SURVEY OF U.S. MINERAL AND METAL PROCESS RESIDUES

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Abstract

The U.S. mineral processing industry produces over 30,000,000 metric tons per year of process residue and waste that may contain hazardous species as well as valuable by-products. Copper, lead, and zinc commodity sectors generate between 23,300,000 and 24,000,000 metric tons per year of process residue. An evaluation of these sectors resulted in mining process flow diagrams and technical descriptions, and evaluation of major sources of process residue by commodity sector [1]. This survey identified the following process residues and waste as having by-product recovery potential:

- copper-dust and fine particles, tailings, slag waste, and gas cleaning sludge;
- lead-dust and fine particles, tailings, slag; and
- zinc-dust and fine particles, liquor residues, undesirable elements in solution, and slag.

Metal concentrations in process residue can exceed metal concentration in the natural ore and may therefore present opportunities for by-product recovery. The economics of by-product recovery are influenced by the cost of managing process residue as a waste (e.g., storage and/or disposal), the cost of the process residue before additional processing, the value of residuals and products after processing, and the processing cost. Since "productivity gains tend to increase as value is added to a product while it moves downstream," process residue generated by downstream processes present opportunities to recover by-products returning value to the mining industry [2].

Introduction

The U.S. Department of Energy (DOE) Office of Industrial Technologies, Mining Industry of the Future Program, works with the mining industry to further 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]. DOE formed an alliance with the National Mining Association (NMA) to strengthen the basis for research projects conducted to benefit the mining industry. The research described in this paper resulted from the collaboration between DOE and NMA. In fact, NMA and industry representatives reviewed the results of this DOE project that was conducted by Oak Ridge National Laboratory (ORNL) and Colorado School of Mines engineers.

This paper generally describes copper, lead, and zinc mining and their associated process wastes and residues. This description can serve as a basis for identifying the process residues and waste that contain both impurities and products which currently cannot be economically recovered. This information can 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. Accordingly, this paper is intended to facilitate discussions between researchers and mining company representatives to clarify by-product recovery opportunities by providing easy-to-understand descriptions of mining processes. When by-product recovery opportunities are identified, they can be evaluated by using criteria such as favorable economics and reduced environmental impact. Collaboration between research and industry representatives can identify by-product recovery research on processing methods that promise to improve the economics of mining.

Copper process

ORNL engineers evaluated copper mining operations, prepared flow diagrams of those operations, and identified process residues with by-product recovery potential (Figure 1) [4]. The United States currently holds 16% of the world's refined copper reserves in 30 active mines. Fifteen copper mines located in Arizona, New Mexico, Utah, Michigan, and Montana produced 99% of domestic production in 2000 [5].

The U.S. copper sector generates 10,500,000–11,000,000 metric tons per year of process residues [6]. Hydrometallurgical processing is important. In 1991, ~~for example,~~ U.S. mines leached 15.7 million metric tons of copper ore to recover 441,000 metric tons of copper. However, 80% of the world's ~~primary~~ supply of copper ~~in the world~~ comes from low-grade ~~or poor~~ sulfide ores with concentrations of 0.7% or less copper. These ores are treated by pyrometallurgical methods that generate major process residue streams. Ore b~~B~~eneficiation by sizing and froth flotation of-ore-concentrates copper ~~and~~ producing~~es~~ dust, fine particles, and tailings. Smelting concentrates copper to matte ~~and~~ producing ~~es~~ slag waste. Gas cleaning and acid production generates sludge. Depending on processing details, each of these residues presents differing opportunities for by-product recovery.

Dust, fine particles, and tailings

Beneticiation of copper ore by sizing and froth flotation concentrates the copper while producing dust, fine particles, and tailings. Excavated ores are reduced to pulp by adding water and crushing in jaw, gyratory, and cone crushers, then sized with vibrating screens. Pulp is ground in rod and ball mills, followed by semi-dutogenous or autogenous milling before particles are separated according to size using classifiers and ~~hydro cyclone~~hydrocyclones.

