

REMOVAL OF ARSENIC FROM LEAD SMELTER SPEISS

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Summary

The removal of arsenic from lead smelter speiss by volatilization techniques has been investigated. Elemental arsenic removal greater than 98 percent has been achieved by treatment of speiss and a sulfur source in a carbon monoxide atmosphere.

Introduction

Speiss is created during lead smelting. It is a valuable product because of the relatively high silver content. The composition of speiss is variable, but it generally contains appreciable amounts of recoverable metal constituents and arsenic. The composition of speiss used in the present experimental study is presented in Table 1.

There is only one facility in the United States that currently treats lead smelter speiss. Arsenic is removed from the speiss by roasting with pyrite in an oxidizing environment to produce arsenic oxide. The handling and processing of arsenic oxide is difficult because it is an EPA designated toxic material. The toxicity of arsenic is believed to be related to its valence

TABLE 1

Lead smelter speiss composition

Element	Concentration in speiss (%)
Cu	53.9
Pb	11.1
As	18.7
Sb	9.0
Bi	---
Ag	265 oz/ton ^a
Au	26

^a1 oz/ton = 0.0034%.

state, the trivalent species being the most toxic [1]. Therefore, alternate treatment possibilities have been investigated and are reported in this communication.

Experimental procedure

Studies have been performed to investigate the potential for removing elemental arsenic from speiss. If the arsenic is completely removed or effectively lowered in concentration from the speiss phase, then the resulting residue can be recycled in a conventional copper smelting circuit for recovery of copper and silver. Pyrometallurgical studies were performed in the present research to investigate the removal of arsenic by volatilization processes.

The furnace atmospheres examined included: nitrogen, air, vacuum, and carbon monoxide. The experimental system is depicted schematically in Fig. 1. Each test charge was placed in a preweighed 10 mm Vycor crucible and weighed to ± 0.001 g. The crucible was then positioned in a 25 mm Vycor reaction tube, and sealed with rubber stoppers. The tube was flushed with the chosen cover gas for ten minutes, then placed in a preheated split tube furnace. A thermocouple was positioned in the crucible near the sample to measure the sample temperature. A gas flow rate of $45 \text{ cm}^3/\text{min}$ was maintained throughout the test. The exhaust gas was bubbled through a gas scrubber before being vented to the exhaust hood. Each test required 10–15 minutes for the sample to reach the desired temperature. At the conclusion of the test the Vycor reaction tube was removed from the furnace, and cooled under the cover gas an additional ten minutes before opening the tube and recovering the sample. The sample was then crushed, dissolved and submitted for analysis by induction coupled plasma spectrometry. A nitric, perchloric, hydrochloric acid digestion procedure was used to dissolve the reacted samples.

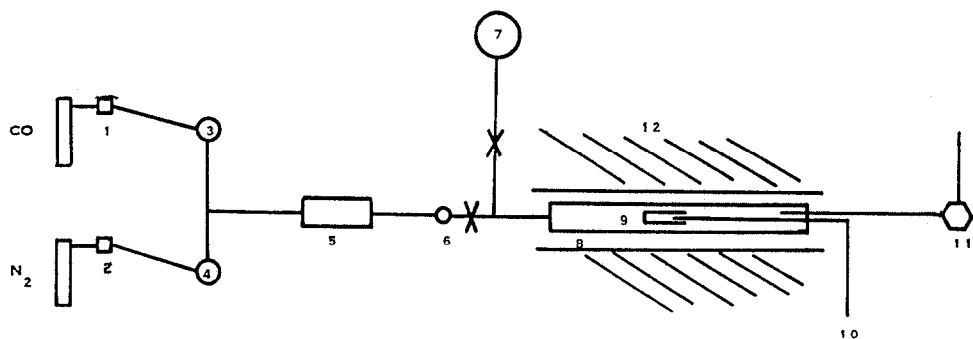


Fig. 1. Experimental system for volatilization testwork. 1, Gas regulator control; 2, gas regulator control; 3, Ascarite drier; 4, deoxidizer; 5, gas drier; 6, flowmeter; 7, vacuum; 8, Vycor reaction chamber; 9, reaction crucible; 10, potentiometer; 11, gas scrubber; 12, split furnace.

Three methods of sulfur addition were studied; preroasting with elemental sulfur; elemental sulfur added but a preroast not used; and pyrite addition. Lead sulfide and iron sulfide (troilite) were also investigated in separate tests as the sulfur source, but were found to have negligible effect on arsenic removal.

A sulfidizing preroast was performed on some of the speiss to produce a completely sulfidized feed speiss of known sulfur content. The sulfidized speiss was prepared by mixing preweighed amounts of sulfur and speiss in a Vycor reaction chamber, then sealing under a vacuum. The sealed tube was then heated for 24 hours at 200°C.

Experimental results

The presence of sulfur is required for the effective volatilization of arsenic from speiss. This is evidenced by the results presented in Table 2. These tests were performed in a nitrogen atmosphere at 700°C using as-received unsulfidized speiss. Only lead and antimony were found to be removed from the unsulfidized speiss, whereas mostly arsenic (as arsenic sulfide) was found to evolve from the sulfidized speiss.

In tests conducted in air, there were no weight losses, and no arsenic removal. Tests performed on as-received speiss under a vacuum showed partial removal of all elements in the speiss. These test results will be discussed in more detail in a forthcoming thesis [2].

