



Project Summary

WME

Investigation of New Techniques for Control of Smelter Arsenic Bearing Wastes

Anil K. Mehta

Arsenic is the twentieth most abundant element in the earth's crust and is known to appear in 245 mineral species. It is found in appreciable concentrations in association with sulfide deposits with arsenopyrite (FeAsS) the most common form. Because of its relative abundance and modes of occurrence, it is a contaminant of coals, iron ore, phosphate rock, and nonferrous metals. Domestically, arsenic is produced as arsenic trioxide recovered as a by-product from copper smelting and is used to produce arsenic metal and some 45 other compounds of commercial significance. Uses include pesticides, animal hide and wood preservatives, feed additives, metal alloys, glass and pigment manufacture, solar cells, and catalysts. Most compounds of arsenic are extremely toxic and the element is also a suspected carcinogen.

Because of the potential hazards associated with arsenic disposal, the Industrial Environmental Research Laboratory at Cincinnati, Ohio, sponsored a research project at the Mineral Research Center, Montana Tech Alumni Foundation, to investigate a variety of approaches to the fixation of arsenic-bearing wastes, particularly smelter flue dusts, to render them harmless to the environment. The program was comprised of three principal elements: (1) separation of

the arsenic from metal values by leaching; (2) incorporation of the arsenic into a fixation matrix; and (3) leach testing of samples of the fixed product to determine suitability for environmental protection. Stabilization of the arsenic by incorporation in slag matrices and in cements, mortars, clays and concrete was investigated. The most promising technique found was stabilization by dissolution in a slag matrix to form a solid solution upon cooling. The slag fixation products yielded leachate concentrations of from 0.02 to 4.5 ppm for arsenics in slag loadings ranging from 7 to 24 percent arsenic.

This Project Summary was developed by EPA's Industrial Environmental Research Lab., Cinn., OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The flue dusts generated in the process of copper smelting contain appreciable amounts of copper and other metal values including precious metals. These flue dusts may also contain appreciable amounts of arsenic trioxide where arsenic (sulfide) occurs in the ore body. In the past, it had been common practice at some smelters to

collect metal values in the flue dust by means of high temperature electrostatic precipitation (ESP), with much of the arsenic trioxide passing the ESP in the vapor state and being emitted to the atmosphere. Now, smelters processing high arsenic concentrates cool the flue gas to desublimite the arsenic trioxide for control by a particulate arrestor. Two types of control are practiced: (1) a high temperature ESP, cooling, and cold ESP; and (2) cooling and cold fabric filter. Therefore, smelters processing concentrates having a medium to high arsenic content generate residuals containing arsenic trioxide. Present practice is to store these dusts. Where the residuals contain metal values, they are stored for retrieval and processing for metal recovery at some future time when economic recovery becomes possible.

There is now only one smelter in the United States that treats flue dust to produce arsenic for sale. The decline in demand and the competition from overseas sources to supply arsenic compounds have created an unfavorable economic condition that has resulted in rather large inventories of accumulated flue dust in storage. Because of the toxic nature of the flue dust, this storage must be in weather proof structures. At this time, it does not appear likely that sufficient market capacity for arsenic or its compounds will be found to consume the stockpiles being generated. Disposal of arsenic in some environmentally acceptable form may, therefore, become necessary. Eventually the main receptor for arsenic will be the land via landfill disposal or solution ponding. If land disposal of arsenic is to be practiced, the volume of dust should be reduced. This can be accomplished by concentrating the arsenic content. The objective is to remove metallic values from the dust, thereby leaving a residue ready for subsequent metallurgical treatment for fixation of the arsenic.

Montana Tech Minerals Research Foundation (MRC) began an EPA supported project in November 1976 (EPA Grant R-804-1-595) to investigate means of treating arsenic containing copper smelter flue dusts. A comprehensive literature survey was initiated to gather information about arsenic that could possibly lead to a technique or techniques for the safe disposal of this material. Information was sought on the general chemistry and geochemistry of arsenic, the extractive metallurgy of

arsenic and its removal as an impurity from metallurgical systems, wastewater purification, and existing control equipment and techniques. The survey resulted in a collection of over seven hundred references. The MRC arranged for the participation of interested industry representatives to provide insight into the potential usefulness of the research and performance of certain aspects of the experimental work.

