Treatment of Copper Smelting and Refining Wastes

By D. K. Steele, K. S. Gritton, and S. B. Odekirk

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Cover: A copper waste dump.

Report of Investigations 9522

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g/L	gram per liter		pct	percent
h	hour		t	metric ton
mg/L	milligram per liter		tr oz/st	troy ounce per short ton
min	minute		V	volt
mL	milliliter		wt pct	weight percent
mV	millivolt		°C	degree Celsius
oz/t	ounce per ton			

TREATMENT OF COPPER SMELTING AND REFINING WASTES

By D. K. Steele,[1] K. S. Gritton,[2] and S. B. Odekirk[3]

ABSTRACT

The domestic primary copper industry generates in excess of 600 million t of mining and mineral-processing waste annually. Most of the waste poses negligible environmental threat, but a small fraction, because of toxic or corrosive characteristics, may be subject to regulation under Subtitle C of the Resource Conservation and Recovery Act (RCRA) or other pertinent regulations. Among the wastes generated by various copper producers are flue dusts, slags, refinery-bleed solutions, and acid-plant wastes. The U.S. Bureau of Mines (USBM) has researched methods to mitigate the environmental threat posed by copper-processing wastes while recovering valuable metals from these materials. Acid-leach processing of flue dusts has been demonstrated feasible along with sulfide treatment of liquid refinery wastes and acid-plant-bleed and gas-cleaning solutions to precipitate dissolved metals. In addition, the feasibility of removing copper and molybdenum from slag, as well as stabilization of precipitated sulfide wastes by vitrification, have been investigated.

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INTRODUCTION

Processing of sulfide ores often results in the concentration of environmentally sensitive, or other deleterious, contaminants into various waste streams. Arsenic, cadmium, lead, and other metals may be concentrated in flue dusts, water-treatment sludges, and furnace liners, as well as refinery and acid-plant solutions. While these waste streams may contain significant amounts of valuable metals, recovery is complicated by the presence of objectionable materials which are difficult to separate from the valuable components. The recovery of metal values from waste materials can mitigate operational costs associated with waste disposal and could also provide opportunities to reduce the environmental risks and liabilities posed by the storage or disposal of the untreated substances.

While the reprocessing of low-volume wastes may not have been economically attractive in the past, waste-management regulations promulgated as a result of the Resource Conservation and Recovery Act (RCRA) require mineral processors to recycle or properly treat potentially hazardous substances prior to disposal. Consequently, the negative economic impact of waste treatment must be evaluated in light of the tremendous liabilities incurred by noncompliance with RCRA and other legal restrictions. As ore reserves continue to be depleted and new, more complex ores are beneficiated, processors will be required to tolerate escalating impurity levels in process streams and the potential for concentration of toxic metals in waste streams will increase. As a result, an increasing number and variety of wastes may come under the purview of the RCRA.

Arsenic has received much attention as one of the environmentally sensitive elements which concentrate in metallurgical-process waste streams. Several processes are available for removal of arsenic from product streams (1),[4] but the ultimate disposition of arsenic-bearing waste still poses a problem for mineral processors. Owing to its well documented toxicity (2) and the mobile nature of dissolved arsenic compounds in ground water (3), the removal of arsenic from process streams and its safe disposal has become a significant problem for some domestic mineral processors.

Stabilization of arsenic as calcium-iron arsenate (4-5) has been suggested as a method for the disposal or long-term storage of arsenic, but some studies suggest the stability of these materials may be limited (6). In addition, the voluminous and fine-particulate natures of these arsenates create handling and storage risks. Removal of arsenic from the wastes prior to any other processing for possible metal recovery, or fixation of the arsenic in a vitrified form, may provide alternative treatment strategies which pose less risk to the environment and provide a dense, stable, and more easily handled form for the waste. The U.S. Bureau of Mines has researched the processing of arsenic-containing waste materials to remove the arsenic and recover metal values (5, 7). Pressurized chloride-oxygen leaching of arsenic-bearing wastes was investigated by Smyres and coworkers (5), although a sulfuric-acid leach may offer some advantages since sulfide-mineral processors generally produce the acid as a byproduct, thus providing a cheap reagent. The acidic bleed streams from electrolytic metal refineries, or the bleed solution from sulfuric-acid plants, could also provide acid for leaching. Since these acid-bearing solutions must be removed to control impurities in the refining and acid-production processes, coprocessing of flue dust with such solutions may provide treatment options for the utilization and disposal of both wastes.

The USBM has also investigated the leaching and recovery of metals from a variety of arsenic-bearing dusts (8). Acid-leach processing of an arsenic-laden smelter flue dust and options for recovering metal values from the resulting leach solutions are described in this report along with sulfidization as a means to purify refinery and acid-plant-bleed solutions. Detailed leaching studies investigated the effects of temperature, residence time, and sulfuric-acid concentration, as well as the use of refinery- and acid-plant-bleed solutions on the solubility of the metal values in the dust.

Subsequent investigations of leach-solution processing steps included cooling to precipitate copper sulfate, sulfur dioxide reduction to precipitate arsenic trioxide, solvent extraction to remove arsenic, neutralization to precipitate calcium-iron arsenates, neutralization to precipitate bismuth, sulfidization to precipitate arsenic and or copper sulfides, and cementation to recover copper.

Bismuth is extremely detrimental to the electrowinning of copper, and the copper-bismuth separation is critical if copper values are to be recovered from bismuth-bearing byproducts. The removal of bismuth from flue dust leach residue is also discussed in this report.

Additional research discussed in this report includes stabilization of arsenic sulfide by vitrification, removal of heavy metals from synthetic acid-plant-blowdown solution (APBD), and leaching of copper smelter slag.

Objectives of the research were to examine and develop alternatives for the treatment of copper industry wastes and bleed streams which mitigate environmental threats posed by copper-processing wastes. The separation and recovery of arsenic into a nonhazardous, storable, or salable product was a primary objective. Minimizing volumes of solid and liquid bleed streams, while rendering them nonhazardous, and recovering copper were also included as research objectives.