Results are presented in Table 3 for volatilization from sulfidized speiss at various times and temperatures under a carbon monoxide cover gas. The striking difference between the testwork performed in nitrogen and in carbon monoxide was the form of the arsenic deposited on the reaction

TABLE 2

Comparison of element removal from sulfidized and untreated speiss in nitrogen at 700°C

Test	Time (min)	Element removed (%)		
		As	Pb	Sb
<i>Untreated speiss</i>				
V-6	60	0	12.5	5.8
V-7	90	0	12.0	7.6
V-8	120	0	15.9	13.2
<i>Sulfidized speiss</i>				
SV-13	30	29.8	0	0
SV-11	60	44.4	0.2	0
SV-10	90	61.1	0	0.3
SV-20	120	71.4	0.6	8.1

TABLE 3

Arsenic removal from sulfidized speiss under a carbon monoxide atmosphere

Test	Time (min)	Temp (°C)	Element removed (%)		
			As	Pb	Sb
SVC-10	15	700	27.5	0.2	—
SVC- 9	30	700	57.7	4.3	—
SVC- 8	90	700	77.6	1.7	3.9
SVC- 7	120	700	82.5	0.9	4.9
SVC-12	20	800	33.0	—	—
SVC-11	120	800	92.2	—	5.4

tube wall. Examination of the deposits by energy dispersive X-ray (EDX) analysis showed that the deposit from the nitrogen atmosphere tests was arsenic, sulfur and antimony, i.e., sulfide deposits formed. The deposit from the tests using the carbon monoxide cover gas contained only arsenic and antimony. Semi-quantitative analysis of the metallic deposit by EDX analyses showed 95% As and 5% Sb.

A summary of arsenic, lead, and antimony removal results using FeS_2 (pyrite) as the sulfur source is presented in Table 4. The data indicate that pyrite is effective in removing arsenic from speiss. As in the case of sulfidized speiss, the product produced by pyrite—speiss roasting was elemental arsenic and antimony not sulfide compounds.

TABLE 4

Arsenic removal from speiss in the presence of FeS_2 under a carbon monoxide atmosphere

Test	Time (min)	Temp (°C)	Element removed (%)		
			As	Pb	Sb
<i>21.7% Sulfur</i>					
FVC-2	120	650	76.0	—	13.6
FVC-1	120	700	91.1	—	59.1
FVC-5	30	800	96.0	—	69.7
FVC-4	120	800	96.9	—	51.5
<i>27.8% Sulfur</i>					
FVC-8	120	800	98.8	—	65.3
<i>25.0% Sulfur</i>					
FVC-7N	120	800	98.8	—	68.8
<i>16.1% Sulfur</i>					
FVC-9H	120	800	40.4	—	30.9

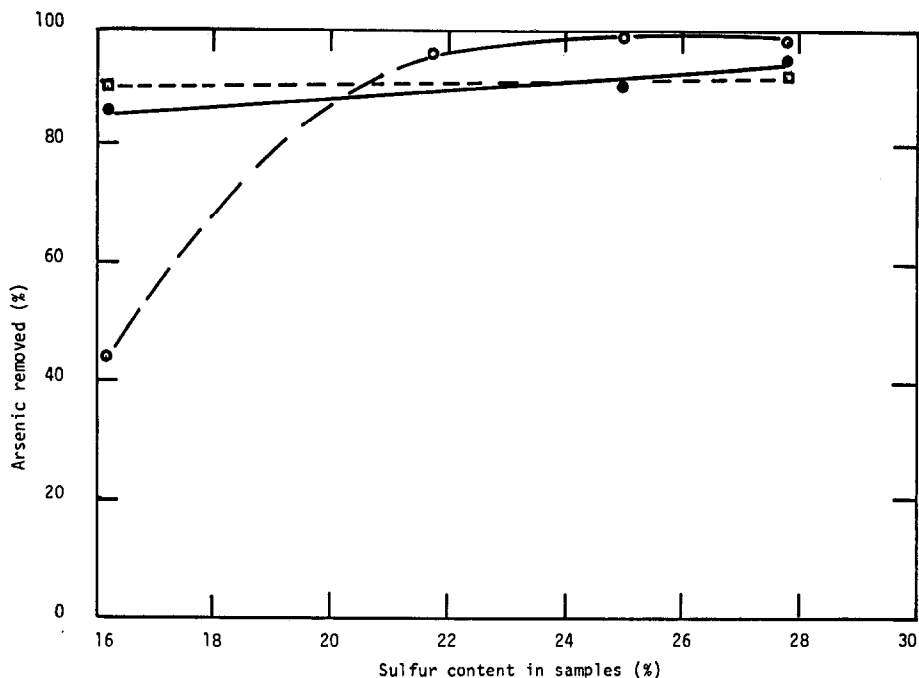


Fig. 2. Arsenic removal from speiss as a function of sulfur content and sulfur source. Source of sulfur: ○, FeS₂; ●, sulfur; □, sulfur pre-roasted with speiss.

Arsenic removal as a function of sulfur source and sulfur content is depicted in Fig. 2. These results were for tests carried out at 800°C for two hours under a carbon monoxide atmosphere. When pyrite additions were below 20% available free sulfur, arsenic removal was considerably lessened.

Acknowledgement

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References

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