

The Chemistry of Sulfur and Arsenic in Airborne Copper Smelter Particulates

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There have been few published reports on the chemical states of sulfur and arsenic released by a copper smelter. These reports have generally assumed that sulfur oxides are present in particulates as sulfates and/or sulfuric acid and that arsenic is present as arsenic trioxide (NELSON, 1968). Results obtained using a recently developed analytical technique (HANSEN, et al., 1975) indicate that neither of these assumptions is true of the workroom environment of the copper smelter studied in this report.

The data reported in this communication are taken from a small series of air samples collected in a large copper smelter near Salt Lake City, Utah. The smelter has 3 reverberatory furnaces (5 m. high, 10 m. wide, 35 m. long) and 9 converters (5 m. in diameter, 10 m. long) which are used to produce copper metal from copper sulfide concentrates by pyrometallurgy. A diagram of the plant is shown in Figure 1. This plant uses a direct charging process in which the concentrates are fed directly into the reverberatory furnaces without a preliminary roasting step. In the furnace the concentrates melt and separate into two molten layers; iron silicate slag on the top and copper sulfide on the bottom. The copper sulfide is tapped out of the furnace into ladles of 9 metric ton capacity and transferred into a converter. The converter is a large cylinder which functions as a reaction vessel where copper sulfide reacts with oxygen to produce copper metal and sulfur dioxide gas. Copper metal is poured out of the converter into a ladle and taken to the smelter anode plant where it is treated with natural gas to remove excess oxygen and cast into anode form. The anodes are shipped by rail to another location for electrolytic refining.

METHODS

Size classified particulate samples were collected on glass fiber filters (without organic binder) mounted in high volume samplers equipped with Andersen cascade impactor sampling heads (BURTON, et al., 1973). Samplers were operated at 20 cfm for approximately 8 hours, 8:00 a.m. to 4:00 p.m. The sampling locations are given in Table I and Figure 1.

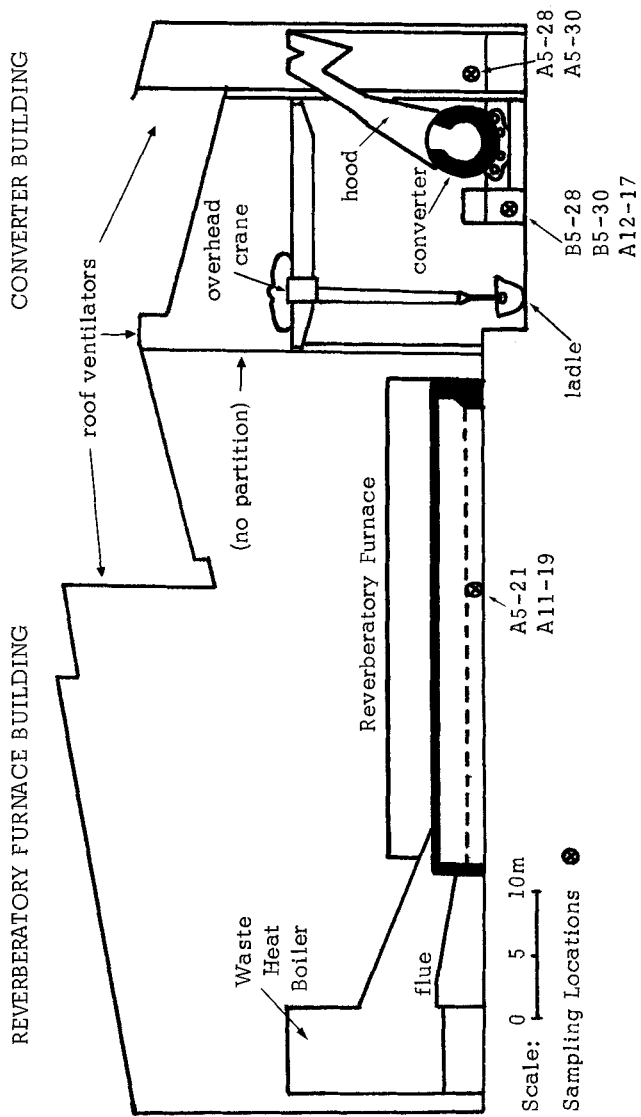


Figure 1. Cross section of the copper smelter reverberatory furnace and converter buildings showing air sampling locations.