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[4]Italic numbers in parentheses refer to items in the list of references at the end of this report.

LEACH STUDIES

WASTE CHARACTERIZATION

Waste materials used in these studies consisted of arsenic-laden smelter flue dusts, acidic bleed solutions from an electrolytic copper refinery, a finely ground copper-smelter slag, and simulated acid-plant-bleed solutions. Compositions of the solid materials are summarized in table 1 and compositions of liquid materials are listed in table 2.

Table 1.—Compositions of solid copper-processing wastes used in treatment studies, wt pct

Elemental component	Dust A	Dust B	Dust C	Dust D	Slag
As	4.7	1.8	3.6	7.3	NA
Bi	1.4	0.2	0.12	1.5	NA
Cd	0.1	0.05	0.13	0.15	NA
Cu	25.1	29.0	23.9	17.08	0.18
Fe	8.2	20.0	13.5	7.2	41.0
Mo	2.1	4.0	0.3	2.3	0.80
Pb	5.7	0.7	2.0	8.8	NA
Sb	0.1	0.04	0.14	0.14	NA
Zn	1.4	0.9	1.2	1.8	NA
Smelter type	Bath	Flash	Flash	Bath	NA

NA   Not available.

Table 2.—Compositions of liquid copper-processing wastes used in treatment studies, g/L

Element	Acid plant weak-acid-bleed (synthetic)	Acid-plant blowdown (industrial)	Refinery-bleed solution
As	4.4	0.048	0.6
Bi	0.044	0.0014	0.001
Cd	0.275	0.01	<0.02
Cu	2.95	0.0026	<0.05
Fe	<0.002	0.0044	0.3
H_2SO_4 ..	160	28.8	270-370
Mo	<0.006	NA	NA
Pb	<0.025	0.0044	0.02
Sb	NA	0.0005	0.02
Zn	<0.003	0.024	0.2

NA   Not available.

The flue dusts contained significant amounts of copper, iron, and lead. Three of the dusts, A, B, and D, also contained appreciable concentrations of molybdenum; molybdenum recovery was, however, not extensively investigated in this work due to time restrictions and investigation priorities. Total amounts of minor elements in the dust depend largely on ore content and not so much on smelting technology. The differences in dust composition are largely due to the amount of dust generated with respect to the amount of ore treated. Flash smelting can generate 10 times more dust than a conventional bath melt. When recycling or treating the dust, each copper-producing operation has to be considered separately to determine recycle limits with respect to secondary or contaminate metals such as bismuth. Those operations in which the dust is the outlet for a given metal must remove the offending metals prior to recycling any of the dust. Some copper smelters have no problem recycling all their dust while others cannot tolerate particular metal buildups and must separately process their dust.

The acidic waste solutions from sulfuric-acid production and copper-refining processes contain low levels of impurities of insufficient concentrations for individual recovery. The acid concentration, however, is sufficient for leaching flue dusts or other wastes that contain similar impurities; thus, the acid can be useful rather than a liability. The weak-acid-bleed solution used in these studies was a synthetic solution blended to replicate a bleed stream from the acid production process at a domestic copper refinery. The blowdown and refinery-bleed solutions used in these investigations were actual industrial effluents obtained from domestic copper producers.

LEACHING OF BATH-SMELTER FLUE DUST

Sulfuric Acid Leach

Limited availability of solid samples required most of the leach tests to be carried out in batch mode. Batch leaching of various dust samples was performed using reagent-grade sulfuric-acid solutions, refinery-bleed electrolyte, and weak-acid-bleed solution. In each case, the available acid in the solutions dissolved significant amounts of metals from the solid waste; however, leach residues typically contained up to 5 pct Cu, 2 pct As, and various other metallic contaminants. The residues were not suitable for landfill disposal since most did not pass requirements as outlined in the Toxicity Characteristic Leaching Procedure (TCLP) (9).

Much of the early test work was performed on dust sample D because it was the most plentiful of the flue-dust samples. Batch test results obtained using this dust identified acid concentration, solids content in the slurry, and residence time as the parameters having most influence on the solubility of metals contained in the dust (10). Detailed results of the leach tests have been previously published (10-11) and the optimum leach conditions for maximizing copper and arsenic solubility while minimizing bismuth solubility were identified as 20 to 25 wt pct H_2SO_4, 20 pct solids, and 55 °C, with a residence time of 30 min.

The reason for minimizing bismuth extraction was to preclude the need to deal with this element in two recyclable streams. If all of the bismuth remained in the leach residue, the need for a copper-bismuth separation would be eliminated in the processing of the leach solutions. Conversely, if all of the bismuth were leached, the leach residue could be recycled to the smelting operations without the need for a separate bismuth-removal step. Leaching the flue dust at a higher temperature of 80 °C, 25 wt pct H_2SO_4, and 20 pct solids increased bismuth extraction from approximately 20 to 40 pct which was not sufficient to preclude treating the residue for bismuth removal. Selection of the most prudent strategy would, however, be site specific.

Bleed Electrolyte Leach

Bleed electrolyte, diluted and undiluted, was used to leach flue dust sample D and results were compared with data obtained using reagent-grade sulfuric acid solutions. Tests utilized 25 wt pct H_2SO_4, undiluted-electrolyte-bleed solution, or an equal-volume mixture of the two solutions. A 30-min leach was performed at 20 pct solids and 55 °C. Similar comparative leach tests using other dust samples were not performed owing to the limited amount of materials available.

Metal extractions were similar using either electrolyte-bleed solution or fresh acid as shown in table 3. Therefore, the use of this bleed stream as a source of sulfuric acid to leach flue dust is feasible.

Table 3.—Comparison of metals leached, in wt pct, from flue dust D using various leaching solutions

Lixiviant	As	Bi	Cd	Cu	Fe	Mo	Zn
Reagent-grade acid	97	20	94	87	50	92	92
50:50 mixture, H_2SO_4 and refinery bleed solution ..	97	21	90	82	51	91	88
Refinery bleed	96	20	90	84	48	91	88

LEACHING OF FLASH-SMELTER FLUE DUST

Acid Leach

Flash smelter flue dust, flue dust B, was also investigated in batch leach tests to allow for comparison with leach results obtained using sample D (sample D was generated using conventional bath-smelting technology). The dust was leached at 55 °C for 30 min using 25 wt pct H_2SO_4. The percent solids concentration, however, was reduced to 12 wt pct to limit copper concentration in the leach filtrate to 35 g/L Cu; this is near copper saturation

for the solution. This was necessary to prevent copper precipitation during downstream processing steps.