An experimental research program was devised and initiated in March 1977. This program was structured to investigate methods to separate the arsenic from the flue dust so that the metal values could be recovered, and the arsenic fixed in a form which would be stable in the environment, this permitting disposal to the land without extraordinary safety precautions. A number of approaches were investigated, and extensive leach tests of the fixed products were conducted over periods ranging from 6000 to 9000 hours.

The experimental program was initially structured around the hydrometallurgical treatment of smelter flue dust to separate metal values from the arsenic trioxide and subsequent recovery of the arsenic through precipitation as an arsenate or by sorption. In an indepen-

dent approach, a number of schemes for arsenic fixation in the form of flue dust, arsenic trioxide, and calcium and iron arsenates were investigated. This work led to the discovery that calcium arsenate was an excellent form for fixation in selected media. Because of this, methods to convert the arsenic in flue dust to calcium arsenate in a dry, elevated temperature process was pursued. A technique for using calcium compounds such as lime was developed for possible use for converting the arsenic trioxide in flue dust to form suitable for fixation.

Extraction of Arsenic from Flue Dusts

A program of leaching experiments was organized to investigate the solubility characteristics of a variety of arsenic-bearing flue dust materials collected from domestic primary producers of copper, zinc, and lead (Tables 1 and 2). Leaching experiments were conducted using six conventional lixiviants (water, sulfuric acid, ferric sulfate, ferric chloride, aqueous ammonia, and sodium hydroxide) in various combinations. Leach extraction was determined as a function of time, temperature, and reagent concentration.

Table 1. Copper Smelter Flue Dust Composition Ranges

Element	Percent in dust
Cu	5-15
Pb	8-15
Zn	5-15
As	3-30
Bi	0-2
Ag	3-13 oz/ton
Au	0-0.2 oz/ton

Table 2. Example Copper Smelter Flue Dust Assays

Element	Assay, %			
	Dust I	II	III	IV
As	20.0	29.4	25.6	3.54
Bi	0.65	0.94	0.88	0.33
Cd	0.94	0.65	0.89	0.41
Cu	4.76	3.91	4.19	19.2
Fe	6.1	1.43	1.43	14.6
Pb	5.8	5.3	5.43	5.01
Sb	0.63	1.26	0.74	0.16
Sn	0.75	1.60	0.5	—
Te	0.27	0.69	—	.046
Zn	14.3	12.3	14.2	7.12
S	10.0	7.9	9.1	12.4
Mo	—	—	0.09	—
Ag	—	—	5.4 oz/ton	10.31 oz/ton

Results of the leaching tests indicated that up to 99 percent of the contained arsenic in several of the dusts examined could be solubilized by at least one of the lixivants tested under appropriate conditions. Due to the complex and variable mineralogy of the arsenic in the dusts examined, no universally effective method of leaching capable of complete dissolution of arsenic was found. The complexity of both the chemical and mineralogical compositions of smelter flue dusts also resulted in widely dissimilar solubility characteristics of other heavy metal constituents giving rise to a wide range of solution treatment problems following leaching. All leach tests performed resulted in the dissolution of significant amounts of copper, iron, zinc, cadmium, antimony, and tellurium in addition to arsenic.

Although a solvent that would be applicable to all flue dusts was not identified, each flue dust responded effectively to at least one of the solvents. Specific parameters of reagent concentration, time, temperature, and liquid-solid ratio must be determined experimentally for each individual flue dust in order to maximize arsenic extraction, achieve selectivity with respect to other metal constituents, and to conserve chemical reagents. No single combination of lixiviant composition and leaching conditions is considered optimum for a diversity of flue dust waste materials.

Most flue dusts responded well to a combination of sulfatization followed by either water or sulfuric acid leaching. The added advantage of nearly complete extraction of copper, zinc, and cadmium favors the use of sulfuric acid as opposed to the other reagents examined by providing a degree of segregation of other dust constituents in addition to nearly complete arsenic extraction. In this way, a sizable fraction of the original dust containing a variety of impurities deleterious to most nonferrous smelting operations can be isolated from the arsenic as well as several important metals of value. Such a solid residue constitutes an important means of impurity rejection in most smelting operations.

