SUSTAINABLE RECOVERY OF BY-PRODUCTS IN THE MINING INDUSTRY

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ABSTRACT

The U.S. Department of Energy (DOE) teamed with the National Mining Association (NMA) to select research projects that could significantly benefit the mining industry. This paper describes one such project—By-Product Recovery from Mining Process Residue—that is being conducted by Oak Ridge National Laboratory (ORNL) and Colorado School of Mines engineers. This project has two objectives: (1) compiling information on the mining industry to identify process residue with by-product recovery opportunities; and (2) engineering development of an innovative by-product recovery system—the SepraDyne® process—a high vacuum, indirectly heated rotary kiln that operates at temperatures of up to 750EC.

This paper describes copper, lead and zinc mining operations in simple terms while identifying major opportunities for by-product recovery. In some cases, these process residues contain higher concentrations of minerals than the raw ore. Process residues with by-product recovery potential include:

- Copper: dust and fine particles, tailings, slag waste, and gas cleaning sludge.
- Lead: dust and fine particles, tailings, slag.
- Zinc: dust and fine particles, liquor residues, suppression of undesirable elements in solution, slag.

Favorable economics encourage market penetration. Key factors that influence the economics of by-product recovery are the value (may be negative) of the process residue before additional processing, the value of residuals and products after processing, and the processing cost.

The engineering development project improves by-product recovery for a copper mining operation—providing one example of how government and industry collaboration can result to improve mining productivity. SepraDyne® operates its rotary vacuum kiln commercially at a copper mine separating mercury from sulfuric acid plant blow down sludge. The "mercury-free" residue can be either recycled to recover additional copper or sold to recover lead, bismuth, and trace gold and silver.[1] Our collaborative research improves the process by modeling and evaluating: (1) process and thermodynamic variables, and (2) kinetics and thermodynamic experimental results from investigations of two mixtures—mercury, sulfur and oxygen, and mercury and selenium—concluding that the presence of oxygen affects separation of mercury compounds and the recovery of elemental mercury.[2]

The paper summarizes the results of this Mining By-product Recovery project: (1) copper, lead and zinc mining process residue assessments, and (2) research and development of the SepraDyne® process.

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.[3]

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.[4] The National Research Council (NRC) recently evaluated and recommended research and technology development opportunities in the mining industry.[5] By considering waste produced in the mining industry, which can range from 10wt% of the mined material to well over 99.99 percent, by-product opportunities were identified:

- tailings;
- fine particles and dust;
- dewatering and conserving water;
- suppression of undesirable elements in solution;
- removal of metals and nitrate from large volumes of wastewater; and
- solvent exchange and electrowinning (SXEW).

The NRC is also responding to a Congressional mandate by conducting "a study that will examine . . . potential alternatives for future coal waste disposal."[5] This study will evaluate the benefits of each alternative which include by-product recovery opportunities such as reducing the amount of slurry disposal needed, and options for the coal waste product to be processed further in order to produce marketable products.

These collaborative assessments highlight the importance of mining by-product recovery. The National Mining Association (NMA) and DOE's Office of Industrial Technologies has further emphasized this important area of research by asking Oak Ridge National Laboratory (ORNL) to evaluate mineral mining operations for by-product recovery opportunities. Project engineers concluded that gold mining is highly developed presenting little opportunity for additional by-product recovery. While the other mineral mining operations are also efficient, opportunities for by-product recovery may exist. For example, one mine recently started a by-product recovery project by processing tailings with concentrations of 0.1-0.7 % Cu. Compare this with copper concentrations of about 0.3-0.5-wt% in the raw ore

This paper generally describes copper, lead, and zinc mining operations. This description can form a basis for identifying process residues that contain both impurities and products, which currently cannot be economically recovered. This information could be used to develop a market-based approach to by-product recovery by evaluating potential revenue generated from the sale of by-products along with innovative recovery techniques. ORNL engineers' preliminary evaluation of mineral mining operations identified opportunities for by-product recovery in the following categories:

- Dust and fine particles
- Tailings
- Slag waste
- Gas cleaning sludge
- Liquor residues
- Suppression of undesirable elements in solution

COPPER PROCESS

The United States currently holds 16% of the world's refined copper reserves in 33 active mines. Copper mines are located in Arizona, New Mexico, Utah, Michigan, and Montana.[6] Oak Ridge National Laboratory evaluated copper mining operations, as described below, and compiled flow diagrams of unit operations.[7] We prepared both detailed and simplified flow diagrams of copper mining operations and identified process residues that have by-product recovery potential as follows (see Figure 1):