As indicated by the data in table 4, the leaching chemistry of the flash-smelter dust was significantly different in terms of bismuth and zinc solubility. Approximately 60 pct of the bismuth in this dust was soluble in a sulfuric acid leach compared with approximately 20 to 25 pct solubilized from the bath-smelter dust.

Table 4.—Metal leached using reagent-grade acid and weak-acid-bleed solutions

Acid	Extraction, wt pct						
	As	Bi	Cd	Cu	Fe	Mo	Zn
Flue Dust D:							
Reagent-grade	95	25	90	85	50	90	90
Flue Dust B:							
Reagent-grade	95	60	90	90	80	90	75
Weak-acid-bleed solution ..	95	80	90	90	80	95	75

Note.—Extraction values represent lowest values from several tests.

Although temperatures above 55 °C showed no improvement in leaching dust sample D, a temperature of 80 °C improved leaching of flash-smelter flue dust B. This, in conjunction with the use of synthetic weak-acid-bleed solution, increased the dissolution of bismuth over that obtained using reagent-grade sulfuric acid at 55 °C as shown in table 4. The synthetic weak-acid-bleed solution contained in grams per liter: 160 H_2SO_4, 1 HCl, 2 HF, and 1 NaCl.

To determine the cause of increased bismuth extraction, which resulted when leaching with weak-acid-bleed solution, the effect on bismuth dissolution of varying concentrations of hydrochloric and hydrofluoric acids was investigated. Leaching was performed at 80 °C since higher bismuth extractions were obtained previously at the elevated temperature. The addition of a small amount of hydrofluoric acid resulted in increased bismuth extraction, from 67 pct in the absence of hydrofluoric acid to 75 pct using 2 g/L HF, as shown in table 5. Both leach solutions contained 1 g/L HCl. The presence of hydrofluoric acid in an industrial leach, however, is undesirable. Bismuth solubility increased 11 pct by increasing the hydrochloric acid concentrations from 1 to 5 g/L, but further increase in HCl concentration had little effect on bismuth solubility.

These data suggest that weak-acid-bleed solution is a suitable leach solution for flash-furnace flue dust and that bismuth solubility may be enhanced by the presence of the halogenated acids, HF and HCl. Detailed results of leaching with weak-acid-bleed solution have been previously published (12).

Table 5.—Effects of chloride and fluoride concentration on solubility of bismuth when leaching flash-smelter flue dust

HCl, g/L	HF, g/L	Metal extraction, wt pct Bi
1	2	75
5	2	86
10	2	86
1	0	67

Note.—The bismuth extractions presented in this table are slightly lower than those reported in table 4 for the same conditions. These tests were performed on a small scale due to short supplies of flue dust. Scale-up tests performed later, however, resulted in increased metals extractions from which data for table 4 were compiled.

Water Leach in Conjunction With Weak-Acid-Bleed Leach

Leaching would unavoidably occur if water was used for dust control during handling and transportation of the dust as a slurry. The water should leach some copper, cadmium, zinc, and iron from the dust while the weak-acid leach that followed would remove additional copper, bismuth, arsenic, etc. Tests were carried out to determine what effect a water leach might have on subsequent leaching of flash-smelter flue dust with simulated weak-acid-bleed solution. Batch leach tests were performed at ambient temperature in tap water for 30 min using solids concentrations ranging from 6.7 to 23 pct. The leach slurries were filtered and the filtrates and residues assayed for metal contents. No rinse between tests was performed since this would not likely be part of a practical application of this process. A temperature increase during the water leach was noted due to exothermic dissolution reactions. The pH of the final filtrate from the water leach ranged from 3.5 to 3.8. The metal extractions were unaffected by pulp solids contents over the range studied. The metal extractions were typically, in weight percent, 7 As, 0 Bi, 79 Cd, 33 Cu, 7 Fe, 2 Mo, and 44 Zn.

Batch leach tests of the water-leach residue, using weak-acid-bleed solution, were performed at 80 °C for 30 min. Solids contents were again adjusted to obtain a maximum of 35 g/L Cu in the final leach solution to avoid saturation with copper. The reduced copper content in the solids, due to the water leach, resulted in higher ratios of other metals to copper in the water leach residue for a net increase in dissolved metals concentration in the acid leach solution as shown in table 6. Bismuth extractions were notably lower, as compared to a single acid leach, but data presented in table 7 show increased bismuth extraction was achieved by increasing the hydrochloric acid content in the weak-acid-bleed solution.

Table 6.—Composition of flash-flue-dust leach filtrates, g/L

Component	Weak acid	Water-Weak acid	
As	2.5	0.13	2.8
Bi	0.25	<0.001	0.38
Cd	0.07	0.14	0.01
Cu	40.0	28.0	34.0
Fe	26.1	4.1	31.0
Mo	1.6	0.01	2.0
Zn	1.0	1.1	0.23

Table 7.—Weight percent metal extracted from flash-smelter flue dust using water and simulated weak-acid-bleed solution with varying amounts of hydrochloric acid in weak-acid-bleed solution

Component	1 g/L HCl	2 g/L HCl	3 g/L HCl	4 g/L HCl	5 g/L HCl
As	86	84	85	85	89
Bi	83	82	87	85	91
Cd	90	89	89	90	99
Cu	91	89	90	91	93
Fe	68	71	71	69	71
Zn	62	65	59	59	62

CHARACTERIZATION OF LEACH RESIDUES

Acid Leach Residues

Solid residues from the batch-leach studies using flue dust sample D were subjected to the Environmental Protection Agency's TCLP to determine characteristic toxicity (9). Typical residues contained, in weight percent, 2 As, 3 Bi, 0.04 Cd, 6 Cu, 27 Pb, and 10 Fe. Unwashed and washed residues were subjected to TCLP. Unwashed leach residues met TCLP requirements for lead, but not for arsenic and cadmium. The stability of lead may be due to the presence of sulfuric acid retained in the leach residue; this acid would tend to keep the lead in an insoluble, sulfate form. Washed residues did not meet TCLP limits for lead solubility while the arsenic and cadmium levels in the effluents were barely acceptable.