TABLE I
Copper Smelter Sampling Locations

Sample No.	Location
A5-21 A11-10	Four feet above ground level, south side, 10 ft. out from the center of #2 reverberatory furnace.
A5-28 A5-30	Eight feet above the edge of walkway 15 ft. east of #3 converter. Walkway lies level with converters, and is approximately 15 ft. above ground level.
B5-28 B5-30 A12-17	Four feet above ground level, on the east edge of the crane aisle, approximately 15 ft. below the south end of #3 converter.

One quarter of each filter was extracted using either cold 0.1 M HCl (HANSEN, et al., 1975) or hot water (INTERSOCIETY COMMITTEE, 1972). All HCl extracts and selected hot water extracts were analyzed by a thermometric procedure (EATOUGH, et al., 1974; HANSEN, et al., 1975). In this technique, S(IV) oxides are determined by a thermometric redox titration and S(VI) oxides are determined as sulfate by measurement of the heat associated with BaSO₄ precipitation. This method is specific for S(IV) oxides, S(VI) oxides, and As(III) oxides. It should be noted that S(IV) oxides include any particulate adsorbed SO₂ as well as sulfite compounds. S(VI) oxides would include any particulate adsorbed SO₃ or H₂SO₄ as well as soluble sulfate compounds. For convenience, S(IV) and S(VI) oxides will be referred to as sulfite and sulfate, respectively. The HCl extracts were also analyzed by proton induced x-ray fluorescence spectroscopy, PIXE (MANGELSEN, et al., 1974; WALTERS, et al., 1974), which measures total S, As, Fe, Cu, Zn, Mn, and Pb in the sample analyzed. The hot water extracts were all analyzed by an atomic absorption spectroscopy, AAS, technique (WOLLIN, 1970) for sulfate. The existence of sulfite was independently confirmed by photoelectron spectroscopy, ESCA, for two of the samples (HANSEN, et al., 1974). Possible absorption of SO₂ by the filters during sampling was checked by drawing 0.78 ppm SO₂ from a permeation tube apparatus (SALTZMAN, et al., 1971) through three 7.9 cm² sections of the backup filters at 1.6 l/min. for 4 hours. In all cases the thermometric measured levels of sulfite and sulfate for these exposed filters were the same as the normal blank values.

RESULTS

Table II shows the results of the sulfur analyses for a set of seven particulate samples. It was found that the hot water extraction results for sulfate were consistently higher than the hydrochloric acid extraction results using either the thermometric or PIXE total sulfur reported as sulfate. The thermometric total sulfur (as sulfate) and AAS sulfate results were similar for all blank samples and for sulfate in hot water extracts (HANSEN, et al., 1975). The combined sulfate and sulfite concentrations as measured thermometrically in the HCl extracts accounted for all the sulfur observed with PIXE in the same extractant solutions. The thermometric method gave slightly higher values on the average. Regression analysis of thermometric vs. PIXE results for wt% total sulfur gives a correlation coefficient of 0.88, a slope of 1.09 ± 0.41 and an intercept of 0.53 ± 0.52 wt% SO_4^{2-} .

The airborne concentrations of sulfate and sulfite averaged 109 ± 73 $\mu\text{g SO}_4^{2-}/\text{m}^3$ (mean \pm SD) and 54 ± 39 $\mu\text{g SO}_3^{2-}/\text{m}^3$ in the six samples on which complete data are available. Respirable (particles $< 7 \mu$ diameter) sulfate and sulfite averaged 93 ± 68 $\mu\text{g SO}_4^{2-}/\text{m}^3$ and 23 ± 29 $\mu\text{g SO}_3^{2-}/\text{m}^3$. The majority of the sulfate, 85%, was found in respirable particles, whereas only 43% of the sulfite was in respirable particles. The results in Table II show different particle size distributions for sulfate and sulfite. The percentage of sulfate (column 5, Table II) increased markedly with decreasing particle size. A similar but less pronounced trend was observed with the absolute concentration of airborne sulfate. The percentage of sulfite was relatively constant regardless of particle size. The airborne concentration of sulfite, however, decreased with decreasing particle size.

