SUSTAINABLE PRODUCTION IN THE MINING INDUSTRY: BY-PRODUCT RECOVERY

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ABSTRACT

The U.S. mining industry produces over 7,000,000 tons/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. [1] The right technology may be able to recover marketable by-products from this process residue to generate revenue and reduce disposal costs for the mining industry. In fact, such a technology was invented by a small U.S. business, SepraDyne, and is being developed and commercialized at an Arizona copper mine to treat smelter off-gas cleaning sludge. The process separates mercury from lead, copper, gold and silver so the residue is either recycled to recover additional copper or sold to recover lead, bismuth, and trace gold and silver. [2]

The following paper reviews the processing steps used to mine and refine copper at this particular location in Arizona. This overview provides background for understanding the source of the process residue being treated by SepraDyne – smelter off-gas cleaning sludge called acid plant blow-down. Mineral-rich process residues generated by copper refining step may also be amenable to by-product recovery. The paper describes the SepraDyne process—the high vacuum, indirectly heated, rotary kiln operates at temperatures up to 750°C. The paper also summarizes factors that influence the economics of by-product recovery. If, for example, 30% of the industry's residues were to be processed, then mercury removal could generate $400M/year in revenue from the recovered metals, and avoid $1B in waste disposal and energy costs.

Based on recommendations from the National Mining Association, the U.S. Department of Energy and SepraDyne have recently initiated jointly funded research and development of this process at Oak Ridge National Laboratory.

INTRODUCTION

The U.S. Department of Energy (DOE) Office of Industrial Technologies, and the Mining Industry of the Future are working with the mining industry to continue the industry's advances toward environmental and economic goals. Two of these goals are (a) responsible emission and by-product management and (b) low cost and efficient production. (3) Oak Ridge National Laboratory, in collaboration with the Colorado School of Mines, is working with the mining industry, separation-process industry, and government to develop a process that is both environmentally responsible and economically attractive—to help work toward sustainable production in the mining industry.

By-product recovery provides an opportunity for the mining industry to move toward sustainable production. SepraDyne, a small U.S. business, has patented a technological breakthrough that is advancing by-product utilization. The technology uses an improved separation process to recover metals from mining process residue. The heart of the process is an indirectly heated, rotary kiln that operates in a vacuum at high temperature. These conditions produce the ideal 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.

The operating conditions create unique process advantages. Because the unit is heated indirectly and operates under a vacuum, the treated material is not mixed with combustion gases as in incineration. This means that the process does not require large-scale equipment for treating process off-gas. The vacuum provides an additional advantage: equipment failure modes are inherently safe. Since the retort rotates, process residues are thoroughly mixed ensuring that volatile species are exposed to the operating temperature. The process is not regulated under the Resource Conservation and Recovery Act (RCRA) because products are recycled instead of becoming waste. These process advantages can translate into improved economic viability for recovery of mining by-products.

To realize the potential of this technology, DOE and SepraDyne have recently initiated co-funded work at Oak Ridge National Laboratory and the Colorado School of Mines. The purpose of this work is to (a) identify mining process residues that would benefit from treatment using the SepraDyne process and identify the conditions that influence the economic viability of mining by-products recovery; (b) model process performance; (c) analyze the process chemistry by conducting experiments on interactions between sulfur, mercury, and oxygen; and (d) improve the process by developing materials that enhance kiln performance and longevity in highly corrosive operating environments.

This work should enhance the market for separation-technology companies and related mining service industries, advance technological innovation and its transfer to industry. Full deployment of this technology should reduce hazardous wastes and damage to the environment. By optimizing the SepraDyne process, this work will generate revenues for mining companies by increasing the sale of valuable by-products and this work will reduce their costs for energy and waste disposal—thus contributing to more sustainable production in the mining industry. This paper covers the following topics:

- copper mining operations of the particular region in Arizona including identification of major products, process residues, and the source of treated process residue,
- the traditional residue treatment technique and the SepraDyne process,
- parameters that influence the economic viability of mining by-products recovery, and
- additional mining residue that may be amenable to SepraDyne processing.