Water-Weak-Acid Leach Residues

Solid residues from the batch-leach studies on flue dust B that used water and weak-acid-bleed solution in series typically contained, in weight percent, 1 As, 0.2 Bi, 11 Cu, 0.03 Cd, 25 Fe, and 3 Pb. This leach residue should be suitable for direct recycle to the smelter owing to the low bismuth content. It did not pass the TCLP requirement for lead solubility.

POSTLEACH PROCESS FLOWSHEET OPTIONS

PROCESSING OF FLUE DUST LEACH RESIDUE

Owing to bismuth insolubility, the residue from conventional bath-smelting technology (sample D) contained most of the bismuth (the extraction of which was minimized in the leach) that must be removed before the dust can be recycled to the smelter for metals recovery; the residue not only contains copper and lead, but other valuable metals which can be reclaimed. Flue dust sample D, for example, contained 0.2 tr oz/st gold and 6 tr oz/st silver.

Residues were leached with mixtures of sulfuric and hydrochloric acid at 55 °C for 2 h. Slurry conditions for the leach ranged from 5 to 20 pct solids, 2.5 to 20 pct H_2SO_4, and 0 to 5 pct HCl. Hydrochloric acid was the main constituent affecting bismuth extraction with 5 pct HCl leaching 90 pct or greater bismuth consistently.

PROCESSING OF LEACH SOLUTIONS

Typical leach solutions contained significant amounts of dissolved metals and their recovery was the primary research objective. The composition of an average leach solution obtained by leaching dust sample D in 20 pct H_2SO_4 is presented in table 8, along with the amount of metal typically dissolved at the conditions defined as optimal for maximizing metals extraction while minimizing bismuth extraction (13), i.e., 20 wt pct solids, 20 to 25 wt pct H_2SO_4, 55 °C for 30 min.

Table 8.—Composition of typical leach solutions produced at defined optimal conditions, dust sample D

Elemental component	Solution composition, g/L	Metal leached, wt pct
As	12.0	97
Bi	0.8	22
Cd	0.4	91
Cu	38.0	84
Fe	9.0	49
Mo	5.0	91
Zn	4.0	89

Overview

Four postleach processing options were investigated for the recovery of metal values from the leach solutions. The first option included copper removal as a hydrated sulfate with subsequent arsenic recovery by reduction and precipitation of arsenic trioxide using sulfur dioxide. A second option employed neutralization of acidic leach solutions using calcium carbonate to selectively precipitate calcium-iron arsenate; copper was subsequently recovered by cementation on iron. The third option utilized solvent extraction with tri-n-butyl-phosphate (TBP) to remove arsenic and molybdenum from the leach solutions. The arsenic and molybdenum were selectively stripped with water and ammonia, respectively, and copper was then precipitated from the arsenic-free leach solution via cementation. A fourth option employed calcium carbonate and sulfur dioxide to selectively precipitate bismuth. Copper and arsenic were then precipitated with hydrogen sulfide. The suitability of byproducts for resale or stabilization by vitrification was considered for each of these process options.

Copper Recovery as Sulfate, Arsenic Removal Using SO₂ Reduction-Precipitation

Saturated salt levels were attained in leach solutions by recycling of filtrates back to the leach process with added sulfuric acid to maintain the H_2SO_4 concentration at 20 wt pct; filtrates were oxidized by sparging with air to convert arsenic to the pentavalent state. Copper sulfate was precipitated from 80 °C, copper-saturated solutions by cooling to 10 °C at which temperature only 25 g/L Cu remained in the leach solutions.

Pentavalent arsenic in the leach solutions was reduced to the less-soluble As(III) by sparging with SO_2 for periods of 1 to 6 h. Arsenic trioxide precipitated leaving 8 g/L As in the leach solutions. The leach solutions were then recycled with added sulfuric acid to extract more copper and arsenic. Molybdenum precipitated with the arsenic, reducing arsenic purity and making the product unsuitable for sale or for stabilization by vitrification since molybdenum contamination precluded glass formation in subsequent vitrification tests.

Precipitation of Arsenic as Calcium-Iron Arsenate

Despite preferring to provide waste-management options that circumvented the material-handling problems associated with traditional calcium-iron precipitation of arsenic, the use of calcium and iron in the treatment of leach solutions was investigated to determine whether an arsenic-copper separation could be effected by proper control of process variables. Experiments to optimize the separation of arsenic and copper via selective precipitation as calcium or iron arsenates from leach solutions using $CaCO_3$ yielded promising results. The effects of temperature, redox potential (ORP), and the molar iron-to-arsenic

ratio at the pH where arsenic and copper precipitated were studied. Test conditions and results are summarized in table 9. Chlorine gas was used to oxidize the solutions and ORPs were measured using a platinum electrode with a silver—silver-chloride reference.

Table 9.—Test conditions for selective precipitation of arsenic from acidic leach solutions

Temper- ature, °C	Potential, mV (Ag/AgCl refer- ence)	Fe-to-As molar ratio	pH of maximum As precipi- tation	pH at onset of Cu precipi- tation	ΔpH at onset of Cu-As precipi- tation
50	700	1	4	4	0
55	700	3	4	4	0
85	700	1	1.8	2	0.2
85	700	3	2.8	4	1.2
70	900	2	2.8	4	1.2
70	900	2	1.8	3.8	1.8
70	900	2	1	3	2
70	900	2	1.8	4	2.2
55	1,100	1	2	4	2
55	1,100	3	2	3	1
85	1,100	1	2	2.5	0.5
85	1,100	3	1	3.8	2.8

Tests were performed in batch reactors using 7.8 wt pct $CaCO_3$ slurry to adjust the pH. Measured aliquots of the slurry were added to the leach solution in the reactor and stabilized pH readings were recorded. A sample of the reactor contents was then withdrawn and filtered, and the solid and liquid phases analyzed for metal content. This semi-continuous sampling procedure made direct comparison of results from test to test difficult since dilution due to the addition of the $CaCO_3$ slurry was not constant. However, some important trends were identified.