Fixation of Arsenic

The recovery and fixation of arsenic forms from the leach liquors and other arsenic compounds readily available in the lab, such as arsenic trioxide, calcium, and iron arsenates, was the subject of broad based investigation. A number of arsenic "getter" compounds

were considered in this screening study. The fixed products were subjected to leach tests to determine the stability of these products. Additionally, a program of arsenic fixation experiments was organized to investigate the stabilization of arsenic by dissolution in slag matrices, and by encapsulation in cements, mortars, clays, and concrete. The success or failure of the stabilization was determined by reasonably long-term leach tests. These investigations were based upon the use of a suitable dry form of arsenic as a starting material for the fixation experiment. Such forms included unprocessed flue dust, calcium arsenate, iron arsenate, and arsenic trioxide. Both ambient and elevated temperature approaches were studied.

Sorption/Fixation from Leach Solutions

Laboratory tests to effect the recovery of arsenic from pregnant leach solutions included precipitation of arsenic by chemisorption on hydrated ferric oxides generated by hydrolysis of ferric sulfate present in the leach liquor, and on particulate surfaces of phosphate rock, bentonite clay, and cement plant cottrell dust. The arsenic content of sulfate-based leach liquors can be effectively recovered as a solid residue by coprecipitation with hydrated ferric oxide at mildly acidic solution pH. Residual arsenic concentration in solution can be reduced to well below one part per million when such precipitation is carried out in the presence of naturally occurring calcium phosphate (collophanite), although a reversion of arsenic solubility to approximately one part to seven parts per million occurs when arsenic-bearing hydrated ferric oxide precipitates are equilibrated with pure water over periods of several months. The use of particulate material to chemisorb arsenic from solutions does not appear to be a viable technique. Excessively large quantities of solid particulate would be required for successful removal of arsenic to desirable concentration levels. Therefore, large quantities of sludge material would have to be handled and stored

Clays

The concept employed here was to cause physical entrapment of the arsenic with a clay matrix. Bentonite and Kaolin were used as the clay sources. Bentonite contains a high percentage of montmorillonite clay

mineral. Arsenic sources used were arsenates of iron and calcium and arsenic trioxide

The mixtures in specified weight ratios were mechanically pelletized, then roasted to give dense and physically strong structures. The pellets were formed with specific arsenic concentrations and then heated at various roasting temperatures and times. As a variation, some pellets were coated with ceramist's glazing compound and glazed. These pellets were subjected to the immersion type leach test.

The pH of the solution was allowed to take its own course in most of the cases unless specified. For arsenic analysis, two ml of the leach solution were taken out at specified time intervals and replaced with two ml of the distilled water. The pellets of iron or calcium arsenates resulted in very low leaching (i.e., less than 1 ppm, with most samples less than 0.5 ppm) at arsenic loadings as high as 75 percent. However, the arsenic trioxide pellets proved to be unsuitable, yielding high leachate concentrations of from 40 to 100 ppm, as for pellet loadings as low as 0.5 to 1.0 percent.

Cement

Arsenic compounds were mixed in different proportions with the cements. Three treatments were investigated:

- (a) The materials were mixed with water, cast, and cured.
- (b) Materials were mixed and roasted at different specified time and temperatures. Water was added next, the resulting mixtures were cast and cured.
- (c) Materials were mixed with water, cast, and cured. The cubes were then roasted at specified time and temperatures.

A major reason for setting of cements into hard and dense structures is the crystallization of tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$). Arsenic trioxides and calcium arsenates have been used in portland cement mixtures for special uses (i.e., retarded early-setting time, early high strength, and resistance to chemical action of water). Addition of arsenic compounds is limited to certain quantities as they retard the setting of cements. Failure to achieve a good sample which is solid, unfractured, and hard to break is the result of retardation in crystallization of tricalcium silicate compound in the cements. Retardation by admixtures like arsenic compounds

is so enhanced at higher concentrations that cement setting does not take place and the final product is soft and crumbly.

The cast samples of arsenic cement mixtures were leach-tested for arsenic release using a shaker test. Leaching characteristics of roasted arsenate containing cements are good.