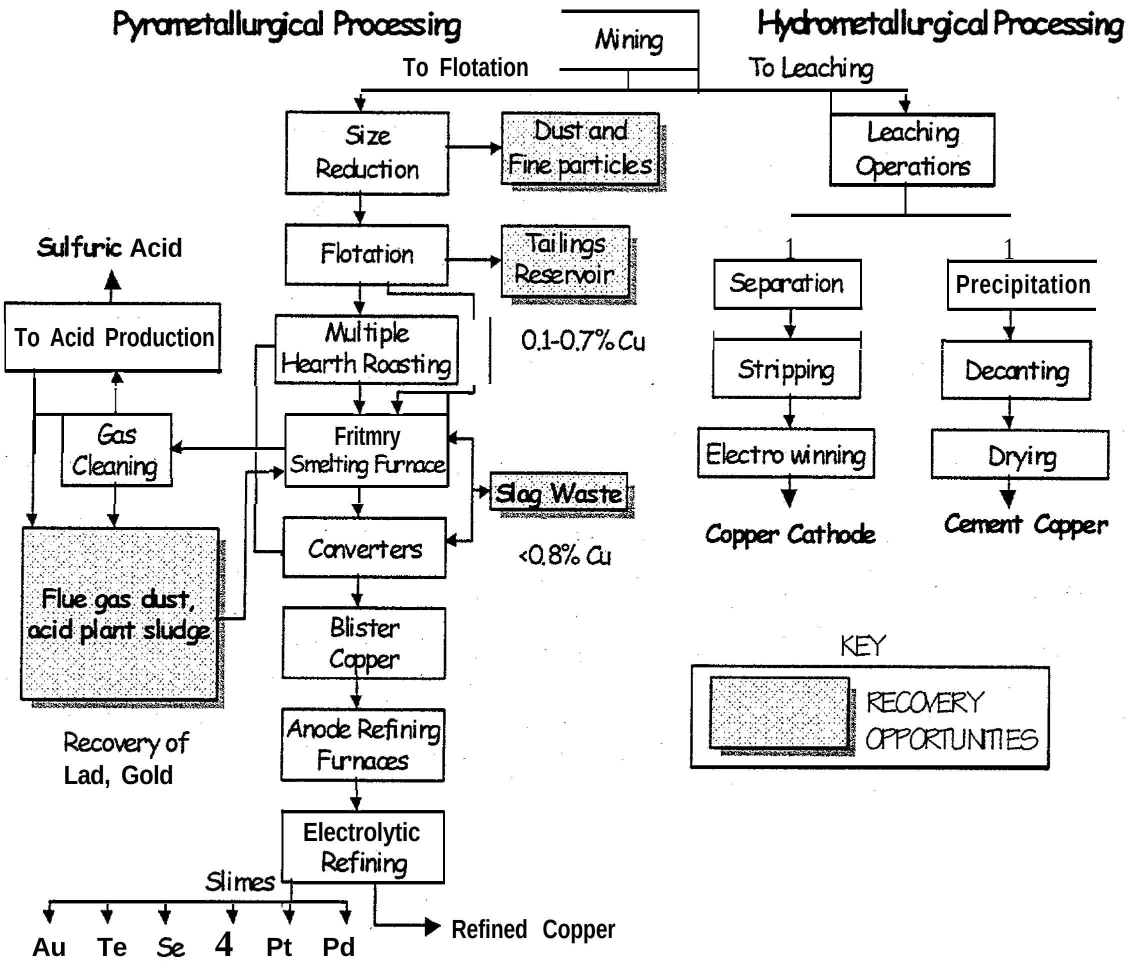

Figure 1. Copper mining operations and by-product recovery opportunities

Sulfide copper ores are beneficiated to increase metal content. There are three types of flotation cells: rougher flotation for sorting into pre-concentrate and tailings, cleaner flotation for post-treatment of the pre-concentrate, and scavenger flotation for post-treatment of the tailings. The next step is solid-fluid separation using sedimentation in settlers and thickeners with vacuum filtering by drum and disk filters. The copper content of dried chalcopyrite concentrates ($CuFeS_2$) averages 20-30 wt %.

