

Short Communication

SAFE DISPOSAL OF ARSENIC BEARING FLUE DUST BY DISSOLUTION IN SMELTER SLAGS

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Summary

The Environmental Protection Agency's EP Toxicity Test has been applied to smelter slags containing dissolved arsenic concentrations up to 23.50 per cent. The test results show that the release of arsenic is, in all cases, below the EPA designated concentration of contaminants for characteristic toxicity. Also, the results of over five years of exposure of slag to an aqueous environment are reported. The test results for the long-term exposure show that, in some cases, the release of arsenic is minimal and that solid slag is a safe means of storing arsenic.

Introduction

Flue dust is created during copper smelting. This dust is collected in the exhaust ductwork and in baghouses. The disposal of this dust is a problem. The composition of the flue dust is variable, but it generally contains appreciable metal values, many trace metal constituents, and is usually contaminated with arsenic. Flue dust composition ranges are presented in Table 1. Example dust compositions are presented in Table 2.

TABLE 1

Copper smelter flue dust composition ranges [1]

Element	% in dust
Cu	5-15
Pb	8-15
Zn	5-15
As	3-25
Bi	0-2
Ag	3-13 oz/ton*
Au	0-0.2 oz/ton

*1 oz/ton = 0.0034%

TABLE 2

Example copper smelter flue dust assays [1]

Element	Assay (%)			
	Dust I	II	III	IV [2]
As	20.0	29.4	25.6	3.15
Bi	0.65	0.94	0.88	0.94
Cd	0.94	0.65	0.89	0.54
Cu	4.76	3.91	4.19	17.5
Fe	6.1	1.43	1.43	17.0
Pb	5.8	5.3	5.43	4.7
Sb	0.63	1.26	0.74	0.14
Sn	0.75	1.60	0.5	—
Te	0.27	0.69	—	0.05
Zn	14.3	12.3	14.2	7.5
S	10.0	7.9	9.1	11.3
Mo	—	—	0.09	—
Ag	—	—	5.4 oz/ton	9.6 oz/ton

Smelter operators are currently stockpiling most of their dust until an appropriate disposal technology can be developed. Storage in a dry manner is expensive, but storage outdoors is a potential health hazard because of the possible leaching by rain water of arsenic and other heavy metals. Therefore, an alternative means of treating and storing this dust is desirable from an environmental viewpoint.

Twidwell and Metha [3] have developed a technique for containment of arsenic in an environmentally safe form, i.e., dissolution of the arsenic in a reverberatory slag phase. To accomplish the dissolution in the slag phase requires that a high-temperature stable form of arsenic be produced in the flue dust. This can be effectively accomplished by low-temperature (200–400°C) roasting of pelletized lime and flue dust, by which means the arsenic oxide is converted to $\text{Ca}_3(\text{AsO}_4)_2$. The calcium arsenate is non-volatile when heated in air, i.e., its pyrometric cone equivalent temperature is 1290°C.

Calcium arsenate bearing flue dust effectively dissolves in molten smelter slag when added to the slag in this non-volatile form. The resulting product, a slag phase containing dissolved arsenic, is stable against weathering and can be stored in conventional slag dump areas [1].

Experimental procedure and results

A previous investigation by Twidwell and Metha [3] produced arsenic containing slags: (a) to demonstrate the effectiveness of dissolution of arsenates in molten smelter slags and (b) to produce arsenic containing slags for subsequent stability studies.

TABLE 3

EP Toxicity Test results for doped slag systems

% As in slag	Analysis of leach solution from extraction test (mg/litre)												
	As***	Cd***	Cr***	Pb***	Al	Bi	Ca	Zn	Cu	Mo	Ni	Fe	
0.5*	0.016	0.093	0.016	0.226	0.004	0.068	0.037	0.030	0.239	0.039	0.050	0.008	
0.8*	0.047	0.000	0.007	0.149	0.090	0.013	0.435	0.010	0.474	0.020	0.018	0.032	
2.1	0.448	0.000	0.006	0.169	0.083	0.024	0.064	0.082	0.526	0.022	0.020	0.092	
3.3	0.421	0.000	0.004	0.150	0.085	0.047	0.156	0.084	0.270	0.029	0.018	0.049	
5.2	0.901	0.000	0.007	0.150	0.088	0.046	0.126	0.151	0.294	0.029	0.017	0.165	
9.1	0.415	0.001	0.007	0.148	0.087	0.056	0.410	0.060	0.050	0.023	0.018	0.002	
19.4	0.802	0.002	0.007	0.149	0.088	0.044	0.722	0.036	0.008	0.023	0.025	0.047	
23.5	1.791	0.001	0.008	0.142	0.084	0.055	1.501	0.041	0.004	0.024	0.020	0.010	
0.3**	0.007	0.080	0.014	0.202	0.010	0.053	0.094	0.033	0.086	0.034	0.051	0.025	
9.0	0.337	0.004	0.010	0.179	0.044	0.001	0.617	0.034	0.011	0.031	0.029	0.043	
12.4	0.115	0.003	0.007	0.245	0.066	0.038	0.128	0.034	0.008	0.023	0.025	0.001	
13.7	0.308	0.002	0.007	0.145	0.080	0.060	0.480	0.029	0.015	0.023	0.020	0.039	
16.4	0.377	0.009	0.011	0.182	0.045	0.018	0.601	0.030	0.012	0.030	0.035	0.040	
20.7	0.846	0.004	0.008	0.167	0.052	0.011	0.732	0.036	0.016	0.023	0.029	0.036	

* As received (undoped) copper reverberatory slag.

