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# SUSTAINABLE BY-PRODUCT RECOVERY IN THE MINING INDUSTRY

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## ABSTRACT

The U.S. mining industry produces over 7,000,000 tonnes/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 tonnes/yr; and (b) bag house dust and wastewater treatment—2,100,000 tonnes/yr (U.S. Environmental Protection Agency, 1995). 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 has been commercialized at an Arizona copper mine to treat smelter off-gas scrubber 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 (U.S. Environmental Protection Agency, 1991).

The following paper reviews the processing steps used to mine and refine copper at this Arizona facility. This overview provides background for understanding the source of the process residue being treated by SepraDyne—smelter off-gas cleaning sludge, called "acid plant sludge." The paper describes the SepraDyne system—a high-vacuum, indirectly heated rotary kiln that operates at temperatures of 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 treated, at a treatment cost of $1,000/tonne, mercury removal could generate $400 million/yr in revenue from the recovered metals, avoid over $80 million/yr in waste disposal costs, and contribute to energy savings.

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.

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## 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 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 (U.S. Department of Energy, 1998). Oak Ridge National Laboratory 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 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 have recently initiated co-funded work at Oak Ridge National Laboratory, in collaboration with the Colorado School of Mines and the University of Arizona. 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 paper documents progress on tasks (a) and (b) by covering the following topics:

- copper mining operations at the Arizona facility that hosts the SepraDyne process, including the source of major products, process residues, and treated process residue;
- the traditional residue treatment technique and the SepraDyne process; and
- preliminary analysis of the economic viability of mining by-products recovery.

## 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, and Montana. One of these Arizona mines hosts the SepraDyne by-product recovery system. This facility also hosts complex, linked copper processing operations. Combined smelter and refinery operations make the facility efficient and self-sufficient. Additional efficiency gains are realized because by-products are recovered from acid plant sludge. An overview of these copper mining operations provides background for the analysis of process residues that are candidates for by-product recovery (see Fig. 1), (U.S. Environmental Protection Agency, 1994 and U.S. Department of Energy, 1980).

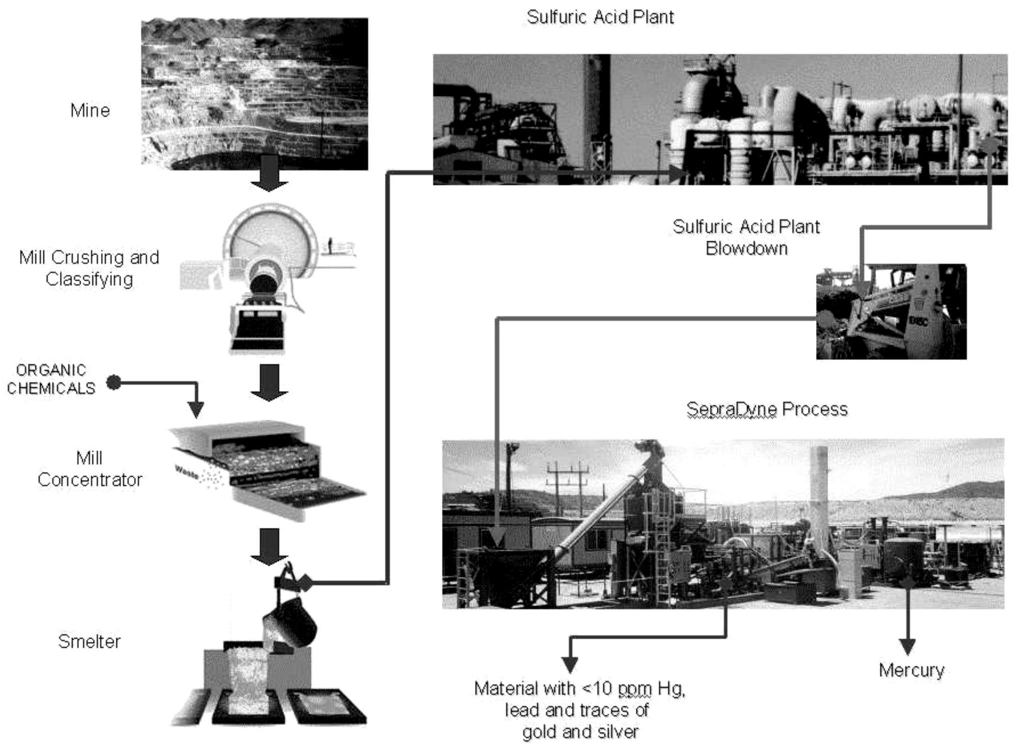



Figure 1. Copper mining and by-product recovery.