Results indicated a copper-arsenic separation is feasible if pH is maintained in the range of 1.8 to 3. The compositions of the precipitates removed from the reactor at various pH values clearly indicated arsenic precipitated prior to copper. Arsenic precipitation typically commenced around pH 1 and was complete by pH 2, and copper precipitation was initiated in the pH range of 3 to 4. Copper precipitation showed no statistical dependence on any of the test parameters and was minimal at slurry pH values less than 3.

The pH at which arsenic precipitation was maximized decreased as temperature and ORP increased, and was independent of the iron-to-arsenic ratio for the range evaluated. Additionally, the filtration characteristics (speed

and washability) of precipitated slurries were greatly improved at higher temperatures, i.e., 70 and 85 °C, and higher ORPs, i.e., 700 and 1,100 mV.

The $CaCO_3$ precipitation option, however, generated significant amounts of arsenic-containing waste which were difficult to handle. The voluminous and easily air-borne nature of the precipitated arsenic compounds could preclude application of selective precipitation to separate copper from arsenic because of material-handling difficulties.

Arsenic Removal by Solvent Extraction

A third arsenic-copper-separation option involved removal of arsenic and molybdenum from the leach solutions by extraction with TBP. Leach solutions generated in a semi-continuous leaching process were contacted with undiluted TBP at an aqueous-to-organic (A-O) ratio of 1:1 at room temperature to determine which metals would be extracted. No adjustments to solution pH were made before or during extraction, and 30-min contact times were used. Typically, the aqueous-solution pH ranged from 0 to 1, and, while the composition of solutions used in the batch solvent-extraction tests varied, a typical leach solution contained, in grams per liter, 12 As, 0.2 Bi, 0.1 Cd, 25 Cu, 2 Fe, 2 Mo, and 1.5 Zn.

TBP extracted arsenic and molybdenum from the leach solutions while exhibiting virtually no affinity for other metallic ions in the liquors. The nature of the extracted species, whether an arsenic-molybdenum complex or individual ions, is unknown, but the extracted metals were selectively stripped from the loaded solvent. Arsenic was stripped with water while molybdenum required $0.5\ N\ NH_3$ for removal from the organic phase. Solvent losses and reagent consumptions were not determined.

Copper Recovery by Cementation on Powdered Iron

Processing simplicity made cementation the preferred method for recovering copper from arsenic-free leach solutions. When arsenic was removed by either solvent extraction or precipitation with lime and iron, copper was subsequently recovered by addition of powdered iron. Test results are summarized in table 10. Arsenic removal by solvent extraction results in a more pure copper product, but both solvent extraction (SX) and lime precipitation processes allowed for complete copper recovery.

Table 10.—Cementation of copper after arsenic removal

As removal method	Fe addition, pct of stoichiometric	Cu recovery, pct	Product composition, pct		
			As	Cu	Fe
SX	75	35	<1	68	21
	100	89	1	86	7
	200	100	6	70	13
Lime-iron	75	72	11	36	7
	100	99	11	24	8
	200	100	10	23	33

Neutralization of Weak-Acid-Bleed Leach Filtrate for Bismuth Removal

Neutralization of weak-acid-leach liquors from flash-smelter flue dust B with a calcium-carbonate slurry was investigated to selectively precipitate bismuth from solution. Reduction, using sulfur dioxide, and oxidation, using chlorine, were investigated to determine whether bismuth could be selectively precipitated.

Neutralizations were performed at 60 °C since some cooling would be expected following an initial leach at 80 °C. Oxidized solutions measured greater than 1,000 mV and reduced solutions measured less than 250 mV before neutralization and less than 150 mV after neutralization. Chlorine addition was continuous during oxidized neutralization, but the sulfur-dioxide sparge was discontinued just prior to neutralization of reduced solutions.

Neutralization was accomplished in batch tests by adding a 60 °C slurry of 120 or 140 mL of water containing various weights of calcium carbonate to 140-mL aliquots of pretreated (oxidized or reduced) leach filtrate. The combined solutions were mixed for 1 h, filtered, and the solids were washed with sulfuric acid solutions having the same pH as the filtrates to preclude further neutralization from the entrained solution. The amount of calcium carbonate added to the slurry controlled the final pH.

As shown in figure 1, arsenic precipitation occurred before complete bismuth precipitation under oxidized conditions, and bismuth precipitated prior to complete arsenic precipitation under reduced conditions; see figure 2. Under oxidized conditions, iron also precipitated with arsenic implying that an iron arsenate may be forming. Large continuous simulated-neutralization tests, where calcium-carbonate slurry and weak-acid-leach filtrate were added to neutralized slurry, showed even greater bismuth selectivity when washing of the gypsum precipitate was adequate to remove entrained liquor.

Characterization of Bismuth-Rich Gypsum

Gypsum samples generated by calcium carbonate neutralization of reduced (<250 mV) leach solutions were subjected to TCLP to determine characteristic toxicity. Results in table 11 indicated the solids to be stable with respect to TCLP. The solids typically contained in percent, 0.07 Bi, 0.1 Cu, 0.02 As, 0.002 Cd, 0.005 Zn, 0.07 Fe, with the remainder comprised of gypsum and very small amounts of other elements.