OVERVIEW OF COPPER MINING OPERATIONS

The United States currently holds 16% of the world's refined copper reserves in 33 active mines. In addition to the 13 copper mines located in Arizona, copper mines are operated in New Mexico, Utah, Michigan, Montana. One of these Arizona mines hosts the SepraDyne by-product recovery system. An overview of copper mining operations provides background for the analysis of process residues that are candidates for by-product recovery (see Fig. 1). [4, 5]

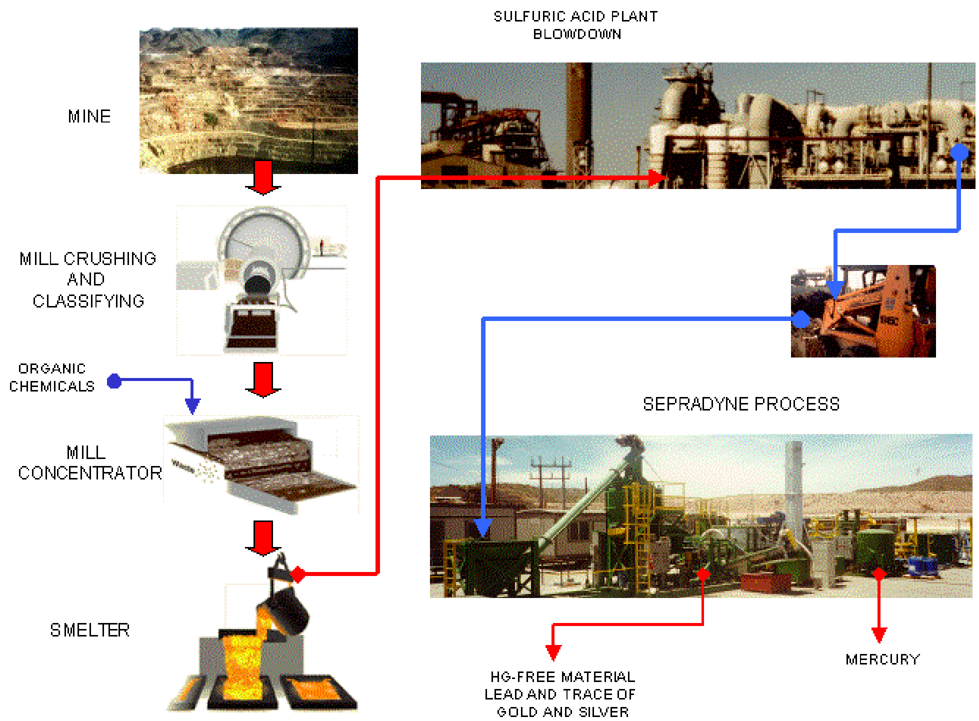

Figure 1. Copper Mining and By-Product Recovery

Ore Mining

There are three basic methods of extracting copper ore: surface, underground, and solution mining. Representing 83% of domestic mining capacity, open-pit mining is the predominant method used today by the U.S. copper mining industry. However, solution mining of copper oxide and sulfide ores has increased since 1975. In this method, dilute sulfuric acid is percolated through or contained in formerly active mining sites including dumps, leach pads, or underground broken rubble. In 1991, U.S. mines leached 15.7 million metric tons of copper to recover 441,000 metric tons of copper. Approximately 75% of these facilities are in Arizona.

Leaching

Leaching methods include dump, heap, and vat leaching techniques, as well as underground (or in situ) leaching methods. Leaching of ores and concentrates is limited to acid-soluble ore oxides that are not associated with calcite rock that consumes acid. A variety of techniques are used to extract copper – some ore is roasted or calcified before leaching while other ore is subjected to microbial leaching. Copper is recovered from leach solutions through precipitation or by solvent extraction/electrowinning. Solvent extraction is typically preferred over ion exchange to extract copper from the leachate (weak sulfuric acid solutions). The organic solvent is separated in a settler and stripped with concentrated sulfuric acid to produce a clean, high-grade solution of copper for electrowinning.