## Ore Mining

There are three basic methods of extracting copper ore: surface, underground, and solution mining. Representing 83% of domestic mining capacity, surface 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 1991, U.S. mines leached 15.7 million tonnes of copper ore to recover 441,000 metric tonnes of copper. Approximately 75% of these facilities are in Arizona. The Arizona facility that hosts the SepraDyne process extracts ore in both open-pit mining and in-situ leaching operations. This ore contains mercury (Hg) in the form of cinnabar (HgS).

## 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. 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.

**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. Methods include the following:

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

***Sizing and classification.*** Crushing and grinding are sequential size-reduction stages. Secondary and tertiary crushing are performed in cone crushers, roll crushers or hammer mills. 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. 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. The Arizona facility that hosts the SepraDyne process concentrates copper sulfide using two froth flotation systems. Flotation cells keep the particles in suspension through chemical reaction and agitation. The reaction between sulfide minerals and sulfide collectors (such as xanthates) results in insoluble metal xanthates that are strongly hydrophobic. The hydrophobic copper particles are attracted to air bubbles—these particles float to the top of the cell and overflow for collection. Minerals that are not reacted sink to the bottom of the cell and are removed for disposal.

***Electrowinning.*** Electrowinning uses inert anodes made of lead or stainless steel to produce the final copper product. Copper is plated on cathodes of stainless steel or on thin-copper sheets. The Arizona facility that hosts the SepraDyne by-product recovery operation also includes extensive electrowinning processing. Copper is refined in the on-site solvent extraction-electrowinning plant that produced 65,000 tonnes of copper in 1996 and a 173,000 tonne-per-year electrolytic refinery. This facility includes a 135,000 tonne-per-year rod plant that produced 125,000 tonnes of copper rod in 1996. Concentration of copper produces a sulfuric acid by-product, anode or tank-house slime, that contains molybdenum and precious metals.

**Smelting**

Smelting is a critical step in copper refining. The product of flotation, copper mineral concentrate, contains 60–80% water. After filtration a relatively dry copper concentrate is processed in a smelter. The smelter at the Arizona facility is patented in conjunction with the Mount Isa (from Mt. Isa in Australia) smelting process. Following ignition of the combustible fluid, the process propagates with exothermic reactions in the ores. Hot gases are vented to the acid plant via draft fans pulling at 5,000 rpm and moving nearly 3,900 $m^3$/min (138,000 $ft^3$/min). The smelter is capable of producing 900 tonne/day of copper anodes.

In 1996, the 650,000-tonne-per-year-capacity smelter processed 633,000 tonnes of copper concentrates. The smelter 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 then cast into anodes for electrolytic refining (i.e., electrowinning).

The sulfur dioxide gas generated by the 1,150°C smelting process potentially contains inorganic molecules of iron, lead, copper, cadmium, mercury, bismuth and selenium. Common ionic species include sulfites ($SO_3$), sulfates ($SO_4$), and chlorides. Typically, there are also trace quantities of hydrocarbons and precious metals present in the gas stream. In a two-stage cleaning process, 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 solids that are entrained in the off-gas are transferred to the acid plant to produce sulfuric acid (J. B. Berry and H. Patton, 2000).

**Acid Plant**

Sulfur generated by the smelting process is retained and processed to make a sulfuric acid by-product. The acid plant consists of venturi scrubbers, wash towers, and electrostatic precipitators. The vapor stream entering the acid plant is fed counter-flow through a spray of diluted sulfuric acid in the scrubbers. The scrubbers produce a large quantity of wet solids. The gas stream exiting the scrubbers is fed to the wash towers. Again, the vapor stream is fed counter-flow through a spray of sulfuric acid acting as a scrubber. The wash towers also produce a wet solid, which is fed via slurry pumps to a storage tank. The process re-circulates most of the scrubber water, however, a small percentage of the stream must be purged (i.e., blown down) periodically to prevent buildup of solids and to minimize corrosion of the scrubber systems. The vapor stream leaving the wash towers enters a series of electrostatic precipitators. The $SO_3$ contained in the gas is converted to $SO_4$ using vanadium pentoxide ($V_2O_5$) at 430°C (J. B. Berry and H. Patton, 2000).

**Process Residues**

The wet solids collected in the acid plant storage tank are periodically pumped to the filter press to separate the liquid. Liquid is pumped to a holding pond and solids, termed acid plant sludge, are stored in ambient conditions on a solar pad. Since the Arizona mine typically receives only 6 inches of precipitation each year, periodic rain or snow has little affect on the liquid content. The acid plant sludge is moved via front-end loader to an uncovered storage bunker. The composition of this material remains relatively stable because composition is process dependent and the process is not changed. The SepraDyne process separates mercury from the acid plant sludge so that copper, gold, lead, and silver can be recovered from the sludge.