Table 11.—Concentrations of metals in TCLP leachates obtained from bismuth-rich precipitates, mg/L

| Sample	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
1 . . .	3.2	5.6	<0.02	<0.02	<0.8	<0.02	<0.1	<0.2
2 . . .	0.02	0.5	0.7	<0.01	<0.4	0.002	<0.1	<0.1
3 . . .	0.3	0.4	0.8	<0.01	<0.4	<0.01	<0.1	<0.1
TCLP limit	5	100	1	5	5	0.2	1	5

Sulfide Precipitation of Arsenic and Copper

Following the neutralization of flash-smelter flue dust-leach liquors to remove bismuth, a separation of copper and arsenic was achieved by the addition of hydrogen sulfide at 60 °C. As illustrated in figure 3, the ORP of the neutralized solution initially increased as the hydrogen sulfide gas was added. It was during this increase that 90 pct of the copper in the solution was precipitated while less than 10 pct of the arsenic was precipitated; thus, using ORP to control the reaction, a separation of copper and arsenic was effected. At lower temperatures, the copper precipitation decreased and that of arsenic increased in the region of increasing ORP of 0.255 to 0.335 mV, thereby making separation of copper and arsenic less selective.
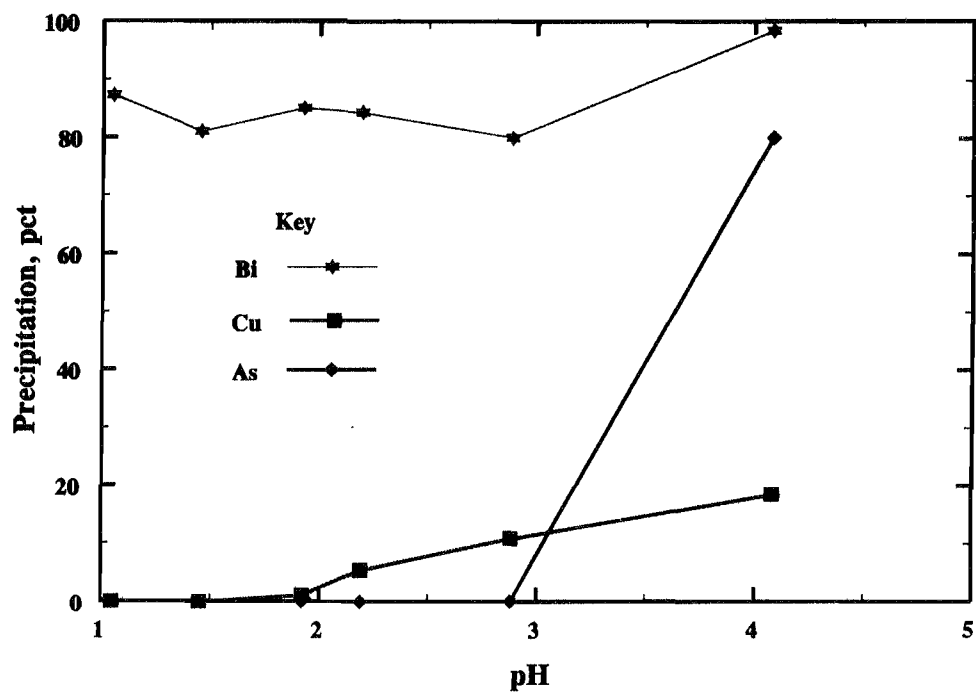
VITRIFICATION OF SULFIDES

The stabilization of arsenic removed from copper-processing wastes in a dense, easily handled form, such as a vitrified glass, was a principal research objective. Thus, preliminary tests, using pure arsenic-sulfide compounds mixed with varying amounts of sulfur, were performed to determine proper vitrification temperatures and optimum mixture ratios. Sulfur additions were necessary to facilitate formation of a vitrified, glassy product. Arsenic-disulfide-sulfur mixtures containing 32 to 52 pct arsenic were vitrified at temperatures from 350 to 500 °C for 2 h under a nitrogen atmosphere. Vitrification was incomplete at temperatures below 375 °C. Weight loss due to
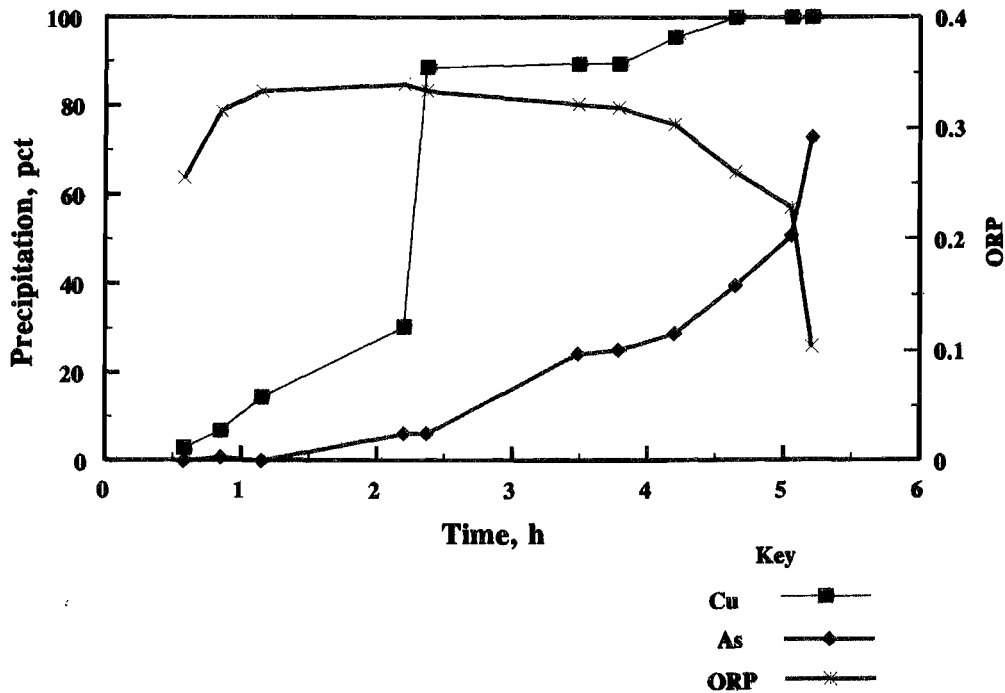
Figure 1
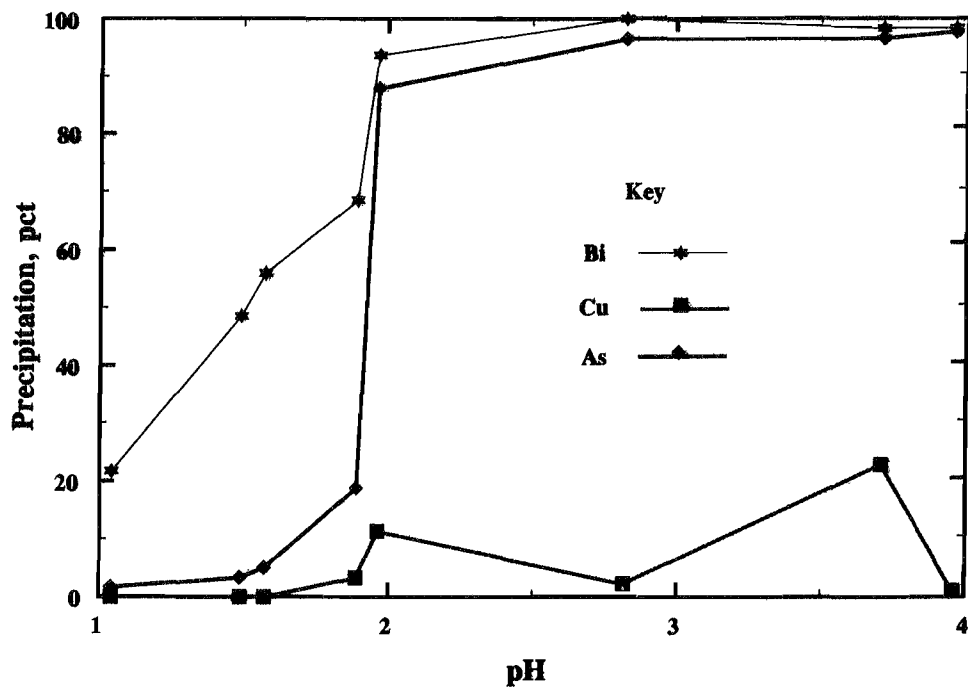
Bismuth precipitation under oxidized conditions.