Copper companies are recovering copper from tailings piles; Magma BHP-Billiton Pinto is mining tailings deposited between 19 11, and 1932 at its Pinto Valley operation. Pinto Valley hydraulically mines the tailings pile, leaches the tailings, and produces copper using a solvent extraction/electrowinning facility. After the tailings are leached and washed, the remaining slurry is pumped 5 miles to an abandoned open-pit copper mine for disposal. The pile's oldest tailings contain 0.72% Cu, while more recent deposits contain 0.11% Cu. Magma strips the top layer of tailings to gain access to older material that can be economically recovered [7].

Slag waste

The product of flotation, copper mineral concentrate, contains 60–80% water that is filtered before processing in a smelter. Roasting may be used to prepare sulfide concentrates for subsequent pyrometallurgical or hydrometallurgical operation by decreasing the sulfur content prior to smelting. Smelting of sulfur-containing, copper concentrate produces two immiscible molten phases: a heavier sulfide phase containing most of the copper, the matte, and an oxide phase, the slag. Matte is an intermediate phase in the copper pyrometallurgical processes because of the extractive metallurgy of copper. The pyrometallurgical process separates three main chemical species: crude copper, iron (II) silicate slag, and sulfur dioxide. Modern copper smelting processes produce high-grade mattes-the short residence time of the materials in the reaction chamber does not allow chemical equilibrium. These factors contribute to produce a high concentration of copper in the slag, generally >1 wt %. Aggressive processing would be -required to recover copper from slag which is in a glassy state.

Gas cleaning sludge

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% SO_2 and inorganic metals. Common ionic species include sulfites (SO_3), sulfates (SO_4), and chlorides. Trace quantities of hydrocarbons and precious metals are 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 of copper, lead, and zinc and other sulfates, as well as some volatile compounds of arsenic, antimony, bismuth, and selenium. The cleaned off-gas is usually processed to form sulfuric acid.

Sulfur dioxide generated by the smelting process is retained and processed to make commercial-grade sulfuric acid by-product. The gas cleaning section of an acid plant scrubs these gases with dilute sulfuric acid using venturi scrubbers, wash towers, and electrostatic precipitators. The process re-circulates scrubber water; however, ~~a~~ some of the stream must be purged periodically to prevent buildup of solids and to minimize corrosion. Filtered wet solids can be processed for recovery of by-products such as copper, gold, lead, and silver.

Lead process

ORNL engineers evaluated and prepared a flow diagram of lead-mining operations [8], and identified process residues with by-product recovery potential (Figure 2). The U.S. lead commodity sector generates 3,000,000–3,200,000 metric tons per year of process residues Some minerals (e.g., galena) contain up to 86% lead while other lead minerals contain only 30% lead. Ore b~~B~~eneficiation by sizing and froth flotation ~~of ore~~ concentrates lead while producing dust, tine particles, and tailings. Sintering and blast furnaces are used to produce lead bullion and also generate slag waste. The processes that generate dust and fine particles, tailings, slag waste, and gas cleaning sludge are described below. It should be noted that lead recycling accounts for a large fraction of the lead market.

Dust. fine particles. and tailings

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 directly smelted-beneficiation must be used to concentrate the lead. Ore beneficiation normally includes crushing, dense-medium separation, grinding, froth flotation, and drying of concentrates [9], [10].