Slags

Arsenates were used as starting materials mainly for their arsenic carrying ability (i.e., they have a low vapor pressure and will not boil out of the system before the slag becomes molten). Flue dust or arsenic oxide cannot be used directly because it will vaporize away from the system before it has a chance to dissolve.

The solvents chosen for study are based on two primary considerations:

1. The availability and low cost of the materials, and
2. The potential for high arsenic dissolution.

The first of these considerations is fulfilled by both by-product slags from smelting operations and impure clays. The second consideration (i.e., the concentration of arsenic that can be dissolved), can only be postulated because only a few phase diagrams are available for arsenic containing systems.

These considerations are no more important than the requirement for the solvents to retain arsenic in such a way as to restrict its release to the environment. This requirement may be termed as chemical fixation of arsenic. Chemical fixation is defined for the purpose of this report as the formation of a chemically stable compound containing arsenic that upon weathering will not release arsenic to the environment in detrimental quantity. Arsenic containing glass (slag) is one of the chemical fixation possibilities.

Glasses are defined by the American Society for Testing Materials as "an inorganic product of fusion which has been cooled to a rigid condition without crystallization." For the purposes of this summary, a slag will be considered a glass. Slag is a multicomponent oxide mixture generated as a by-product from many smelting operations. It is normally treated for storage either by water quenching it or slow cooling it. The water quenched product is mostly non-crystalline while the slow cooled product is a matrix of crystalline and non-crystalline phases.

The experimental procedure used for preparation of the arsenic containing slag was as follows: The solid arsenate was weighed in the desired proportion and added to a fireclay crucible. The material or a mixture of the materials to be used as the solvent was added to the crucible in solid form. The crucible was then placed in an electric muffle furnace at the desired temperature. Furnace atmosphere was not controlled and was assumed to be of slightly oxidizing nature. The samples were melted, removed, and poured into sample recovery pans. They were allowed to cool in air.

Lime Roasting for Arsenic Fixation

Because of the success with the high temperature techniques for arsenic fixation, a pyrometallurgical route to conversion of arsenic trioxide to a refractory compound was sought. Based upon the literature review and the results obtained from the pellet roasting experiments, a number of arsenic gettering compounds were screened for their ability to retain arsenic trioxide under oxidative roast conditions as an arsenate form.

Many getter compounds were considered in this screening study (e.g., iron bearing compounds such as Fe_2O_3 , FeS_2 , reverberatory slag); aluminum bearing compounds (e.g., Al_2O_3 , kaolin); and calcium bearing compounds (e.g., CaO , CaCO_3 , power plant fly ash, phosphate ore and phosphate slag). The experimental procedure was to mix proportioned amounts of the getter material with either As_2O_3 or flue dust, pelletize (1/2-inch diameter spheres), and dry at 50°C for 24 hours. The pellets were then stored in vials until roasted. Roast tests were performed in an air atmosphere in a muffle furnace. The temperature range investigated was 200° to 400°C . After roasting, the pellets were weighed, ground, and analyzed for arsenic content by standard analytical procedures. Identification of the arsenic compound present was by x-ray diffraction.

The most effective calcium containing getters were CaO and $\text{Ca}(\text{OH})_2$. Those found to be ineffective were waste products that contained calcium, such as cement plant dust (75% CaCO_3), a power plant fly ash (calcium dissolved in slag), phosphate ore [calcium as $\text{Ca}_3(\text{PO}_4)_2$, CaF_2] and a phosphate slag (calcium as CaSiO_3). This study shows that the

arsenic trioxide can very effectively be converted to calcium arsenate by low temperature, short time air roasting. This approach permits conversion of arsenic-bearing flue dusts to a form suitable for incorporation into a slag for disposal. Alternatively, the process may potentially be adapted to permit recovery of metal values either through: (1) separation and recovery of the arsenic trioxide from the flue dust by volatilization and condensation; (2) separation of the arsenic trioxide from the flue dust by volatilization and recovery by reaction with a high temperature lime bed; or (3) return of the roasted pellets to the smelting furnace where the calcium arsenate is incorporated in the slag.