Figure 2

Bismuth precipitation under reduced conditions.

Figure 3

Hydrogen-sulfide-induced precipitation of copper and arsenic at 60 °C.

volatilization was less than 10 pct below 450 °C, but increased greatly at higher temperature. Selected vitrified products were subjected to TCLP protocols. The TCLP analysis showed that extracts from vitrified arsenic-sulfide glasses formed at 375 and 400 °C were below the allowable limit of 5 mg/L As.

Products derived from the vitrification of arsenic-trisulfide-sulfur mixtures could not be distinguished from those formed using arsenic disulfide. Similar tests were performed to determine the proper arsenic-to-sulfur ratio in the mixture to minimize product volatilization. Data presented in table 12 indicate the vaporization loss to be higher in sulfur than in arsenic. This suggests the volatilization of elemental sulfur may be responsible for the major portion of the weight loss.

Table 12.—Compositions (wt pct) of vitrified products produced using various mixtures of arsenic-trisulfide and elemental sulfur

Initial composition		Final composition, test 1			Final composition, test 2		
As	S	As	S	wt loss	As	S	wt loss
32	68	37	58	35	37	59	29
37	63	42	54	50	42	58	32
42	58	46	52	53	45	54	42
47	53	50	48	50	49	49	46
52	48	52	46	43	50	46	36

A tube furnace was used in the vitrification tests; examination showed the solids which condensed in the cooler end of the tube furnace to be mostly arsenic trisulfide. The quickly condensed material could be easily collected and returned to the vitrification process.

The arsenic trisulfide used in these tests was formed by hydrogen-sulfide-sparging of sulfuric-acid solutions which contained dissolved arsenic oxides. The resultant precipitates contained arsenic trisulfide with some arsenic oxides and arsenic pentasulfide. Arsenic sulfide for the two-test series was made in two separate batches. The composition of the sulfide products probably varied in composition. Differences in the amount of arsenic pentasulfide or oxides would explain differences in overall weight loss during vitrification. The arsenic pentasulfide, which does not vitrify, was either converted to a trisulfide or fumed off in the furnace. The final composition of the vitrified products is based on actual assays and the percentages of arsenic and sulfur do not sum to 100, possibly due to experimental error in assaying procedures.

Arsenic-sulfur mixtures containing as much as 52 pct As, with the balance sulfur, were vitrified at temperatures between 400 and 500 °C providing a solid, dense, vitrified product which can be safely stored in an open area without harming the environment.

Vitrification of Contaminated Arsenic Sulfides

Copper waste streams typically contain copper, bismuth, molybdenum, and cadmium; each of these metals forms a stable sulfide at approximately the same ORP as arsenic in a given pH range. Although careful ORP control provides some selectivity in the removal of arsenic by sulfide precipitation, coprecipitation of other metallic sulfides is inevitable. Because of the inability to precipitate a pure arsenic sulfide for vitrification, the effect of metallic contamination on the TCLP stability of vitrified arsenic products was studied. Synthetic samples of arsenic-trisulfide were contaminated with copper, cadmium, molybdenum, and bismuth sulfides. Metal contamination levels ranged from 1.5 to 20 pct, and all metals, except arsenic were present in equal mass percentages. A tube furnace temperature of 450 °C and residence times between 1 and 2 h under nitrogen atmosphere minimized weight loss due to volatilization. The TCLP results for arsenic and cadmium, and weight loss data are presented in table 13.

Data indicate that arsenic was contained in a glassy matrix, but that vitrified material containing more than trace amounts of cadmium did not pass TCLP requirements for cadmium. In addition, increasing the amounts of metals, other than arsenic, in the sulfide mixture to levels above 10 wt pct, often resulted in the formation of a brittle product which could pose handling difficulties.