- Dust and fine particles
- Tailings
- Slag waste
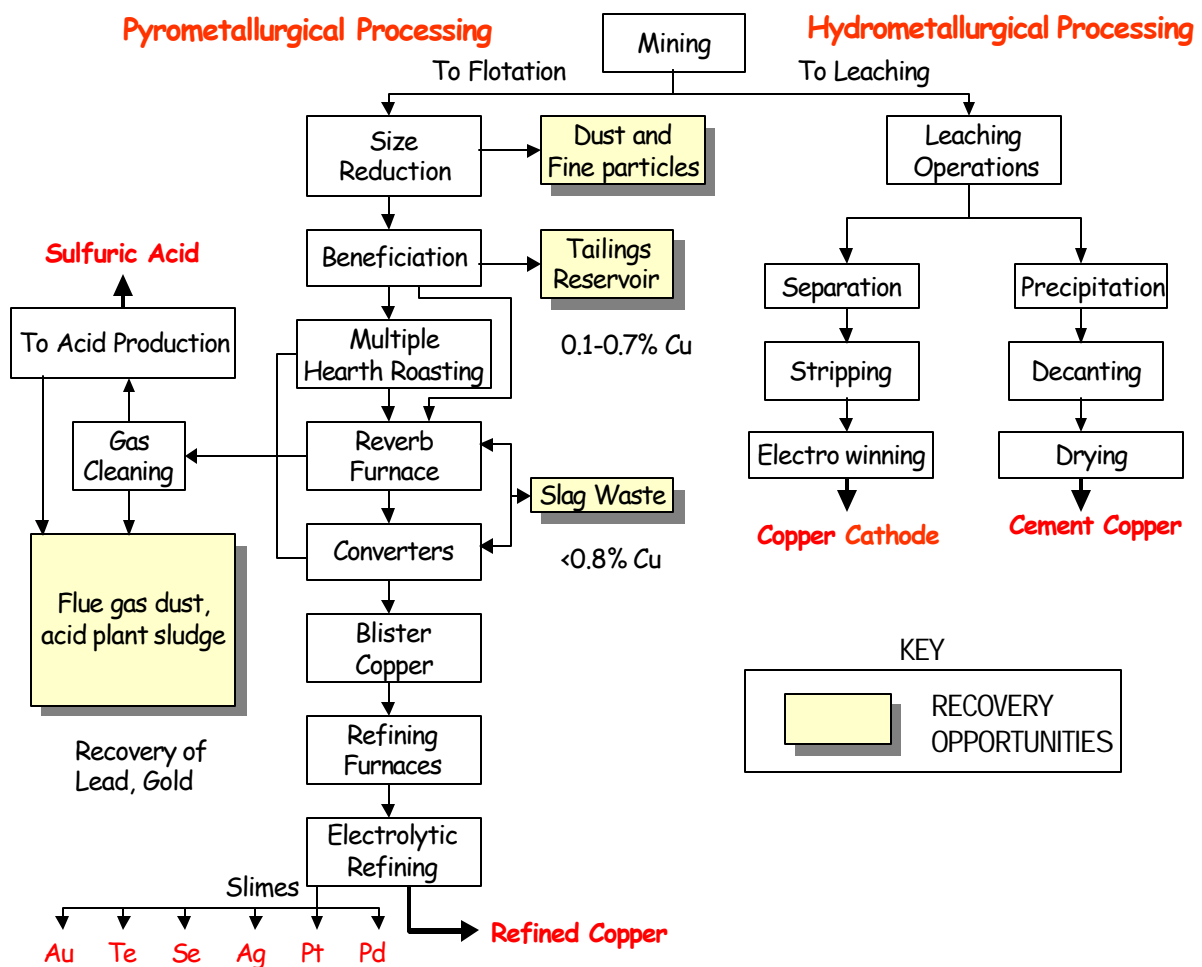- Gas cleaning sludge

Figure 1. Copper Mining Operations and By-product Recovery Opportunities.

Copper Ore Extraction

There are three basic methods of extracting copper ore: surface, underground, and solution mining.   Surface open-pit mining is the predominant method used today by the U.S. copper

mining industry, representing 83% of domestic mining capacity. Ore mined from open pits contains about 0.3-0.5-wt% Cu, typically in the sulfide form. Copper concentrations of at least 1 wt%, along with other valuable metals, are obtained from underground mines. Solution mining of copper oxide and sulfide ores has increased since 1975. In 1991, U.S. mines leached 15.7 million tons of copper ore to recover 441,000 metric tons of copper.

Hydrometallurgical Processing

The leaching process extracts copper by dissolution in sulfuric acid. This method is suitable for low-grade copper ore bodies for which customary mining operations would be uneconomical, as well as for the leaching of remnant ores from abandon mines. 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. These processes produce copper cathode and cement copper. Analysis of hydrometallurgical processing did not reveal opportunities for by-product recovery.

Pyrometallurgical Processing

About 80% of the primary copper in the world comes from low-grade or poor sulfide ores, which are usually treated by pyrometallurgical methods, generally in the following sequence:

- Beneficiation by froth flotation of ore to copper concentrate
- Optional partial roasting to obtain oxidized material or calcified material
- Two-stage pyrometallurgical extraction
  - Smelting concentrates to matte
  - Converting matte to blister copper
- Refining the crude copper, usually in two steps:
  - Pyrometallurgically to fire-refined copper
  - Electrolytically to high-purity electrolytic copper

Size Reduction and Beneficiation Operations

Lumpy ores are reduced to a pulp by crushing in jaw, gyratory, and cone crushers, then sized with vibrating screens. The wet ore is ground in rod and ball mills or, more recently, autogenously milled before particles are separated according to size using classifiers and hydro cyclones.