Electrowinning

Electrowinning uses inert anodes made of lead or stainless steel to produce the final copper product. The electrochemical reaction at the lead-based anodes produces oxygen gas and sulfuric acid by electrolysis. Copper is plated on cathodes of stainless steel or on thin-copper sheets. In addition, molybdenum and precious metals are recovered in the sulfuric acid by-product that is called "anode slimes."

Beneficiation Operations

Beneficiation includes several steps that extract and concentrate the copper contained in raw ore. The beneficiation method(s) selected varies with mining operations and depends on ore characteristics and process economics and can include:

- Sizing and classification: crushing, grinding; washing; filtration; sorting; sizing; gravity concentration;
- Concentration: froth flotation; ion exchange; solvent extraction; electrowinning; precipitation; amalgamation; roasting; autoclaving; chlorination.

Sizing and Classification. A conventional milling and flotation process is used for copper sulfide ores. Crushing and grinding are followed by sequential size reduction stages, normally accomplished by a jaw or gyratory crusher. Secondary and tertiary crushing usually are performed in surface facilities in cone crushers, although roll crushing or hammer mills are sometimes used. Grizzlies and screens control the size of the feed material between the crushing and grinding stages. Most copper facilities use a combination of rod and ball mills to grind sulfide ore. Typically, crushed ore and water enter the rod mill so that material of a specific size is suspended in the slurry. Oversized material passes to the ball mill for additional grinding. After grinding, ore slurry is classified according to particle size between 20 and 200 mesh using equipment such as a hydrocyclone. Undersized material moves to the next phase of beneficiation.

Concentration. U.S. mines concentrate about 75% of their copper sulfide by operating 11 froth flotation concentrators in Arizona and New Mexico. Flotation cells keep the particles in suspension through chemical reaction and agitation. Chemical reagents make the copper minerals hydrophobic without affecting the other minerals. These reagents are targeted to specific ores. For example, typical copper froth collection reagents are ethylxantate, amylxantate, thionocarbamate, while froth reagents for molybdenum copper ore are ethylxantate, alkyl dithiophosphate, fuel oil, kerosene. The reaction between sulfide minerals and sulfide collectors (such as xanthates) results in insoluble metal xantathes that are strongly hydrophobic. Copper sulfide mineral reacts to form a surface covered with air-avid hydrocarbon non-polar ends seeking an air bubble attachment.

Air is pumped through the solution to produce a bubbly froth. The hydrophobic copper particles are attracted to these air bubbles—these particles float to the top of the cell and overflow for collection. Un-reacted minerals sink to the bottom of the cell and are removed for disposal. The separation of different types of minerals in the ore is a delicate operation—continued monitoring of the ore feed mineralogy is critical to maintain steady-state control of the flotation units.

Smelting

Smelting is a critical step in copper refining. The product of flotation, copper mineral concentrate, contains 60–80% water. This concentrate is thickened, using a flocculent such as a polymer or nonionic surfactant, and filtered, using disc or drum filters, producing a relatively dry product. This copper concentrate is processed in a smelter that uses a series of furnaces to burn off and separate non-copper material.

The smelter furnace generates sulfur dioxide ($S0_2$) gas and produces two separate molten streams: copper-iron-sulfide matte, and slag. The copper-iron-sulfide is sent on to converters, where a silica flux and compressed air or oxygen are used to remove the iron and sulfur, respectively, leaving blister copper that is ~99 % copper. The blister copper produced by the converter is the cast into anodes for electrolytic refining (i.e., electrowinning).