Conclusions

A summary of the most significant results from the leach tests is given in Table 3. These results show that arsenic in the form of calcium or iron arsenate can be incorporated into a variety of matrices, yielding stabilized products which, when subjected to extensive leach testing, permit only minimal releases to the environment. Limited testing with arsenic oxides showed that this form is not suitable for direct fixation in any of the matrices investigated in this study because sufficiently low leachability could not be obtained at reasonable arsenic-to-matrix ratios.

Hydrometallurgy

The results of the experimental leaching studies on the dissolution of arsenic from smelter flue dust wastes indicate that leaching can be an effective impurity rejection method dependent upon the specific chemical and mineralogical compositions of such materials. Specific parameters of lixiviant composition, time, temperature, and liquid-to-solids ratio must be determined empirically for each individual flue dust in order to maximize arsenic extraction, achieve selectivity with respect to other heavy metal constituents, conserve chemical reagents, and mollify reaction conditions. No single combination of lixiviant composition and leaching conditions is considered optimum for a diversity of flue dust waste materials.

The arsenic content of sulfate-based leach liquors can be effectively recovered as a solid residue by coprecipitation with hydrated ferric oxide at mildly acidic solution pH. Residual arsenic concentration in solution can be reduced

Table 3. Summary of Fixation Test Results

Matrix	Arsenic form	Arsenic loading	Leach time (hrs)	Arsenic concentration	Treatment
Clay	As ₂ O ₃	1%	168	40-100 ppm	Pelletize and roast
Cement	As ₂ O ₃	≤25%	9,000	≤25	No roasting
None	Iron arsenate	100%	1,700	6-7	Precipitate from flue dust leaching
Cement	CA or FA	25%	9,000	≤2.0	No roasting
Cement	FA	25%	9,000	.7 < C ≤ 1.0	Cast, cure, roast or no roasting
Clay	CA or FA	to 75%	9,000	≤1.0 Most < 0.5	Small pellets roasted Glazing showed no influence
BF slag	FA	<20	8,000	≤0.25	
BF slag	CA	<25	8,000	≤0.25	
RF slag	FA	<10	8,000	≤0.25	
RF slag	CA	<20	8,000	≤0.15	
Cement	FA	≤10%	9,000	≤0.15	Roast, cast, cure
Cement	CA	≤25%	9,000	≤0.01	Cast, cure; no roasting
Cement	CA	≤25%	9,000	≤0.04	Cast, cure, roast
Cement	CA	≤10%	9,000	≤0.02	Roast, cast, cure
Concrete	CA or FA	4%	6,000	≤0.02	Cast with CA or FA slag
Clay slag	FA	≤15	7,800	≤0.004	

to well below one mg per liter when such precipitation is carried out in the presence of naturally occurring calcium phosphate (collophanite), although a reversion of arsenic solubility to approximately one mg per liter occurs when arsenic-bearing hydrated ferric oxide precipitates are equilibrated with pure water over periods of several months. This concentration is, however, less than the five mg per liter specified as the designated concentration for a hazardous waste (EPA)

Pyrometallurgy

The major emphasis in the pyrometallurgical treatment study was to convert the volatile arsenic compounds to a non-volatile form (at smelting temperatures of 1250° to 1300°C) such as calcium arsenate. This compound was then dissolved in smelter slag and subjected to long term exposure in an aqueous environment to determine stability of the product. The results show that the slag product is sufficiently stable for conventional dump storage. Several types of slags and arsenate forms have been investigated. Only the results using calcium arsenate dissolved in copper reverberatory slag are reported

here (Table 4). In all cases, the slag product showed less than the EPA designated characteristic arsenic toxicity level (i.e., five mg per liter). All of the leach tests resulted in the extraction of less than the designated toxicity level for the elements As, Cd, Cr, and Pb (Table 5).

Encapsulation

A large number of experimental tests were performed to determine the stability of admixtures of arsenic bearing materials and clays, cements, and concretes. The arsenic forms studied included arsenic oxides, arsenic bearing flue dusts, arsenates, and arsenic slags. The results showed that arsenic oxides in clay and cement matrices deteriorated rapidly when exposed to water. Encapsulation in clays, cements, and concretes as a form of containment is completely inappropriate for arsenic oxides.