Most sulfide copper ores must be beneficiated to increase the metal content. The essential operation is froth flotation, which is usually carried out in two successive steps: the first is collective or bulk flotation for concentrating all the metal-containing minerals, and the second, if necessary, is selective flotation to separate various minerals. Flotation using frothers, collectors, activators, depressors, and reagents to control the pH (e.g., lime) separates the feed pulp into metal sulfide groups. In simple cases, the flotation cells are combined into three groups: (1) rougher flotation for sorting into pre-concentrate and tailings; (2) cleaner flotation for post-treatment of the pre-concentrate; and (3) scavenger flotation for post-treatment of the tailings

from the first step. The next step is solid-fluid separation using sedimentation in settlers and thickeners with subsequent vacuum filtering by drum and disk filters. The copper content of dried chalcopyrite concentrates ($CuFeS_2$) averages 20-30 wt%.

Two copper-containing materials are produced during size reduction and beneficiation operations. The first is dust and fine particles produced during the size reduction stages and the second is tailings generated by the flotation process. Some copper companies such as Magma Pinto is recovering copper from a tailings pile at its Pinto Valley operation. These tailings were deposited between 1911 and 1932. Pinto Valley hydraulically mines the tailings pile, leaches the tailings, and produces copper by using the solvent extraction/electrowinning (SX/EW) facility. After leaching and washing the tailings, the remaining slurry is pumped approximately five miles to an abandoned open copper pit mine for final disposal. The pile's oldest tailings contain 0.72% Cu, while the most recent deposits contain 0.11% Cu. Magma strips the top layer of tailings to gain access to older material that can be economically recovered.[8]

Roasting and Smelting

The product of flotation, copper mineral concentrate, contains 60-80% water. After filtration a relatively dry copper concentrate is processed in a smelter. Roasting may be used to prepare sulfide concentrates for subsequent pyrometallurgical or hydrometallurgical operation. The purpose of roasting is to decrease the sulfur content to an optimum level prior to smelting to form copper matte.

Smelting of un-roasted or partially roasted sulfide ore concentrate produces two immiscible molten phases: a heavier sulfide phase containing most of the copper, the matte, and an oxide phase, the slag. In most copper extraction processes, matte is an intermediate phase. The pyrometallurgical production of copper from sulfide ore concentrates is a rough separation of the three main elements as crude copper, iron (II) silicate slag, and sulfur dioxide. Slag containing <0.8 wt% copper are either discarded as waste or sold as products. Modern copper smelting processes produce high-grade mattes — the short residence time of the materials in the reaction chamber does not allow chemical equilibrium. Both factors contribute to high concentration of copper in the slag, generally >1wt%. Special methods are required to recover copper from such slag.

Prior to the 1960s, the most important method for producing copper was roasting sulfide concentrates, smelting in calciners in reverbatory furnaces, and converting the matte in Pierce-Smith converters. Since that time, the modern flash smelting process with subsequent conversion has become predominant. There are several types of smelting processes that are presently used.

While still in the molten state, matte produced by smelting is concentrated, or converted, using forced air. Copper and iron sulfides, the main constituents of matte, are oxidized to a crude copper, ferrous silicate slag, and sulfur dioxide. Conventional conversion of matte is a batch process. The first step yields an impure copper (I) sulfide containing about 75-80 wt% Cu, so-called white metal. The second step, the converter, produces blister copper that averages 98-99 wt% Cu.

Slag from the first step contains iron (II) silicates (40-50 wt% Fe) with high magnetic content (15-30 wt% Fe_3O_4). Reaction with air and formation of copper (I) oxide can increase the initial copper concentration from 3-8 wt% to 15 wt%. Additional copper can be removed from the slag by returning it to the smelting unit or by froth flotation. The second step uses a high viscosity small-volume converter to form copper (I) oxide or silicate copper (20-40 wt% Cu). When a

sufficient quantity of slag (<0.8 wt% Cu) has accumulated, it is returned to the first converting stage or purged.

Refining

Three stages are involved in conventional refining: (1) pyrometallurgical or fire refining, (2) electrolytic refining, and (3) re-melting of cathodes and casting of shapes. Re-melting of cathodes that are out of spec and casting of shapes. Crude copper is fire refined, such as blister copper produced in converters (97-99 wt% Cu), to form black copper in blast furnaces (90-95 wt% Cu), cement copper from hydrometallurgical operations (85-90 wt% Cu), and anode scrap from electrolytic refining.

About 80% of the world copper production is refined by electrolysis. This treatment yields copper with high electrical conductivity and separates valuable impurities, especially precious metals. Cathode copper is currently produced with purities ranging from 99.97 to 99.99%. Insoluble substances are <1% of the anode weight—these impurities collect on the bottom of the cells as anode slime. Slime contains precious metals (silver, gold, and platinum), selenides and tellurides of copper and silver, lead sulfate, stannic oxide hydrate, and complex compounds of arsenic, antimony, and bismuth. The distribution of the elements varies over wide ranges (see Table 1).

