modeling results

Mercury separation within the retort is the crucial processing step. The quantity of mercury actually collected is less than expected, based on a material balance. Researchers surmised that mercury might be reacting with constituents in the feed, preventing volatilization of elemental mercury. Operators assumed that an increase in temperature would result in better recovery of elemental mercury. However, increasing the process temperature could further jeopardize the structural integrity of the rotary kiln-structural integrity of the kiln is a problem when operating at ~600°C because of the presence of highly corrosive sulfuric acid. Modeling the separation process resulted in a better understanding of parallel reactions as a function of temperature and air in-leakage (see Figure 4).

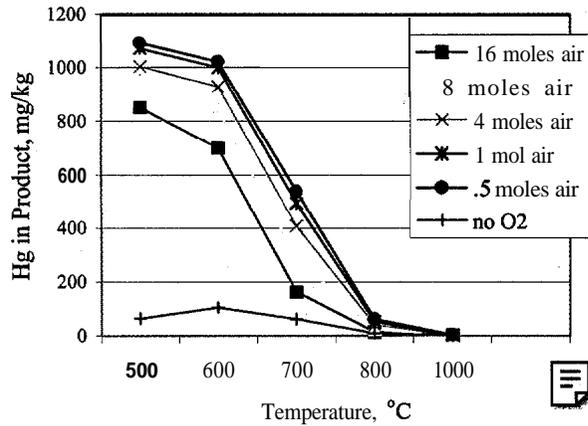


Figure 4. Mercury concentration in product as function of air in-leakage

If the air in-leakage is high (0.5-15 moles), the concentration of air is **sufficient** to form mercury oxidizes which remain in the product. When the presence of air is low enough to provide a reducing environment, elemental mercury vaporizes, leaving a lower concentration of mercury in the product at lower temperatures. Process thermodynamics were modeled at low and high rates of air in-leakage to demonstrate the effect of **SepraDyne's** patented rotary seal design on separation of the species. The redox-chemistry of the process dramatically influences distribution of species' during processing. Because carbon acts as a reducing agent, we also modeled addition of amorphous carbon to the feed.

Partial vacuum (high airflow rate)

With partial-vacuum operation of a hypothetical retort, thermodynamic modeling showed that oxy-sulfate compounds form with mercury such that mercury vapor does not become the dominant species until 600°C, and mercury is not released from the sludge until the process temperature is >400°C (Figure 5). In the absence of oxygen, mercury vapor dominates at temperatures <500°C and the release of mercury from the sludge starts around 130°C. Under partial vacuum, selenium is retained in the product along with commodity metals (e.g., lead, copper, gold and silver because it forms mostly nonvolatile oxide compounds below 250°C.

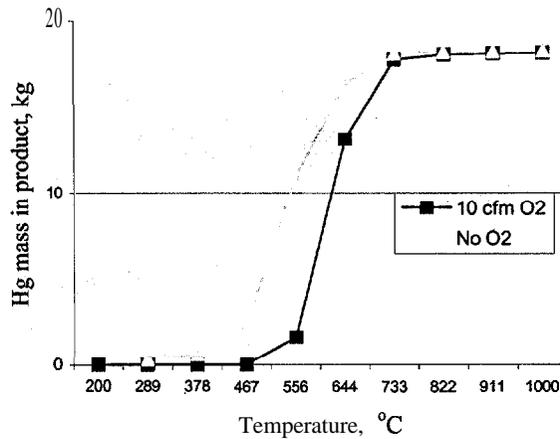


Figure 5. Comparison of mercury release with and without oxygen

SepraDyne system (low air flow rate)

Researchers modeled performance of the SepraDyne process using FLOW to import results from HSC (Figure 6). The system operates at 600°C and maintains a high vacuum with low gas flow rates that are difficult to measure. Researchers estimated air in-leakage by calibrating the mercury content of the product with the air in-leakage (Figure 4). Iterative mass balance calculations converged on the air in-leakage given a concentration of 280 mg/kg mercury in the product: 0.15 moles of air (-0.25 cfm).