Arsenate compounds can be effectively stabilized in cement and concretes. The amount of arsenate in the cement must not exceed approximately 25 weight percent or physical stability of the product is greatly decreased. For appropriate arsenate to matrix ratios, it was found that arsenic loss to an

aqueous environment was less than one mg/liter for periods of up to 9,000 hours of exposure.

Essentially complete containment of arsenic was demonstrated for samples using arsenic bearing slag as the aggregate in concrete (i.e., less than 0.02 mg/liter arsenic was extracted from two 4 percent arsenic concretes) by complete immersion in water after 9,000 hours of exposure. However, this approach does not appear to be economically attractive for commercial application.

Recommendations

This study has resulted in a procedure for conversion of arsenic in smelter flue dusts by low temperature roasting in the presence of lime to produce a non-volatile compound of arsenic (i.e., calcium arsenate). Dissolution of this arsenic compound in a slag solvent produces an environmentally safe form for disposal in conventional slag dumps. However, the use of this procedure means that the metal values in the flue dust are not recovered. This loss is not important at some smelting facilities because the quantity of dust produced is

Table 4. Arsenic Extraction from Arsenic Doped Copper Reverberatory Slag

Arsenic in slag (%)	Arsenic extraction ⁽¹⁾	
	Exposed time (hrs.)	As concentration (mg/liter)
0.54 ⁽²⁾	7320	0.070
0.77 ⁽²⁾	8304	<0.038
2.1	1536	0.24
3.3	1536	0.34
5.2	1536	0.14
8.8	7944	0.48
17.4	7992	2.19
19.2	8309	1.21
23.5	7152	2.21

⁽¹⁾Leachant: deionized water; pH = 6, solid/liquid ratio = 1/100.

⁽²⁾As received commercial copper reverberatory slag.

Table 5. EPA Toxicity Test Results for Doped Slag Systems

Arsenic in slag (%)	Analysis of leach solution from extraction test (mg/l)			
	As	Cd	Cr	Pb
0.54	0.016	0.093	0.016	0.226
0.77	0.047	0.000	0.007	0.149
2.1	0.448	0.000	0.006	0.169
3.3	0.421	0.000	0.004	0.500
5.2	0.901	0.000	0.007	0.150
9.1	0.415	0.001	0.007	0.148
19.4	0.802	0.002	0.007	0.149
23.5	1.791	0.001	0.008	1.142

EPA designated concentration of contaminants for characteristic toxicity (mg/l)

As 5.0
Cd 1.0
Cr 5.0
Pb 5.0

small. But the loss in metal values at smelters that treat high arsenic concentrates would be significant.

It is recommended that further study be directed toward determining the potential for recovering the metal values in the flue dust while disposing of the arsenic via recycling roasted lime-flue dust mixtures back into the reverberatory smelting furnace. The arsenic (now in a non-volatile form) should preferentially distribute to the slag phase and the copper and silver should distribute to the matte phase from which they can be subsequently recovered. Experimental evidence has been generated by Luigi at the Anaconda smelter and shows that, as the lime content of the slag phase is increased, the arsenic content of the slag phase also increases. Therefore, the slag phase should function as an arsenic bleed from the system. If the arsenic is forced into the slag phase by increasing the lime content of that phase, the question then becomes what happens to the distribution of the other constituents? Presently available distribution data show that the copper and silver should distribute to the matte phase.

Anil K. Mehta is with the Mineral Research Center, Montana Tech Alumni Foundation, Butte, MT

John O. Burckle is the EPA Project Officer (see below)

The complete report is in two volumes, and is entitled "Investigation of New Techniques for Control of Smelter Arsenic Bearing Wastes."

Volume I. Experimental Program (Order No PB 81-231 581; Cost: \$21 50)

Volume II Literature Review (Order No PB 81-231 599, Cost: \$12 50)

These reports will be available only from: (prices are subject to change)

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at.

Industrial Environmental Research Laboratory

U.S. Environmental Protection Agency

Cincinnati, OH 45268

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335



Official Business
Penalty for Private Use \$300

RETURN POSTAGE GUARANTEED

Third-Class
Bulk Rate

• IFRLO120880
DAVID KFE
EPA R/O V
A & HM DIV 230 S DEARBURN
FEDERAL PLAZA
CHICAGO IL 60604
•

7