Table 1. Distribution of Elements in Anode Slime

Element	Weight Percent
Copper	20-50
Nickel	0.5-2
Lead	5-10
Arsenic	0.5-5
Antimony	0.5-5
Bismuth	0.5-2
Tellurium	1-4
Silver	<= 25
Gold	<= 4

Copper cathodes are re-melted and cast into final products because their electro-crystalline structure may not be suitable for working to semi-finished products. Although separation techniques differ greatly from plant to plant, anode slimes are generally treated as follows:

- Leaching with dilute sulfuric acid to oxidize copper.
- Recovery of selenium and tellurium by pyrometallurgical or hydrometallurgical methods.
- Removal of un-wanted elements and production of silver alloy.
- Separation of precious metals by electrolysis (silver and gold) and fractional precipitation (platinum metals).

Gas Cleaning and Acid Production

Waste gases from the roasting 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, which contains >8% SO_2, also contains inorganic molecules of zinc, 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. Impurities are removed from the gas stream—typically, gases are routed through bag-houses to remove coarse entrained particulate matter (i.e., bag-house dust). The flue dust consists chiefly of sulfates and basic sulfates of copper, lead, and zinc, as well as some volatile compounds of arsenic, antimony, bismuth, and selenium. The cleaned off-gas is usually processed to form sulfuric acid.

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.[9] Liquid is separated from the wet solids that can be processed for recovery of by-products such as copper, gold, lead, and silver.

LEAD PROCESS

ORNL engineers evaluated lead-mining operations, as described below, and compiled flow diagrams of unit operations.[7] We prepared both detailed and simplified flow diagrams of lead mining operations and identified process residues that have by-product recovery potential as follows (see Figure 2):

- Dust and fine particles
- Tailings
- Slag waste

Sizing and Smelting Lead Ore

Lead most often occurs in association with the sulfide mineral group. Lead ore deposits usually form with other minerals and the host rock. These crude ores cannot be smelted—size reduction and beneficiation must be used to concentrate the lead. Ore beneficiation normally includes crushing, dense-medium separation, grinding, froth flotation, and drying of concentrate.[6, 10]

Sinter oxidation using a blast furnace is the major method for producing lead from sulfide concentrate. In the last two decades, oxygen metallurgy processes have advanced to industrial applications that feature sulfide oxidation in a flash flame or by oxygen injection into a slag bath, followed by reduction of the lead oxide slag.[11]

One type of sintering roaster uses downdraft airflow to produce roasting gases with a concentration of 1-2 vol% sulfur dioxide. Gases are re-circulated until acid-strength gas is produced. In this system, the molten lead flows downward through the sinter bed with the gas stream. Another type of roaster uses updraft airflow—sintering occurs in an ascending gas
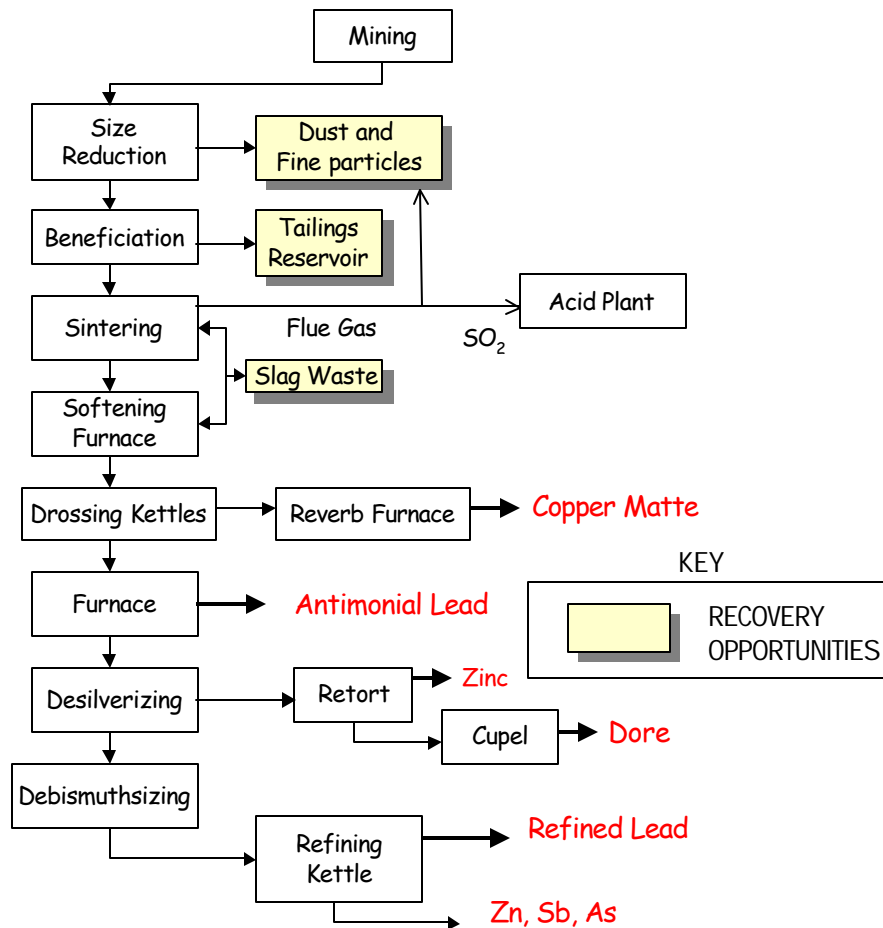
Figure 2. Lead Mining Operations and By-product Recovery Opportunities.