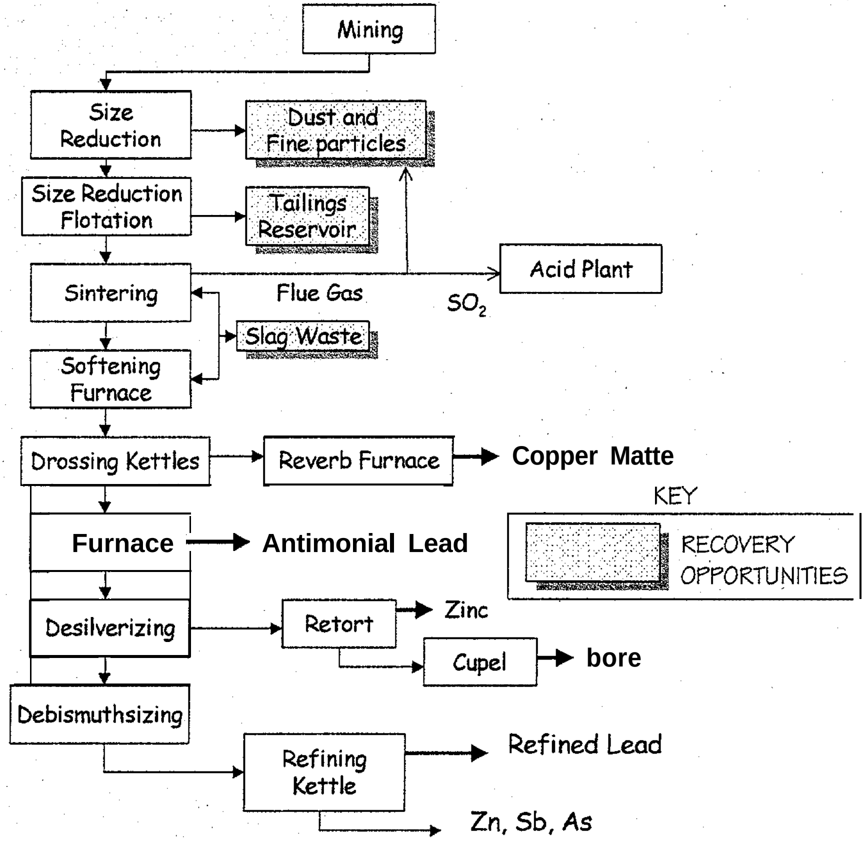

Figure 2. Lead mining operations and by-product recovery opportunities

Slag waste

Sinter oxidation using a blast furnace is the major method for producing lead from sulfide concentrate. In the past 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 l-2 vol % sulfur dioxide. Gases are recirculated 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 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 is mostly ‘oxidized with coke. The sinter is charged to the blast furnace and metals are reduced to metallic lead, 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 corrosion-resistant, metallic elements (e.g., the platinum group, gold, silver, and rhenium) that exchange electrons according to their position in the electrochemical series of metallic elements. Because of this preferential transfer of electrons, 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 the 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, which must be further refined.
- Slag that may contain large quantities of zinc that may be further processed.
- Flue and baghouse dusts that may contain cadmium. Leaching may be used to separate cadmium before dust is recycled to sintering.
- Off-gas, which may contain about 4% carbon monoxide.
- Matte, a sulfidic product of blast furnace smelting, forms only if the concentration of sulfur is high.

Normally, subsequent reverberatory 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 fuming techniques. Zinc oxide in the slag is reduced to metallic zinc (vapor) by carbon, oxidized by secondary air, and exits in the furnace gases for recovery of zinc oxide dust.