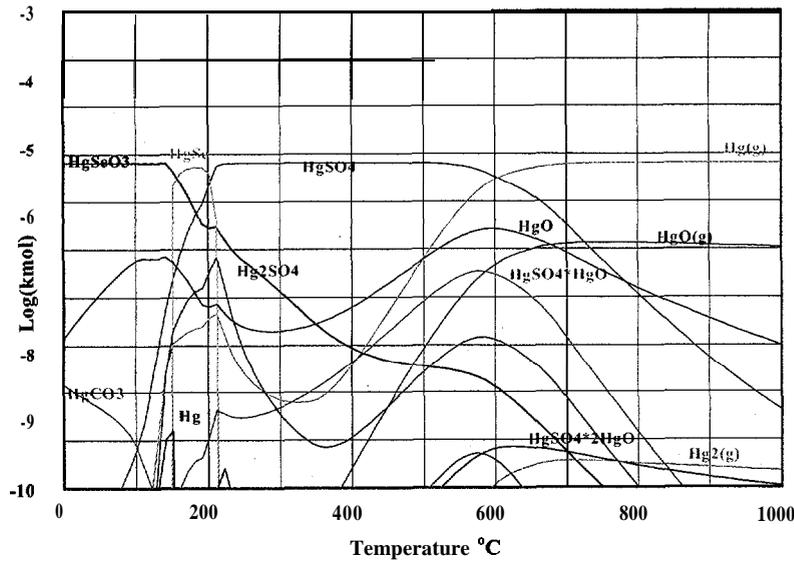
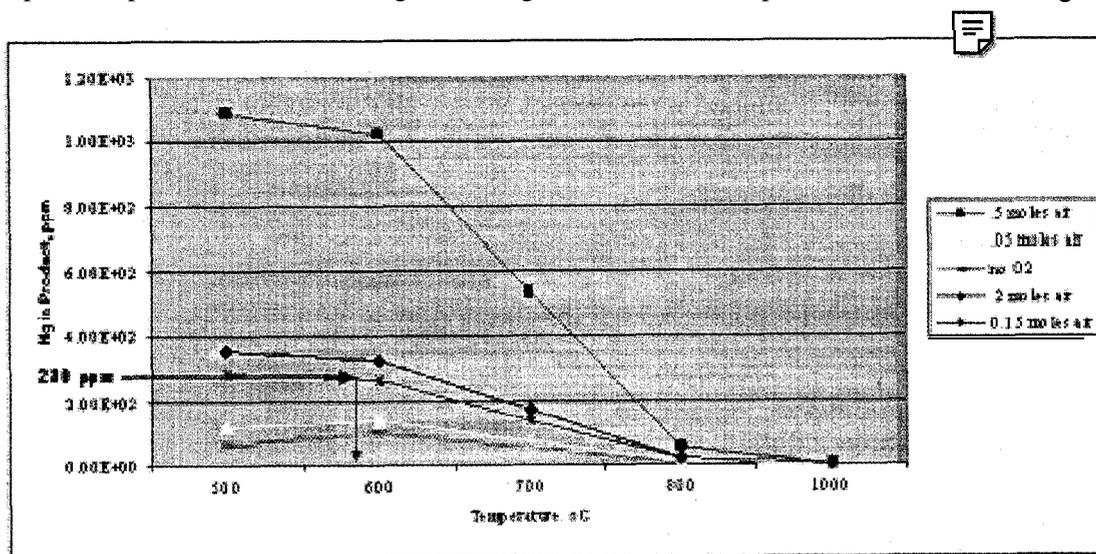


Figure 6. Thermodynamics of current operating conditions in the SepraDyne retort

These results validate the performance of the SepraDyne rotary retort as an effective mercury separation process. If air in-leakage were high, it would not be possible to obtain 280 mg/kg



Thermodynamic modeling tracks other key elements and their compounds during processing. As in the partial vacuum case, selenium forms nonvolatile oxides that report to the product, but also form volatile species including mercury selenide (HgSe) at temperatures ranging from 175 to 300°C . These low oxygen levels allow the formation of HgSe to dominate at around $175\text{--}220^\circ\text{C}$ so that formation of Se species overlaps formation of Hg species. The Se in the off-gas collection system allows the recombination of Fe oxides to predominant, indicating sulfate decomposition at higher temperature, which would complicate the off-gas treatment system and promote species recombining with mercury vapor.

Increased reducing potential represented by carbon addition

Analysis of the presence of oxygen in the system reveals the importance operating the retort system in a reducing environment (devoid of oxygen). Based on model results, adding carbon to the feed could improve operations by consuming available oxygen and providing a reducing environment to improve separation of mercury and selenium. As carbon is increased there is shift from the formation of nonvolatile mercury compounds to more volatile Hg compounds and a reduction in the temperature needed to remove Hg from the acid blowdown sludge. When the concentration of carbon approaches the stoichiometric balance with oxygen in-leakage, the temperature at which mercury volatilizes and mercury vapor predominates starts to drop. Model results indicate at temperatures as low as 100°C , mercury separation would be improved by adding carbon to the feed. At higher temperatures the effect is more dramatic-the reducing environment prevents oxidization of metals and the formation of complex chemical compounds-simplifying the composition of the off-gas stream (Figure 8).

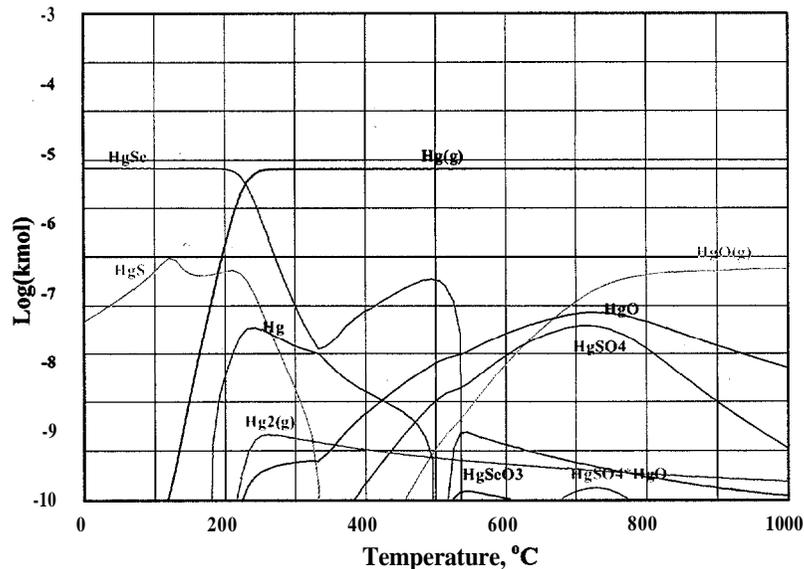


Figure 8. Thermodynamics of reaction system in the presence of carbon.