stream. A major problem for roaster operations is dust collection because high volumes of ventilation air are handled at considerable cost. Dust recovered from baghouses and wet scrubbers must be recycled to the process. The dust from sintering operations is usually collected in high-temperature electrostatic precipitators. Rich gas containing ~6 vol % sulfur dioxide can be delivered to a sulfuric acid plant. Flue dust from lead sintering plants contain 60-70% lead, about 10% sulfur, and varying amounts of zinc, cadmium, arsenic, antimony, and mercury. Flue dusts are recycled to the sinter bed.

The second part of the roast-reduction process is carried out in a blast furnace. The lead, that is mostly oxidized, in coke and sinter charge to the blast furnace is reduced to metallic lead, other metals such as copper, antimony, arsenic, and noble metals. In some blast furnaces the zinc contained in the sinter remains in the slag. In others, zinc off-gas is condensed to liquid zinc metal. Noble metals are largely dissolved in the lead product (bullion), with small amounts distributed to sulfide matte and slag. The copper contained in the sinter is captured in the bullion in form of sulfide or metallic copper depending on the amount of sulfur present. Copper can report to the slag along with the zinc. Antimony and arsenic compounds are reduced to their respective metals, which dissolve in the lead bullion. The products of the lead blast furnace are:

- Lead bullion, that must be further refined
- Slag that may contain large quantities of zinc and require further processing.
- Flue and baghouse dusts that may contain cadmium. Leaching may be used to separate cadmium before dust is recycled to sintering.
- Off-gas, may contains about 4% or carbon monoxide. After dust is removed it is released to atmosphere.
- Matte, a sulfidic product of blast furnace smelting, forms only if the concentration of sulfur is high. Normally, subsequent reverbatory melting of lead bullion dross yields copper matte, lead metal, and slag.
- Speiss is formed when the concentration of arsenic, nickel, cobalt, and antimony is so high that these metals can no longer dissolve in the matte. Speiss is undesirable, because it dissolves large quantities of noble metals and is also expensive to refine.

Lead blast-furnace slag often contains sufficient zinc to make recovery profitable using a rotary kiln or submerged combustion slag fuming. In both cases zinc oxide in the slag is reduced to metallic zinc (vapor) by carbon, oxidized by secondary air, and carried out in the furnace gases for recovery of zinc oxide dust.

Refining lead bullion

The lead bullion contains numerous dissolved impurities. The lead content varies between 90 and 99% depending on the process and feed quality. Lead bullion can contain metallic impurities as shown in Table 2.

Table 2. Weight percent impurity in lead bullion.

Impurity	Percent
Cu	0.2-4.0
Fe	0.-0.5
Zn	0-0.5
Ni	0-0.1
Co	0-0.1
As	0-2.0
Sb	0-6.0
Ag	0-2.0
Bi	0-6.0
Sn	0-4.0
S	typically 0.2-0.3
O	typically 0.1

Pyrometallurgical and electrolytic refining are both used. The latter is generally reserved for high levels of impurity. Pyrometallurgical refining methods include chemical processes, precipitation processes, and distillation processes. In the chemical process, a reagent is added to the parent metal so it reacts with one or more impurity to form a compound that is insoluble in the parent metal. Selective oxidation, sulfurization, or chlorination can be used as the refining step. The precipitation process uses temperature decreases to make impurities insoluble in the metal. Alternatively, suitable reagents can form insoluble compounds that can be skimmed off (e.g., bismuth from lead-bismuth solutions after addition of calcium and magnesium). Distillation processes are employed when a large difference in vapor pressure exists between the parent metal

and the impurity (e.g., in the separation of residual zinc from bullion after desilvering). Typical pyro-refining includes the following steps:

- Removal of copper (decoppering) by precipitation followed by selective sulfidizing of copper.
- Removal of arsenic, tin, and antimony by selective oxidation with injected air or oxidizing agent such as sodium nitrate.
- Removal of noble metals is normally called desilverizing and involves intermetallic precipitation with zinc.
- Removal of residual zinc after desilverizing by distillation.
- Debismuthizing by precipitation bismuth with alkali metals.
- Removal of alkali metals and alkaline-earth metals after debismuthizing is called final refining and is performed by selective oxidation with air under a salt slag cover.

Refined lead contains arsenic, antimony, and tin at a level of 10-20 g/t, zinc corresponding to the final content in vacuum dezincing (30 g/t), and calcium and magnesium corresponding to saturation limit. These impurities are reduced to below 1 g/t by treatment with caustic soda.