** As received (undoped) lead blast furnace slag.

*** EPA designated concentration of contaminants for characteristic toxicity (mg/litre): As 5.0; Cd 1.0; Cr 5.0; Pb 5.0.

This technical communication is to report recent experimental data collected on the arsenic containing slag samples. The new data consist of the experimental results from (a) applying the EP Test [4] (developed since the original study was conducted) to copper reverberatory slags containing from 0.54–23.50 per cent arsenic and (b) determining the influence of continuous exposure of the slag to a water environment for over five years.

EP Test results

Eight arsenic doped slags were subjected to the EP Test [4] procedure. The results for arsenic and a large number of other elements are reported in Table 3. The EPA specified concentration of contaminants for designation as a toxic solid was not exceeded for any heavy metal, e.g., the arsenic extraction even for a starting slag containing 23.50% arsenic did not exceed the designated level of five mg/litre.

Continuous exposure results

The stability of arsenic doped slag samples to continuous exposure to a deionized water environment for 45,330 hours (over five years) has been determined. The influence of slag matrix (either copper reverberatory or lead blast furnace slag: composition for as-received slag are presented in Table 4); solid/liquid ratio (1:1, 1:10, 1:100); pH (5, 7, 9); and particle size (1/4, - 8+10 mesh, - 60+100 mesh) were investigated. The results are presented in Tables 5 and 6.

The experimental results of long-term exposure (45,330 hours) of arsenic containing reverberatory slags show that arsenic release to an aqueous phase is greatly decreased by the slag matrix. As noted in Table 5 the influence of pH on the release of arsenic from the reverberatory slag samples was unimportant for particle sizes of 1/4 inch, i.e., less than 1 mg arsenic/litre (<0.085% arsenic extracted from the solid) was released to the solution. However, the lead blast furnace slags showed a significant arsenic release for the same set of circumstances. The influence of pH on arsenic extraction from smaller particle sizes of reverberatory slag, especially the - 60+100 mesh range, shows the importance of maintaining a basic solution.

The influence of solid/liquid ratio and particle size on arsenic extraction is illustrated in Table 6. Solution pH was uncontrolled in these exposures. The

TABLE 4

Slag compositions [1]: Major constituents

	SiO ₂ (%)	CaO (%)	FeO (%)
Copper reverberatory slag	35–40	6–7	40–45
Lead blast furnace slag	25–30	20–35	33–35

TABLE 5

Influence of pH on arsenic extraction from arsenic doped slag samples in 45,330 hours

Arsenic in slag (%)	Arsenic extracted* (mg/litre)								
	pH 5			pH 7			pH 9		
	Particle size								
	1/4	-8+10	-60+100	1/4	-8+10	-60+100	1/4	-8+10	-60+100
Copper reverberatory									
11.8	<1	1	10	<1	1	<1	<1	<1	6
12.0	1	5	10	<1	<1	<1	<1	3	2
Lead blast furnace									
13.6	8	—	19	4	6	8	2	6	12

*Solid/liquid ratio 1:100. pH maintained at the above levels for over 2300 hours and then allowed to seek its natural values.

TABLE 6

Influence of solid/liquid ratio and particle size on arsenic extracted in 45,330 hours

Arsenic in slag (%)	Arsenic extracted* (mg/litre)								
	S/L = 1:100			S/L = 1:10			S/L = 1:1		
	Particle size								
	1/4	-8+10	-60+100	1/4	-8+10	-60+100	1/4	-8+10	-60+100
Copper reverberatory									
12.0	1	<1	1	—	<1	8	3	38	57
Lead blast furnace									
13.6	2	3	11	4	8	18	8	15	50

*pH uncontrolled; starting pH was 5.7. The pH increased in most samples to 9–10 in the first hour then decreased to 6–7 after about 2300 hours.

arsenic release from the reverberatory slag was small and acceptable for all particle size ranges for S/L ratios of 1/100, for particles to +10 mesh for a S/L ratio of 1/10 and for 1/4 inch particles for a S/L ratio of 1/1. The lead blast furnace slags showed a much higher release of arsenic.

Conclusions

Copper reverberatory slags appear to offer potential for safe long-term disposal of arsenic bearing flue dust. The procedure involves pelletizing the flue dust with lime followed by a low temperature, 400° C, roast. The arsenic in the dust is converted to calcium arsenate and calcium arsenite which, when added to a molten system, effectively dissolves in the slag. The solidified arsenic bearing slag appears to offer the possibility of outdoor storage, especially if the surface area exposed to weathering is kept to a minimum.

References

- 1 A. Mehta, Investigation of new techniques for control of smelter arsenic bearing wastes, Vol. I. Final Report, EPA Grant R804595010, NTIS, PB81-231581, 1981, 177 pp.
- 2 J. Downey, Elemental distribution of lime-roasted smelter dusts in a copper matte-slag system, Master of Science Thesis, Montana College of Mineral Science and Technology, Butte, MT, May 1982.
- 3 L.G. Twidwell and A. Mehta, Disposal of arsenic from smelter flue dust, paper presented at the 108th AIME Annual Symposium, New Orleans, Feb. 1979.
- 4 EPA, Hazardous wastes, proposed guidelines and regulations and proposal on identification and listing, Federal Register, 45 (98) (May 19, 1980) 33121-33132.