If the retort were operated under reducing conditions, the concentration of mercury in the product would be lower at lower temperatures (see Figure 9). Addition of carbon also improves the separation of metals. Model results show that the proper concentration of carbon could prevent formation of compounds of Hg-O-Se, causing mercury and selenium to separate at different temperatures (Figure 10). Mercury is separated at approximately 300°C while selenium is separated at about 790°C . These thermodynamic properties could be exploited to effectively separate both metals resulting in a more pure mercury off-gas stream and a product with or without selenium, depending on the requirements for product purity.

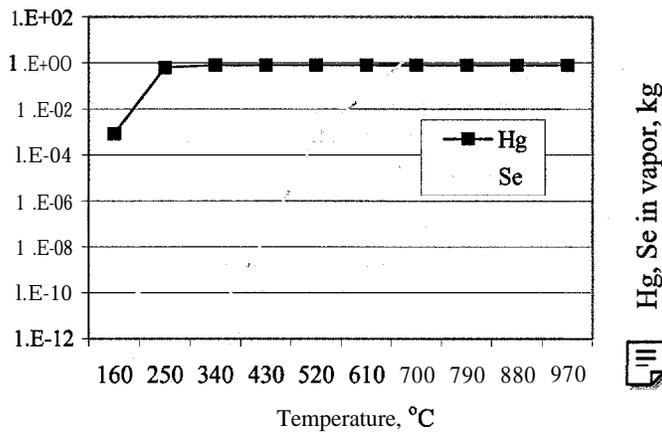


Figure 9. Improved separation reduces concentration of mercury in the product

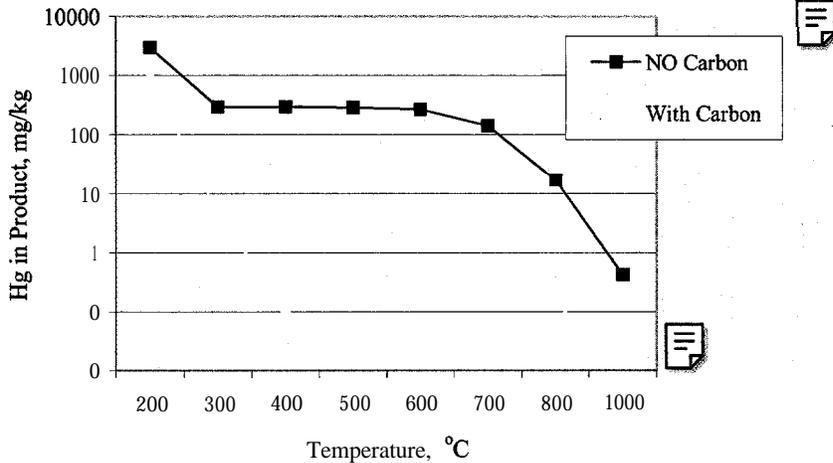


Figure 10. Carbon improves separation of Hg and Se.

Conclusions

The vacuum-retort system, patented by a small U.S. business, **SepraDyne**, improves separation of mercury from acid plant blow-down sludge when compared to systems that allow greater airflow. The Colorado School of Mines (CSM) conducted experiments confirming improved volatilization of elemental mercury under high vacuum. CSM researchers conducted experiments collecting physical property data on Hg-O-S and Hg-Se-O systems. Oak Ridge National Laboratory (ORNL) researchers used these data to model the process. Detailed thermodynamic and mass balance modeling collaborated and provides a theoretical basis for these findings.

Process modeling was supported by field investigation and evaluation of the process. Researchers prepared a sampling plan and conducted a sampling campaign to provide data for a global mass balances. Initial modeling included assumptions regarding the extent of airflow through the vacuum seal and the extent of solids entrainment in the gas stream that exists the



retort. Iterative calculations using FLOW allowed researchers to “close” the material balance and corroborate sampling and modeling results.

A reducing environment provides a clear advantage in elemental mercury separation. Addition of carbon would prevent formation of compounds of mercury and oxygen in the complex mixture of chemicals in acid plant blow-down sludge. By carbon to the system, the temperature at which mercury volatilizes could be reduced by 375°C. This reduction in temperature saves energy and reduces the potential for corrosion of the retort vessel because of sulfuric acid. By controlling the reduction reactions, selenium can be separated at higher temperatures than mercury allowing more effective process control.

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