Zinc process

ORNL engineers evaluated zinc-mining operations, as described below, compiled flow diagrams of unit operations [12] and identified process residues with by-product recovery potential (Figure 3). The U.S consumes 18% of the total world's zinc production while it produces 11% of the world's zinc output [13]. The U.S. zinc commodity sector generates 9,800,000 metric tons per year of process residues. The content of zinc in the raw ore is used to determine how the ore will be processed. Five industrial 'processes produce zinc-one electrolytic and four pyrometallurgical. If zinc content in the ore is greater than 40%, then zinc is produced using pyrometallurgy. If the zinc content of the ore is below 40%, then electrolytic production of zinc may be more economical. Zinc produced electrolytically does not need to be refined. However, crude zinc produced by the pyrometallurgy contains 0.7–3% Pb, up to 0.2% Fe, up to 0.3% Cd, and sometimes small amounts of As, depending upon the production method and the ore composition. Residues and slag from pyrometallurgical processes may contain 8-15% zinc, representing an opportunity for further recovery.

<u>Zinc ore</u>

Zinc is a chalcophilic element, like copper and lead, occurring as the sulfide. The most important zinc mineral today is zinc blende, containing 67.09% Zn and 32.91% S on a theoretical basis. The most important impurity in ZnS is FeS, and concentrations can vary from 0.3 to >20. Sulfides of Pb, Cd, Mn, and Cu are often present. Zinc blende also contains small amounts of As, Sn, Bi, Co, Hg, In, Tl, Ga, Ge, Ag, and Au (Table 1).