## BY-PRODUCT RECOVERY FROM THE ACID PLANT SLUDGE

### Baseline Copper Operations

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; J. B. Berry and H. Patton, 2000). A traditional baking method was used 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 (i.e., >60 ppm), the valuable lead and copper could not be recovered (J. B. Berry and J. Talburt, 1999).

### By-product Recovery Process

SepraDyne has invented a technology breakthrough that is significantly advancing by-product utilization by recovering minerals from process residue—mercury is removed to <10 ppm. Marketable minerals are recovered from acid plant sludge that is generated on site with compact processing equipment that was easily deployed on the Arizona mining site.

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:

- It is easier to site and permit because air pollution is eliminated or reduced.
- Products of incomplete combustion, such as dioxins and furans, are not produced because of the reduced oxygen in the processing environment.
- Complex off-gas treatment systems are not needed, making the process compact while reducing capital and maintenance costs.
- Dust and particulate formation is minimized.

The operating parameters and processing sequence of the rotary vacuum retort (illustrated in Fig. 2) are 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 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 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 organic chemicals are present, cryogenic cooling can be employed to condense these chemicals. Alternatively, gaseous reactants can be introduced to convert the retort off-gases to useful products.

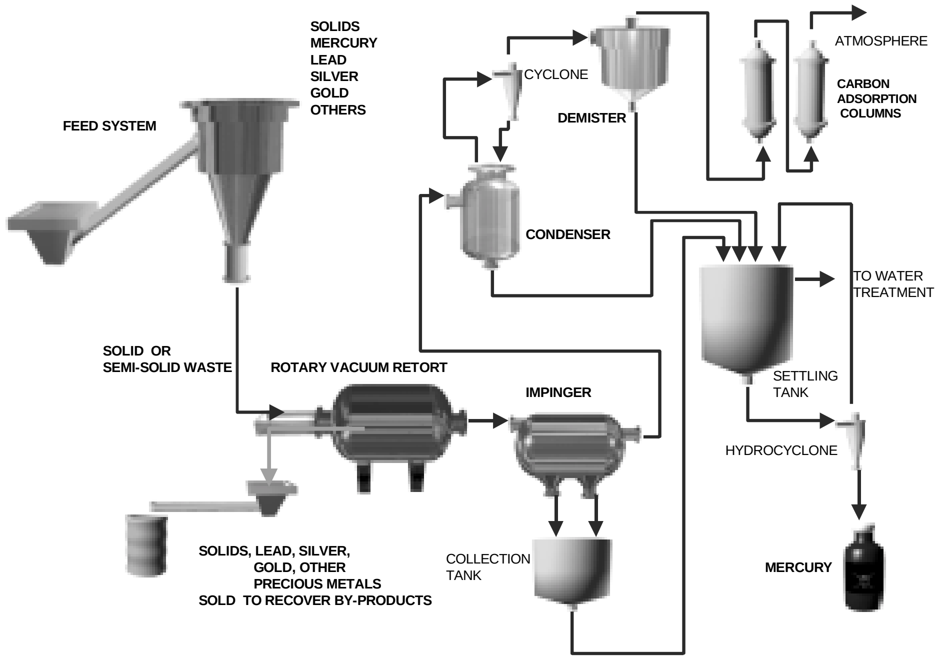



**Figure 2. SepraDyne separation process.**

Once the material is dried, the retort temperature is raised to the target value, at temperatures of up to 600°C to 750°C, 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 will 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 Arizona mines sells the material to an off-site smelter for recovery of lead and trace quantities of gold and silver. Alternately, if the 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 and Chemistry**

Oak Ridge National Laboratory researchers are modeling this system using object-oriented software, FLOW™, so we can analyze the effect of changing process equipment, including improved materials of construction, and operating parameters, including the feed stream composition. Investigations include the performance of metal alloys in the process environment.

Since acid plant sludge 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 (G. L. Fredrickson and J. P. Hager, 1996), the Colorado School of Mines was contracted to conduct experiments on the chemistry of the Hg-S-O systems specific to removal of mercury from acid plant sludge. Demonstrations to date have shown that operating conditions can dramatically influence process effectiveness. Experimental results will be incorporated into the FLOW model to demonstrate the performance of the SepraDyne system.