The electrolytic refining of lead bullion from soluble anodes has been practiced for years in a number of large plants. Because of poor solubility, solutions have been restricted to the lead salts of fluosilicic acid, fluoroboric acid and amido-sulfuric acid. Metals with a higher electrochemical potential than lead (silver, gold, copper, bismuth, antimony, arsenic, and germanium) do not dissolve and accumulate in the anode slime that is processed to recover these valuable by-products.

ZINC PROCESS

The U.S consumes 18% of the total world's zinc production while it produces 11% of the world's zinc output.[5] ORNL engineers evaluated zinc-mining operations, as described below, and compiled flow diagrams of unit operations. We prepared both detailed and simplified flow diagrams of zinc mining operations and identified process residues that have by-product recovery potential as follows (see Figure 3):

- Tailings
- Dust and fine particles
- Slag
- Liquor residues
- Suppression of undesirable elements in solution

Zinc Processing

An engineering evaluation of zinc processing operations identified potential opportunities for by-product recovery. For example, dust and fine particles and slag is produced by thermal zinc operations contains 8-12% zinc. Liquor produced by zinc electrolysis contains 25-30% zinc.

Precipitating the minerals jarosite, geothite and hematite produces zinc. Mineral formation has replaced the precipitation of iron hydroxide worldwide. Jarosite can theoretically contain 37% iron and 13% sulfur as sulfate. However, these values are not achieved in practice so that additional leaching processes are used to obtain zinc content of 4-6% in the residue. The geothite process improves upon the jarosite process because the solution from the first hot leach is treated

with zinc concentrate. Excess zinc concentrate and elemental sulfur are recycled to the roasting process. These process improvements give the geothite the advantage of producing fewer residues. The hematite process enables iron-containing residue from zinc production to be disposed of at a moderate cost and without environmental problems or produced in the form of a useful by-product. However, the cost and complexity of the hematite processing technology restricts more widespread use of the process.[12] As recognized by the NRC, mineral formation processes could potentially be improved by developing methods to suppress the solubility of undesirable elements in leach solutions.
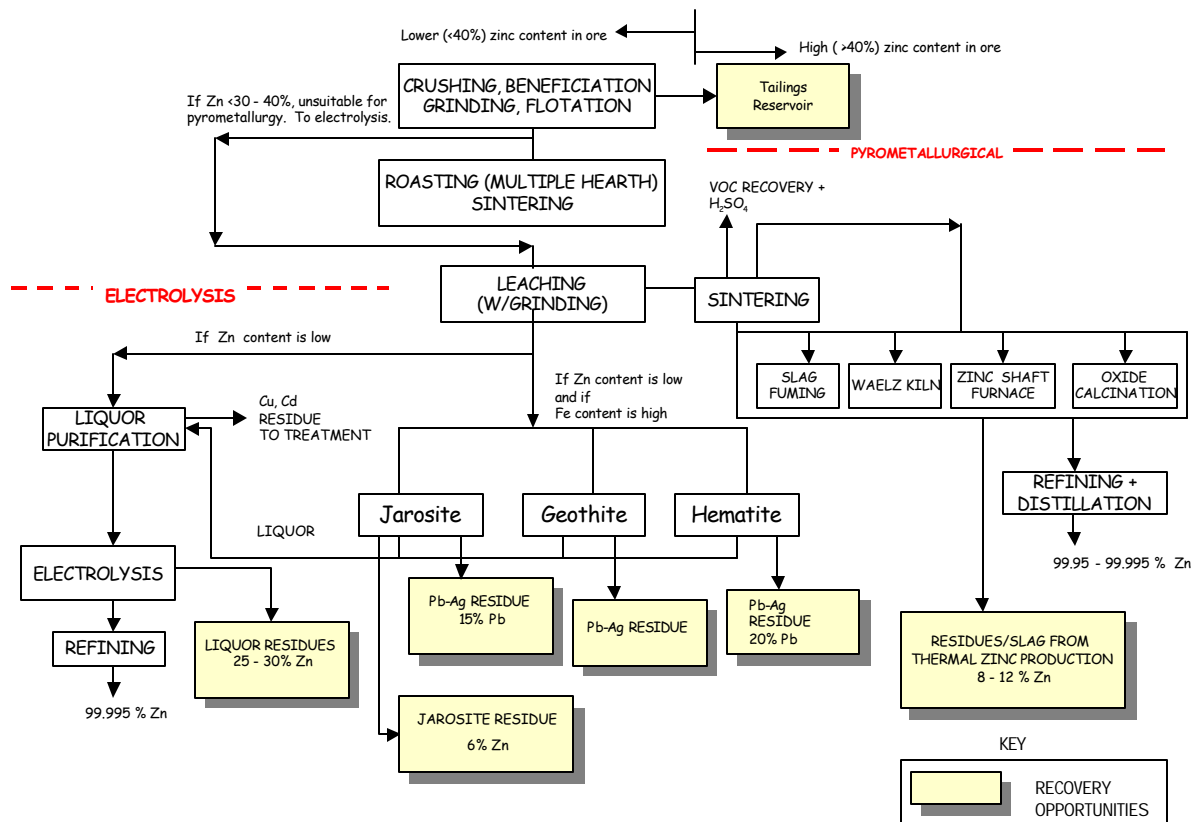
Figure 3. Zinc Mining Operations and By-product Recovery Opportunities.