Total arsenic concentrations as a function of particle size are given in Table III. Total airborne arsenic averaged 6.8 ± 5.2 $\mu\text{g As}/\text{m}^3$, and ranged from 3.0 to 15.4 $\mu\text{g As}/\text{m}^3$ in the six samples in good agreement with the range of 2-22 $\mu\text{g As}/\text{m}^3$ reported by RENCHER and CARTER (1971) for samples from the same smelter. The major fraction of the arsenic was found in particles in the respirable size range. There was a consistent tendency for arsenic content of the particles to increase with decreasing particle size.

Tests were conducted during the development of the thermometric analytical method (HANSEN, et al, 1975) to determine the extent of AS(III) interference in the analysis. It was found that AS(III), as arsenic trioxide or metal arsenites, was oxidized after S(IV) in the thermometric redox titration, and could be detected

TABLE II Analyses of the Extractable Fraction of Seven Atmospheric Samples

Sample No.	Particle Size (microns)	Atmospheric Particulate Concentration (mg/m ³)	HCl Extraction				Hot Water Extraction	
			Thermometric Analysis		PXE Analysis		AAS Analysis	
			wt % S(VI) (as SO ₄ ²⁻)	wt % S(IV) (as SO ₃ ²⁻)	wt % Total S (as SO ₄ ²⁻)	wt % S (as SO ₄ ²⁻)	wt % S	(as SO ₄ ²⁻)
A5-21	>7.0	1.15	0.5	1.8	2.7	3.8	*	*
	1.1-7.0	*	*	*	*	*	*	*
	<1.1	0.26	49.9	1.4	51.6	47.0	*	*
A5-28	>7.0	0.60	2.0	2.5	5.0	3.6	8.5	
	1.1-7.0	0.27	4.7	1.8	6.9	6.0	32.1	
	<1.1	0.22	13.0	1.7	15.1	14.5	22.8	
B5-28	>7.0	1.30	1.3	2.4	4.2	2.9	7.0	
	1.1-7.0	0.33	4.8	1.7	6.8	9.7	22.1	
	<1.1	0.20	12.6	1.6	14.5	12.0	33.9	
A5-30	>7.0	2.75	2.3	1.6	4.2	3.3	7.8	
	1.1-7.0	2.18	0.3	2.2	3.0	4.7	11.1	
	<1.1	1.92	7.1	1.8	9.3	5.7	11.9	
B5-30	>7.0	2.08	1.2	2.1	3.6	2.6	6.1	
	1.1-7.0	0.46	8.8	2.3	11.6	7.6	20.8	
	<1.1	0.32	14.4	2.2	17.1	13.9	29.4	
A11-19	>7.0	0.71	2.4	1.7	4.4	2.9	19.7	
	1.1-7.0	0.22	8.6	1.1	9.9	20.2	33.8	
	<1.1	0.22	0.1	1.1	1.4	4.3	40.3	
A12-17	>7.0	1.59	4.0	2.4	6.9	3.2	10.7	
	1.1-7.0	0.60	12.3	2.3	15.1	12.1	51.8	
	<1.1	0.34	15.1	1.0	16.3	14.7	21.4	

*Data missing

TABLE III
Results of X-ray Fluorescence Analyses for Arsenic

Sample No.	Particle Size (microns diameter)	Atmospheric Particulate Concentration (mg/m ³)	HCl Extraction	
			wt % As	mg As/m ³
A5-21	> 7.0	1.15	0.28	.0032
	1.1-7.0	*	*	*
	< 1.1	0.26	1.60	.0042
A5-28	> 7.0	0.60	0.18	.0011
	1.1-7.0	0.27	0.17	.0005
	< 1.1	0.22	0.65	.0014
B5-28	> 7.0	1.30	0.14	.0018
	1.1-7.0	0.33	0.15	.0005
	< 1.1	0.20	0.86	.0017
A5-30	> 7.0	2.75	0.12	.0033
	1.1-7.0	2.18	0.27	.0059
	< 1.1	1.92	0.32	.0062
B5-30	> 7.0	2.08	0.12	.0025
	1.1-7.0	0.46	0.17	.0008
	< 1.1	0.32	0.53	.0017
A11-19	> 7.0	0.71	0.25	.0018
	1.1-7.0	0.22	0.81	.0018
	< 1.1	0.22	0.42	.0009
A12-17	> 7.0	1.59	0.12	.0019
	1.1-7.0	0.60	0.47	.0028
	< 1.1	0.34	1.81	.0062

*Missing data.

without interference from S(IV). The PIXE analyses indicated that sufficient arsenic was present in the extraction solutions from the smelter samples to have been detected in the redox titrations if it were present as arsenic trioxide or metal arsenites. No oxidizable As(III) was detected in any of the smelter samples analyzed.