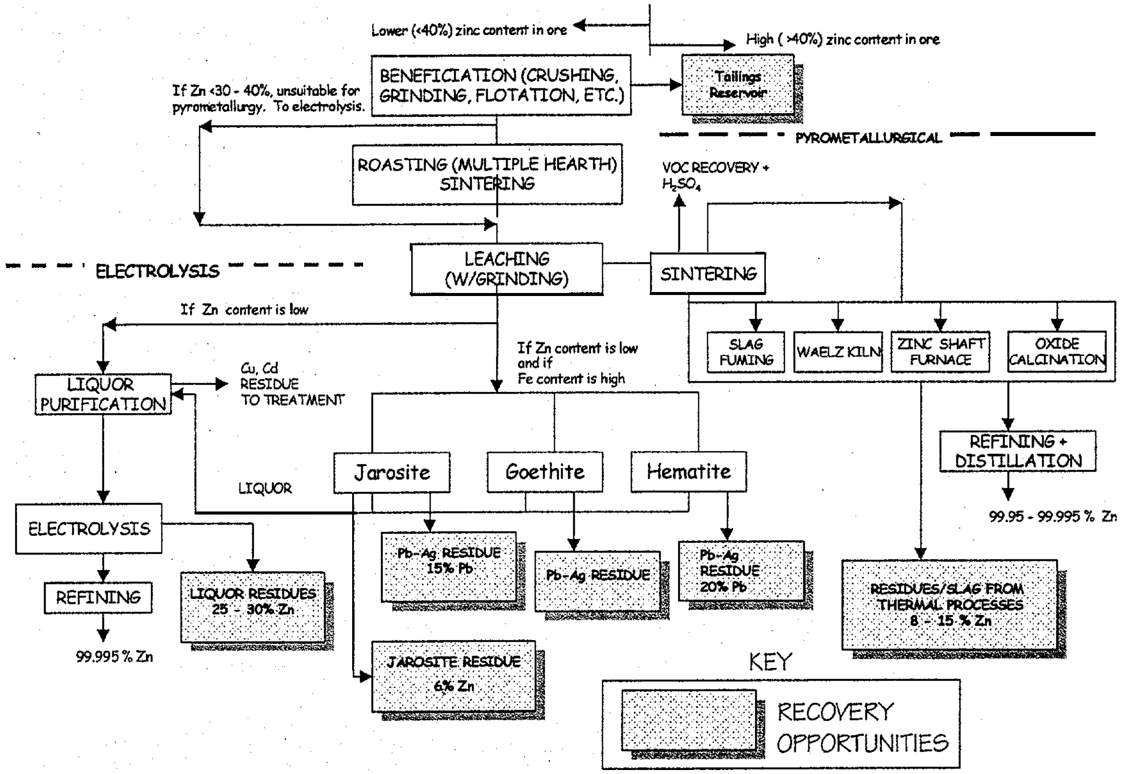

Figure 3. Zinc mining operations and by-product recovery opportunities

Table 1. Zinc content of selected ores

Ore	Zinc content (% by mass)
Smithsonite, ($ZnCO_3$)	52.14 Zn
Hemimorphite, $Zn_2SiO_4 \cdot H_2O$	54.30 Zn
Willemite, Zn_2SiO_4	58.68 Zn
Franklinite, $(Zn,Fe, Mn)O \cdot (Fe_2, Mn,_2)O_3$	21% ZnO

Tailings

After overburden, 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 40–70% liquid mill effluent and 30–60% solids. Most mine tailings are impounded on-site.

Electrolysis liquor residues

Zinc is produced electrolytically from dilute aqueous solutions of zinc sulfate in sulfuric acid although it can also be produced electrolytically from molten salts. The aqueous solution route is adopted in industry. Like the thermal processes of zinc production, the industrial electrolysis of zinc uses oxide starting-materials. The most important natural raw material, zinc blende, still needs to be roasted so it is converted to oxide. Using typical starting materials, the electrolytic process of zinc production consists of roasting, leaching, liquor purification, electrolysis, and finally melting and casting. The main problem in leaching and liquor purification is Zn-Fe separation. High yield of zinc can be achieved only with Fe concentrations of <3%. Because the Fe interferes with the electrolytic process even at low concentrations, it must be precipitated from the zinc sulfate solution. Liquor produced by zinc electrolysiscontains 25–30% zinc.

Mineral formation residue

Mineral formation has replaced the precipitation of iron hydroxide worldwide to enhance zinc production. In the jarosite process, an Fe (3+) compound of the type $X[Fe_3(SO_4)_2(OH)_6]$, -where X represents H_3O^+, Na^+, K^+, or NH_4^+, is precipitated by adding alkali metal or ammonium ions. These compounds correspond to the mineral jarosite. Precipitation of jarosite begins at pH <1 and is complete at pH 1.5. The jarosite process can achieve zinc yields of 96-98%. Iron can also be removed from electrolytic solutions by the goethite process. Goethite is FeO(OH) formed at pH 2-3.5 and temperatures from 70 to 90°C. The goethite process has the advantage of generating fewer residues than the jarosite process, and the zinc yield is comparable to the jarosite process.

The hematite process was developed to enable Fe-containing residues from zinc production to be disposed of at moderate cost and without ecological problems. It differs from the other processes in that the residues are subjected to reductive leaching in which the reducing agent is an excess of zinc concentrate. However, the cost and complexity of the hematite processing technology restricts more widespread use of the process [8]. As recognized by the National Research Council, mineral formation processes could potentially be improved by developing methods to suppress the solubility of undesirable elements in leach solutions.

Thermal processing residue

Thermal processing produces dust, fine particles and slag that can-contain 8- 12% zinc.

Evaluation of by-product recovery economics

Once a process residue is identified as having by-product recovery potential, researchers can evaluate methods to separate impurities from valuable elements (e.g., separate mercury from copper-bearing process residue). Criteria such as favorable economics and reduced environmental impact are used to evaluate these opportunities. However, data are not readily available to describe the market potential and profitability of new technologies. Data on the value of process residue before separating impurities, after separation, and the cost of separation are all necessary in order to evaluate a technology's market potential (Table 2). Additional data are required on the amount of process residue that is available for processing. For instance, consider the cost to recover, by-products from acid plant sludge generated as part of copper smelting operations and the value of those by-products. This process residue (acid plant sludge) has some initial value before impurities (mercury) are separated (Table 2, Row A). This value may be negative because the residue may be designated as "waste" if it cannot be reprocessed to recover some of the valuable components. The value (or cost) could be determined by the cost of transport and disposal of the sludge.