Zinc with Gold Process Residue

Gold process residue, which contains large amounts of silver, presents another opportunity for zinc recovery. Carbon adsorption followed by electrowinning is the most common method of gold recovery domestically. Zinc precipitation is used to recover gold from ore, which contains large amounts of silver using the following processing steps: carbon adsorption; elution of carbon forming a concentrated gold solution, filtration, and mixing with metallic zinc dust causing a chemical reaction, which generates a gold precipitate. The solution is then forced through a filter that separates the gold. The high concentration of zinc in the gold precipitate presents an opportunity for zinc recovery. Gold and zinc process residue and waste may present an opportunity for by-product recovery since these operations produce large volumes of material.

For example, in1992, gold mining alone produced over 540 million metric tones of waste (see Table 3).[1]

Table 3. Gold and Zinc Excess Material

Commodity	Number of mines	Total Commodity Produced (1,000 mt)	Tailings Generated (1,000 mt)	Other Waste Handled (1,000 mt)
Gold	+212	0.329	247,533	293,128
Zinc	25	524	4,227	---

After overburden (surface soils, vegetation) and rock, tailings are a second type of common mining waste. Most beneficiation processes generate tailings, which contain a mixture of impurities, trace metals, and residue of chemicals used in the beneficiation process. Tailings usually leave the mill as slurry consisting of 40 to 70 % liquid mill effluent and 30 to 60 % solids. Most mine tailings are impounded on-site.

EXAMPLE OF IMPROVED BY-PRODUCT RECOVERY

DOE's Mining Industries of the Future Program, and SepraDyne®, a small U.S. business, co-funded a team of ORNL and Colorado School of Mines engineers to develop a by-product recovery process that is making progress toward sustainable mining in a niche market.

The team of engineers (a) modeled and evaluated process performance; (b) conducted process chemistry kinetic and thermodynamic experiments on two mixtures—mercury, sulfur and oxygen, and mercury and selenium; and (c) assessed mining process residues that would benefit from treatment using the SepraDyne process and identified the conditions that influence the economic viability of mining by-products recovery

Process Performance Evaluation

SepraDyne's® patented a rotary vacuum kiln system that processes acid plant blow-down sludge. The objective of this by-product recovery process is to improve the operating 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—generating revenue for the industry. The smelting of non-ferrous sulfide copper concentrates mercury because mercury preferentially reports to the SO_2-rich gas stream that is subsequently processed by the sulfuric acid plant. Mercury exits the processing cycle in the acid plant blow-down sludge. This sludge is filtered and processed to reduce the high concentration of mercury. This filtered sludge represents a potentially valuable by-product since the concentration of copper plus lead can exceed 35%.

SepraDyne's® system (illustrated in Fig. 1) processes this acid blowdown process residue in the following operational sequence. 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. Residue is initially heated to remove the moisture. The water vapor and other liquids impinge on collection plates separating liquids from gases. The condenser separates low-boiling-point gaseous compounds as the first stage in the off-gas treatment train that also includes a cyclone, and a demister. Hazardous vapors that have passed through the off-gas system are removed in the carbon absorption section before treated gas is discharged to the atmosphere (see Figure 4).

Once the material is dried, the retort temperature is raised to 600-750EC, under a vacuum of greater than 0.7 atm (20 inches of Hg). 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. Mercury is recovered from the solids collected in the settling tank using a hydro-cyclone. 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, which contain by-products, are collected in separate containers for shipment. The mine sells this material to an off-site smelter to recover 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. [13]
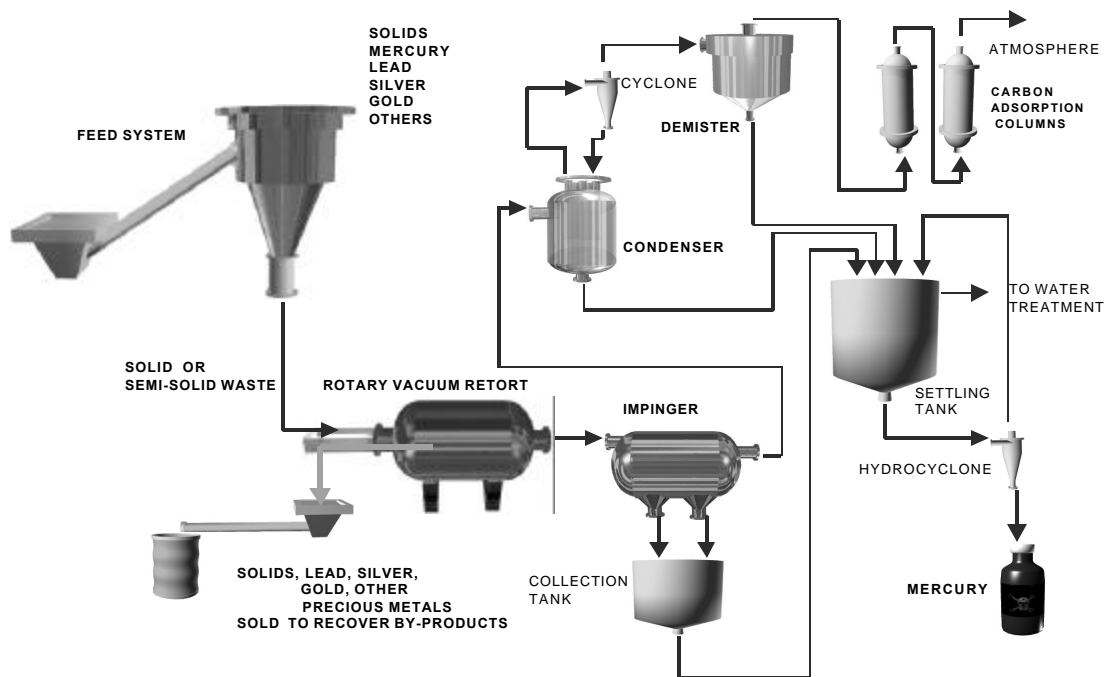