DISCUSSION

The data given in Table II suggest that hot water extraction of sulfur oxides from particle samples apparently leads to the oxidation of virtually all sulfur species present, and subsequently to an overestimation of the sulfate present in the sample. The phenomena of extrinsic oxidation of SO_2 on glass filters leading to high values for the concentration of sulfate in aerosols may be a reflection of sulfur oxidation during the sulfate extraction rather than during the air sampling (LEE and WAGMAN, 1966).

The two sulfur oxides, sulfate and sulfite, show markedly different size distributions, which suggests that they are formed by different mechanisms in the smelter environment and that sulfite is not readily converted to sulfate in the short time period between generation and collection. It has been postulated by HANSEN, et al., (1974) that, in the smelter environment, SO_2 is stabilized by chemisorption on metal oxide (i.e., Fe_3O_4 , CuO) bearing particles to form stable sulfite complexes similar to those observed for Hg(II), Fe(III), and Cu(II) in aqueous solution. This is supported by the finding that the percentage of sulfite in the particulate is highly correlated with iron content (EATOUGH, 1974), correlation coefficient 0.87 ($p < .001$) but not with zinc, copper, manganese, or lead. Further evidence supporting this hypothesis of iron-sulfite formation includes Mössbauer spectra results (HANSEN, et al., 1975) which show that iron is present only as Fe(III) in the particulates, and gas absorption studies (SMITH and WAGMAN, 1969), which show Fe_3O_4 particles and SO_2 gas react and form stable chemisorbed species. The uniform sulfite content with particle size also suggests a mass reaction between SO_2 gas and airborne particles.

The source of sulfate in the smelter environment is unknown. However, because of similarities in the size distribution of sulfate in these samples as compared with results found in ambient aerosols, (NATUSCH and WALLACE, 1974; ROESLER, et al., 1965), it is likely that the sulfate is produced as a very small aerosol by the oxidation of airborne sulfur dioxide within the reverberatory furnaces (1260-1538°C) or converters (1093°C). Such a reaction

could be catalyzed by the metals in the particulates from the smelter (CHUN and QUON, 1973; CHENG, et al., 1971). It should be noted that the same metals which can stabilize SO_2 as sulfite have also been found to catalyze the oxidation of SO_2 to sulfates. These two competing processes are controlled by a number of factors (HANSEN, et al., 1974). The process which will predominate depends on the relative humidity, ambient temperature, the oxidation potential in the particles, the activities of sulfite complexing metal ions, and on the rates of various reactions or processes producing sulfite or removing it as sulfate. The smelter environment provides areas of high temperature and high concentrations of sulfate, SO_2 , and particles.

Arsenic in the HCl extracts of the samples apparently was not present as arsenic trioxide or metal arsenites. It also was not present as arsenic pentoxide, since arsenic pentoxide is readily reduced by sulfur dioxide or sulfurous acid in acid solution to arsenious acid, which would have been detected in the redox titration. Two other forms of arsenic could exist; arsenic sulfides (or related metal containing compounds) and elemental arsenic, As_4 . Both As_4 and arsenic sulfides readily form colloids which would not have been removed in the filtration of the extracts. Visible evidence of colloids was noted in some of the HCl extracts. Arsenic sulfides (As_2S_2 or As_2S_3) are likely to be present because these compounds enter the smelting process with the copper sulfide concentrates. Further, because this smelting uses a direct charging process, the arsenic sulfides would be charged into the reverberatory furnace where they would melt and become part of the molten copper sulfide phase (1300°C). This phase is covered with a layer of silicate slag which would be expected to inhibit volatilization of the arsenic sulfides. Volatilization would take place when the molten copper sulfide is tapped out of the furnace and allowed to run down a 4 meter long open trench into a ladle. The arsenic sulfides presumably are not converted to the oxide at this time, because there is insufficient high temperature contact with oxygen as it vaporizes into the air above the trench. There is currently no evidence to support or reject the possibility of As_4 being present.

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