Table 2. Economic variables for separation of impurities from process residue

	Economic Variable	Concentration of impurities, ppm		
		400	<50	<10
A	Value of process residue before separating impurities	need data-may be negative		
Value of process residue after separating impurities				
B	Primary process residue (e.g., acid plant sludge)	need data	need data	need data
C	Secondary process residue (e.g., mercury)	need data	need data	need data
Gross value after separating impurities				
D	Acid plant sludge (B – A)	calculate	calculate	calculate
E	Secondary process residue (C – A)	calculate	calculate	calculate
F	Target separation cost per ton for new technology	depends on technology	depends on technology	depends on technology
G	Processing cost per ton for existing or next best technology	need data	need data	need data
H	Processing cost per ton saved by new technology (G – F)	calculate	calculate	calculate
Net value of separating impurities				
I	Primary process residue (D – F)	calculate	calculate	calculate
J	Secondary process residue (E – F)	calculate	calculate	calculate
Impurities removal level for highest net benefit based on highest value for each process residue				
	Primary process residue	Highest value in row I		
	Secondary process residue	Highest value in row J		

The primary process residue (acid plant sludge) may have a market value that is a function of the concentration of impurities (mercury) (Table 2, Row B). For example, process residue may be sold to a smelter to recover commodity metals (lead, silver, gold). If the residue includes impurities, such as mercury, the price'the smelter pays the copper smelter could be more or less depending on the amount of impurity. Secondary process residue (mercury) may also have a market value (Table 2, Row C). Separation technology would tend to increase the value of the process residue to buyers because impurities would be removed. In our example, mercury separation technology reduces the concentration of mercury from 1300 to 250 ppm at a cost of $500 (U.S.) per ton (Table 2, Row F).

Mines have existing methods for handling their process residue and could estimate these costs (Table 2, Row G). In our example, the copper mine used a less effective separations technology before using the innovative technology-the cost of this "old technology" would be the "next best" technology referred to in Row G.

By using the heuristic model, cost savings per ton of material processed using a new technology, and the net value of separating impurities from process residue can be calculated. Because of incentives to maintain the confidentiality of cost information, the heuristic model ‘was developed to allow generalized analysis of new technology without revealing sensitive information. Methods for using the model, listed below, may not generate detailed information, but may help establish a dialogue between representatives of the mining industry and technologists resulting in information useful in technology evaluations. One or more of these approaches may provide valuable information that helps the researcher and decision maker gain information for evaluating a new technology.

- Generating information through anonymous responses
- Generating information through range responses
- Generating information from bottom line responses that do not reveal details
- Using the heuristic model as a basis for qualitative evaluation of the technology
- Providing sufficient information to promote voluntary cooperation

Summary

This report points out opportunities for the mining industry to improve operations by responsible emission and by-product management and low-cost and efficient production. The dialogue between the mining industry, government, and the research community has strengthened the potential to capture these opportunities and can help realize A *Vision of the Mining Industry of the Future* [3].

ORNL engineers developed simplified descriptions of copper, lead, and zinc processes that identify process residue with high concentrations of commodity metals. These descriptions serve as a starting point for. clarifying the economic benefit of research into methods to recover these metals, or by-products. By identifying highly beneficial opportunities for by-product recovery, research can result in development of technologies that contribute to a more profitable, safer, and environmentally benign mining industry.

This paper identifies process residues by commodity sector as

- copper-dust and fine particles, tailings, slag waste, and gas cleaning sludge;
- lead-dust and fine particles, tailings, slag; and
- zinc-dust and fine particles, liquor residues, undesirable elements in solution, slag.

Opportunities for technology development that result in economical recovery of by-products in the mining industry can be clarified by evaluating data on the value of process residue before separating impurities, after separation, and the cost of separation. Evaluation of ~~the a~~ the economics of by-product recovery based on a specific technology’s market potential can guide decisions regarding investments in technology development.

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