Acid Plant

The smelting process generates off-gas that is10% sulfur dioxide. The sulfur dioxide is retained and processed to make a sulfuric acid by-product. The off-gas is sprayed with water, cooled, cleaned, dried, and processed 4 times in a catalytic converter. These steps convert the sulfur dioxide to sulfur trioxide (SO_3) that is combined with water (H_20) to make sulfuric acid (H_2SO_4). This sulfuric acid by-product is used in numerous mining operations.

Acid Plant Blow-Down

The sulfur dioxide gas generated by smelting operations is collected to produce sulfuric acid. In a two-stage cleaning process, the impurities are removed from the gas stream. During the first stage, the gases are routed through bag-houses to remove coarse entrained particulate matter (i.e., bag-house dust). In the second stage, remaining entrained solids are removed using a wet scrubbing process. The process re-circulates most of the scrubber water, however, a small percentage of the stream must be purged (i.e., blow down) periodically to prevent buildup of solids and to minimize corrosion of the scrubber systems. Copper, gold, lead, silver, and mercury can be recovered from the solids blowdown.

BY-PRODUCT RECOVERY FROM THE ACID PLANT BLOW-DOWN

Baseline Copper Operations

The Arizona facility that hosts the SepraDyne process also hosts complex, linked copper processing operations. The mine extracts ore in their open-pit mining and in-situ leaching operations. After grinding and crushing, copper sulfide is concentrated using two froth flotation systems. Copper is refined in the on-site solvent extraction-electrowinning plant that produced 65,000 tons of copper in 1996, a 173,000 ton-per-year electrolytic refinery, and a 135,000 ton-per-year rod plant that produced 125,000 tons of copper rod in 1996. Also in 1996, the 650,000 ton-per-year capacity smelter processed 633,000 tons of copper concentrates. The smelter is linked to an acid recovery plant that produces sulfuric acid from smelter gaseous waste. This process residue, called acid plant blow-down residue, is an excellent candidate for by-product recovery. Combined smelter and refinery operations make the facility efficient and self-sufficient as further evidenced by the improved efficiency gained from recovery of by-products from the acid plant blow-down.

Acid plant blow-down contains lead, copper, and bismuth, as well as trace quantities of gold, silver, and mercury sulfide.[2] A traditional baking method was used to reduce the concentration of mercury to acceptable disposal levels for Resource Conservation and Recovery Act (RCRA)-regulated waste. The acid plant blow-down 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 (i.e., >60 ppm), the valuable lead and copper could not be recovered.[6]

SepraDyne Process and By-product Recovery

A small U.S business has invented a technology breakthrough that is significantly advancing by-product utilization by recovering minerals from process residue that could otherwise be RCRA-regulated waste. Marketable minerals are recovered on the site with compact processing equipment that is easily deployed.

The heart of the process is an indirectly heated rotary kiln that operates at a high vacuum and high temperature. These conditions produce an environment that volatilizes water 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 equipment is minimized. The vacuum system has the following advantages over traditional thermal processes:

(a) easier to site and permit because air pollution is reduced;
(b) products of incomplete combustion such as dioxins and furans are not produced because of the reduced oxygen in the processing environment;
(c) complex off gas treatment systems are not needed making the process compact while reducing capital and maintenance costs;
(d) material that would have become air pollution is recovered; and
(e) dust and particulate formation is minimized.

The operating parameters and processing sequence of the rotary vacuum retort (illustrated in Fig. 2) is as follows. Solid or semi-solid waste 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 by an arrangement of burners fueled by natural gas, diesel oil or propane. Alternately, electric heating can be employed in highly sensitive environmental settings, or on sites with low cost electric power. The waste 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 organics are present, cryogenic cooling can be employed to condense these chemicals. Alternately, gaseous reactants can be introduced to convert the retort off-gases to useful products.