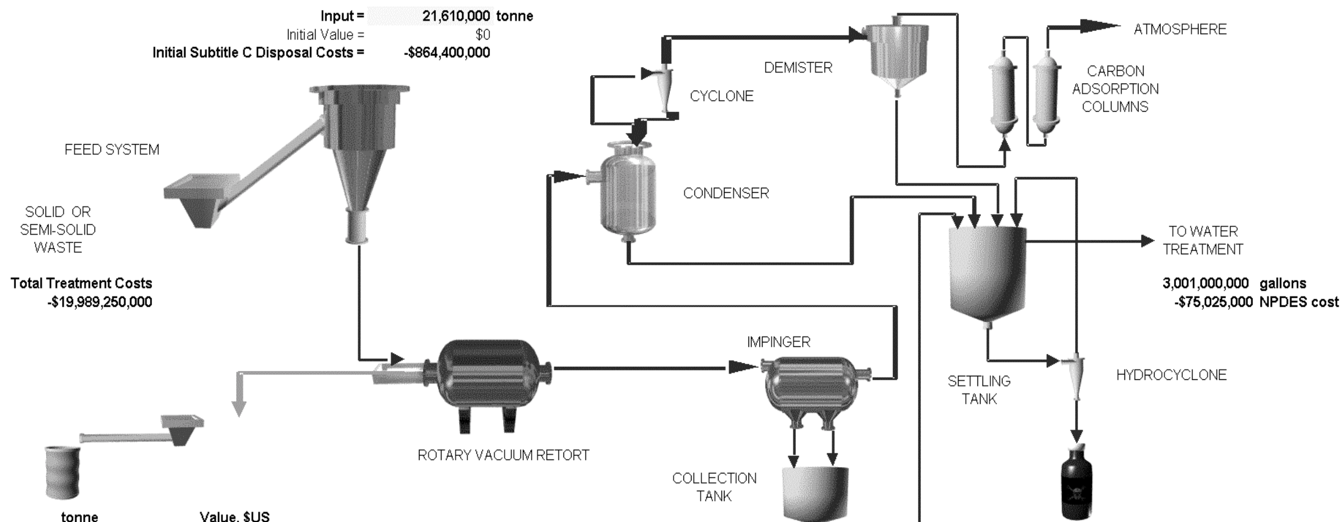
## ECONOMICS OF BY-PRODUCT RECOVERY

Acid plant sludge 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 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 lead and copper. If this additional treatment is not cost-effective, the residue must be disposed of at a cost. If the value of the acid plant sludge is less than the cost of mercury removal to <60 ppm, by-product recovery generates revenue for the acid plant operator that would normally not be available—and consequently generates revenue for the mining operation.

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; however, detailed data are not readily available and may be proprietary. Available data indicate that the mining industry's annual generation of process residues is (a) 5,500,000 tonnes generated by smelter exhaust gas cleaning; and (b) 2,100,000 tonnes generated from bag house dust and waste water treatment (U.S. Environmental Protection Agency, 1995). Using these data, Oak Ridge National Laboratory researchers analyzed the copper industry's potential to generate revenue and avoid cost by removing mercury from the large quantity of mining process residue. If, for example, 30% of the industry's residues were to be treated at a cost of $1000/tonne, mercury removal could generate $400 million/year in revenue from the sale of recovered metals, and avoid >$80 million/yr in waste disposal costs (see Fig. 3). Energy efficiency would also be improved.

## 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 an Arizona mining complex that includes open-pit




| | tonne | | Value, $US |
|---|---|---|---|
| Recycled Copper | 1,005,000 | | 1,852,000,000 |
| Recycled Lead | 8,125,000 | | 3,830,000,000 |
| Recovered Gold | 390 | | 3,492,000,000 |
| Recovered Silver | 84,500 | | 13,930,000,000 |
| Underflow Metals | 9,215,000 | $ | 23,104,000,000 |
| Recycled Mercury | 30,000 | | $157,000,000 |
| All Recovered Metals | 9,245,000 | | 23,261,000,000 |
| Subtitle D Waste | 1,031,000 | | -20,620,000 |
| Avoided Solid Waste | 20,579,000 | | $823,000,000 |

| | tonne | Value, $US |
|---|---|---|
| Recycle Metal | 9,160,000 | 5,839,000,000 |
| Recovered Precious Metal | 85,000 | 17,422,000,000 |
| Final Solid Waste Costs | 1,031,000 | -20,620,000 |
| Treatment Costs | | -19,989,250,000 |
| Waste Water Costs | 11,334,000 | -75,025,000 |
| Totals | 21,610,000 | $3,176,000,000 |
| Initial Overall Value | | -864,400,000 |
| Net Gain in Overall Value | | $4,040,000,000 |

Recycled Mercury

| tonne | Value, $US |
|---|---|
| 30,000 | $157,000,000 |

Figure 3. Cost/benefit of recycling 30% of U.S. copper industry bag house dust and acid plant sludge over 10 years.

mining and leaching copper removal operations, smelting, and acid recovery. The acid plant sludge 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.

Oak Ridge National Laboratory is assisting SepraDyne in researching and developing this technology by (a) aiding understanding of 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, which includes complex interactions of mercury-sulfur-oxygen; and (d) developing metal alloys that will be more corrosion-resistant materials of construction. If the mercury can be removed economically, valuable lead, copper, gold, and silver can be recovered, mining revenue can be generated, and waste disposal and energy costs can be reduced.

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