Figure 4. Vacuum Rotary Kiln Mercury Separation Process.

ORNL analysis of the SepraDyne® technology resulted in the conclusion that the process has advanced by-product recovery by more effectively separating mercury to <10 ppm so that valuable metals, such as lead, can be economically recovered from acid plant sludge. Since air is eliminated from the kiln, the oxidation of mercury and formation of mercury compounds is reduced because of the reduced oxygen in the processing environment.

 Process Performance Modeling

ORNL researchers evaluated 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. 4). FLOW™ is a modular

computer simulation program that models and analyzes emerging chemical and physical processes. FLOW™ predicts process performance by modeling both operational and physical property (e.g., thermodynamic) data. Thermodynamic models would provide information as input to the FLOW™ process model.

ORNL and the Colorado School of Mines used thermodynamic models, enhanced by experimental data,[14] to predict compounds likely to result from critical processing steps. Equilibrium species were estimated by minimizing the collective Gibbs free energies for temperatures between 30E and 600EC (86E to 1112EF). The modeling simulates a vacuum, processing environment by recalculating the equilibrium composition of each 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.[15]

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

ORNL reviewed the economics of this process as background for collecting relevant data from the mining industry. Since the concentration of minerals in the acid plant blowdown can exceed their concentration in ore, the cost of recovering these minerals could be compared with the cost of recovering minerals from the raw ore—this comparison favors by-product recovery. SepraDyne® operates their process under a performance contract eliminating capital investment by the mining company. This contractual operation is external to the primary functions of the mine—the mine hires the processing service when the economics are favorable. 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 influenced by mercury concentration. Key economic data needed to evaluate process economics include the value of process residue after separating mercury at various mercury concentrations, and the processing cost per ton for competing technologies.

Interviews with mining companies indicated that the current application is unique. The copper ore in question contains more mercury than most copper ore, presenting a unique processing challenge. The mine evaluated six technologies prior to selecting the SepraDyne® process for this

unique application. The process is effective in separating mercury from process residue, however, mining company representatives indicated that additional applications in the mining industry are unlikely. High-value, mercury contaminated process residue does not have broad potential to generate mining profit. Therefore, the innovative SepraDyne process meets a niche mining industry market need while contributing to sustainable production in that specific mining application.

CONCLUSIONS

This paper points out opportunities for the mining industry to improve operations by responsible emission and by-product management and low-cost and efficient production. Dialogue between the mining industry, government, and the research community strengthens the potential to capture these opportunities helping to realize A Vision of the Mining Industry of the Future.[4]

Oak Ridge National Laboratory (ORNL) engineers developed simplified descriptions of copper, lead, and zinc processes that can serve as a basis for more specific dialogue on identifying by-product recovery opportunities further clarifying those by-product recovery opportunities that could benefit from joint industry/government research. By identifying highly beneficial opportunities for by-product recovery, it is hoped that research will result in a more profitable, safer, and environmentally benign U.S. mining industry. This paper identifies process residues by mine type as:

- Copper: dust and fine particles, tailings, slag waste, and gas cleaning sludge.
- Lead: dust and fine particles, tailings, slag.
- Zinc: dust and fine particles, liquor residues, suppression of undesirable elements in solution, slag

An innovative by-product recovery process is being operated commercially and improved by a joint industry/government engineering development project. The process solves an environmental problem, reducing costs for the host mine. The patented, high-vacuum, indirectly-heated rotary kiln that operates at temperatures of up to 750EC—the SepraDyne® process—separates mercury from acid plant blowdown sludge. The residue, which contains high concentrations of lead and trace quantities of silver and gold, is sold to a lead smelter.

ORNL engineers have evaluated and modeled the SepraDyne® process leading to recommendations for improving operations and a better understanding of process thermodynamics and kinetics. Experimental results confirm that the absence of oxygen improves separation of mercury compounds and improves recovery of elemental mercury.

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