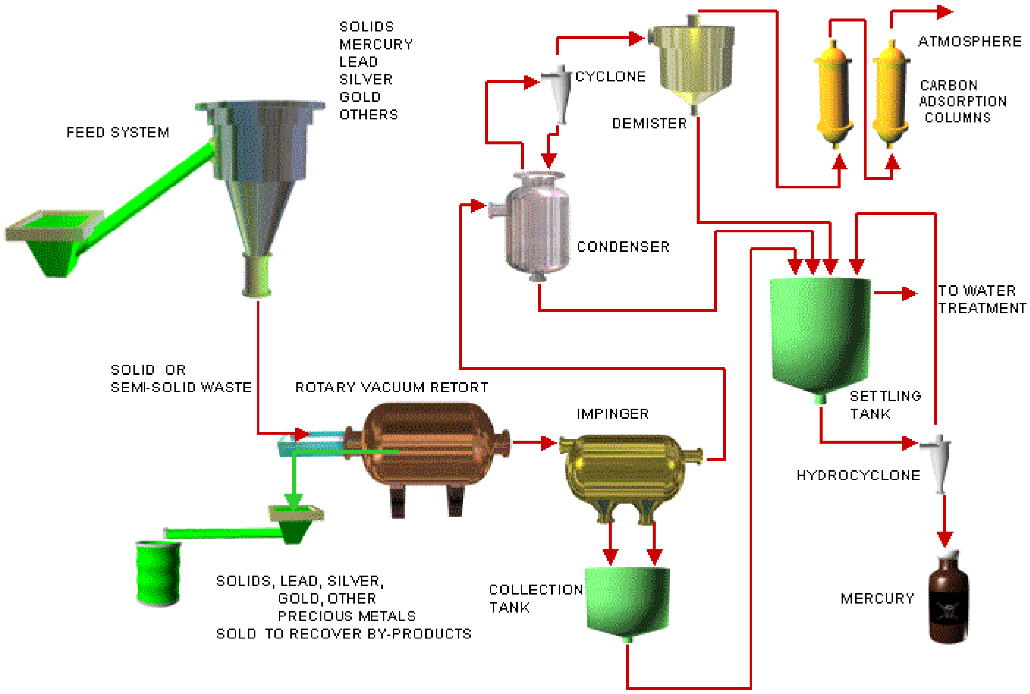

Fig. 2. Sepradyne separation process.

Once the material is dried, the retort temperature is raised to the target value, at temperatures up to 600°C to 750°C, under a vacuum of greater than 0.7 at (20" of Hg) and held at the target temperature for a set time. All additional organic compounds including heavy tars and all compounds of mercury will volatilize under these conditions. Chemicals are separated from the condensed water through traditional or proprietary methods and the water is discharged to on-site wastewater treatments systems or the sanitary sewer. Waste heat from the process is exhausted to the atmosphere. Any trace amounts of hazardous vapors that have passed through the off-gas system are removed in the carbon absorption section. Mercury is recovered from the settling tank.

The condensed concentrated liquids, some of which may be valuable feedstock materials, might also be recovered for heat value, oxidized in an afterburner or disposed of in an approved manner. 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 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. [6] Oak Ridge National Laboratory researchers are modeling this system using object-oriented software, FLOW™, so we can analyze the effect of changing process equipment and operating parameters including the composition of the feed stream.

Process Chemistry

Acid plant blow-down contains high concentrations of sulfur. It is important to understand interactions between sulfur, oxygen, and mercury to better control the process and optimize the removal of mercury. Based on previous experiments [7], the Colorado School of Mines was contracted to conduct experiments on the chemistry of Hg-S-O system specific to removal of mercury from acid plant blow-down. Demonstrations to date have shown that operating conditions can dramatically influence process effectiveness.