Computer modeling of As_2S_3 glass predicts a helical six-member-ring structure (14), and cadmium is sufficiently similar to arsenic in its atomic radius and electronegativity to be stabilized either by lattice substitution or interstitial entrapment to a greater extent than is demonstrated in the above results. In an attempt to increase cadmium stability, a water quench was used to cool the molten glass. As

shown in table 14, quenching with 20 °C deionized water reduced the cadmium and arsenic TCLP leachability by 77 and 21 pct, respectively, using a synthetic sulfide mixture containing in percent: 36.1 As, 0.375 Cd, 0.375 Cu, 0.375 Mo, 0.375 Bi, and 62.4 S.

Table 13.—Weight-loss and TCLP data for contaminated arsenic sulfides

Initial composition, wt pct			Loss due to volatiliza-tion, wt pct	TCLP results, mg/L in leachate	
As	S	Metallic sulfides[1]		As[2]	Cd[3]
42	58	0	7	1	NAp
52	48	0	4	3	NAp
35.3	61.3	3.3	10	1	48
45.3	51.3	3.3	5	4	28
38.6	54.6	6.7	7	5	51
32	58	10	10	3	24
42	48	10	8	19	96
35.3	51.3	13.3	14	4	19
32	48	20	15	7	29

NAp Not applicable.
[1]Equal-mass percentages of Cu, Cd, Mo, and Bi.
[2]TCLP As limit 5 mg/L.
[3]TCLP Cd limit 1 mg/L.

Table 14.—Hazardous elements leached from As_2S_3 glass with 1.5 pct contamination

Sample	As	Cd
Unquenched	1.4	7.9
Quenched	1.1	1.8
Pct change	-21.4	-77.2

SULFIDE PRECIPITATION FROM SYNTHETIC ACID-PLANT-BLOWDOWN SOLUTION

In the production of sulfuric acid from sulfur dioxide-rich smelter off-gasses, particulates are first removed from the gasses using electrostatic and mist precipitators. The liquid from the particulate-removal process is known as acid-plant-blowdown (APBD) solution. The APBD solution contains numerous metal values, including harmful components such as arsenic, cadmium, and lead.

Arsenic-sulfide precipitation followed by vitrification was evaluated as a method to remove and subsequently stabilize the toxic metals from APBD solutions (composition given in table 15). Once the solution was oxidized with air to 425 mV versus a saturated calomel electrode,

H_2S was added until the ORP was 0 mV. Arsenic, lead, and cadmium were precipitated as sulfides leaving concentrations of 0.6, 0.2, and 0.1 mg/L, respectively, in the blowdown solution. The resultant sulfides, with the composition shown in table 16, exhibited characteristic toxicity and vitrification was investigated as a means of stabilization. The sulfides were heated in a nitrogen atmosphere at 450 °C for 1 h and quenched in 20 °C deionized water. Stabilization of sulfides containing only 15 pct As was unsuccessful as TCLP determinations yielded arsenic levels twice the allowable limit.

Table 15.—Composition of synthetic acid-plant blowdown

Element	g/L
As	6.7
Cu	4.1
H_2SO_4	54
Pb	4.7

Element	mg/L
Bi	0.0
Cd	0.3
Sb	0.06
SO_2	4.72

Table 16.—Composition of typical sulfides precipitated from synthetic acid-plant-blowdown solutions

Element	wt pct
As	15.2
Cd	1.1
Cu	18
Pb	0.018

LEACHING OF COPPER SMELTER SLAG

The recovery of metal values from copper-smelter slag was investigated not because of any environmental threat posed by this material, but because the large amounts of this material contain a significant quantity of copper and other metals. Leaching of a finely ground slag material containing in weight percent, 0.18 Cu, 41 Fe, and 0.8 Mo, was pursued using both basic and acidic reagents. Solutions of sulfuric acid, sodium hydroxide, and ammonia were used in attempts to solubilize valuable components in the slag. The objective was to obtain a leach solution suitable for copper recovery by solvent extraction or precipitation.

Slag was leached for 120 min at 80 °C and 20 pct solids, and the results for various leaching agents are summarized in table 17.

Leaching with sulfuric acid dissolved the greatest amount of copper and molybdenum, but iron contamination was significant. Solutions from the acid leach formed a gel upon cooling, making this process undesirable for copper and molybdenum recovery.

The basic reagents, NaOH and NH_3, resulted in more selective copper extraction at the expense of copper recovery. Neither reagent solubilized sufficient copper or molybdenum to warrant further investigation. The feasibility of leaching metal values from copper-smelter slag was demonstrated, but the economics of reprocessing would require nearly complete copper and molybdenum dissolution.

Table 17.—Results of slag-leaching tests

Leach solution	Wt pct metal leached			Total Slag solubilized, wt pct
	Cu	Fe	Mo	
20 pct H_2SO_4	70	60	60	48
10 pct NaOH	25	<1	7	0.5
20 pct NaOH	25	<1	10	NA
5 pct NaOH with 2 pct NaOCL	48	<1	15	1.6
10 pct NH_3	42	<1	15	0.5

NA Not available.

SUMMARY AND CONCLUSIONS

The feasibility of processing arsenic-laden smelter flue dust with either a solution of reagent-grade sulfuric acid or refinery-bleed solution has been demonstrated. Metals from the dust were solubilized by leaching at ambient pressure, and arsenic was separated from other components by either precipitation with lime and iron, solvent extraction with TBP, or sulfide precipitation. Copper was recovered by cementation or by recycle as a sulfide to the smelter.

Bismuth was selectively removed from flue dust leach solutions by reduction with sulfur dioxide followed by neutralization to pH 2.4 with limestone. The gypsum produced was not hazardous according to TCLP testing. Copper was subsequently recovered by precipitation with hydrogen sulfide.

Stabilization of arsenic as a vitrified, glassy-sulfide product was demonstrated, although the presence of contaminants resulted in the formation of a product which did not pass TCLP requirements for metals other than arsenic. Thus, stabilization by vitrification of the mixed sulfides precipitated from some process solutions may not be feasible even though sulfide precipitation was demonstrated effective in the removal of dissolved metals from the synthetic APBD solution.

Leaching of copper and molybdenum from copper-smelter slag was not considered feasible based on low copper and molybdenum extractions using basic reagents and owing to gel formation when using an acid leach.

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