ECONOMICS OF BY-PRODUCT RECOVERY

This acid plant blow-down contains lead and copper, as well as trace quantities of mercury sulfide. It is difficult for mines to recover the value of this acid plant blow-down because it is contaminated with mercury. When the concentration of lead and copper exceed a certain value, brokers may purchase this contaminated process residue and aggressively treat it to recover the value of the lead and copper. If this additional treatment is not cost effective, the residue must be disposed at a cost. If the value of the acid plant blow-down is less than the cost of mercury removal to < 60 ppm, by-product recovery generates revenue for the acid plant operator—and consequently for the mining operation (see Table I).

Table I. Value of treated acid plant blow-down

Concentration of Mercury in Process Residue	Market Value	Disposal Cost
Residue 1. Mercury < 60 ppm	Sell to lead smelter	Non-RCRA
Residue 2. Mercury > 60 ppm	Sell to waste broker	RCRA waste
Residue 1 minus Residue 2 (value of treated acid plant blow-down)	Positive value to acid plant operator	Cost avoidance for acid plant operator

The potential to generate revenue and avoid cost by removing mercury from the large quantity of mining process residue is significant. The mining industry annual generation of process residues is (a) 5,500,000 tons generated by smelter exhaust gas cleaning; and (b) 2,100,000 tons generated from bag house dust and waste water treatment. (1) If, for example, 30% of the industry's residues were to be processed, then mercury removal could generate $400M/year in revenue from the recovered metals, and avoid $1B in waste disposal and energy costs.

Oak Ridge National Laboratory researchers are collecting and analyzing data on U.S. mining process residues to understand if the industry can realize increased revenues and savings by using the SepraDyne process. We plan to apply economic decision criteria to these data; however, detailed data are not readily available and may be proprietary. One of our project's major challenges is to obtain data on mining process residues that can be published.

Economic Decision Criteria

1) Concentration of mercury in:
- **a) ore**
- **b) process residue**

2) Concentration of marketable minerals in:
- **a) ore**
- **b) process residue**

3) Concentration of contaminants such as selenium and organic chemicals that lower the market value of other process residue.

4) Market price of process residue with and without mercury (or other contaminants) removed

5) Cost of non-marketed residuals disposal
- **a) with contaminants removed**
- **b) without contaminants removed**

6) Cost of mercury removal

ADDITIONAL BY-PRODUCT RECOVERY

Concentration and refining of copper produces numerous process residue streams that contain relatively high concentrations of valuable by-products such as lead and copper. Organic chemical reagents are added as frothing agents to the concentration step of beneficiation. These organic chemicals could be destroyed by the high-temperature, rotary retort invented by SepraDyne. Electrowinning concentrates molybdenum and precious metals in a sulfuric acid by-product that is called "anode slimes" or "tank house slimes." These slimes also contain selenium and other hazardous minerals. The application of the SepraDyne process to these mining process residues will be evaluated using the Oak Ridge National Laboratory FLOW™ process model. The process model will be used to direct future development work to those process residues with combinations of hazardous constituents that can be separated or destroyed and valuable mineral by-products that can be economically recovered.

CONCLUSIONS

The SepraDyne process, 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 an Arizona mining complex that includes open-pit mining and leaching copper removal operations, smelting, and acid recovery. The acid plant blow-down solids have an economic value that is now being realized— traditional technologies were less economical in reducing concentrations of mercury to levels which allowed this process residue to be sold or recycled. By economically removing the mercury, valuable lead, copper, gold and silver can be recovered.

Oak Ridge National Laboratory is assisting SepraDyne in researching and developing this technology by: (a) better understanding the economics of by-product recovery; (b) modeling and analyzing the process; (c) subcontracting with the Colorado School of Mines to conduct experiments on the process chemistry that includes complex interactions of mercury-sulfur-oxygen; and (d) developing metals alloys that will be more corrosion-resistant materials of construction. The DOE, Office of Industrial Technologies, Mining Industry of the Future (see http://www.oit.doe.gov/), is co-funding this work based on the recommendations from the National Mining Association. This technology has potential to be extended throughout the industry to recovery by-products from additional process residues, thereby reducing costs and returning revenue to the U.S. mining industry.

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