Original Articles

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Chronic Sulfur Dioxide Exposure in a Smelter

I. Exposure to SO_2 and Dust: 1940-1974

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This article describes environmental conditions at the copper smelter and in a maintenance shop where the subjects tested in Part 2 of this series were employed. Measurements were made at the Garfield, Utah, copper smelter from 1940 to 1974. Previously published data describing workroom air contaminants in copper smelters are contained in the National Institute for Occupational Safety and Health (NIOSH) criteria document, "Occupational Exposure to Sulfur Dioxide," and a related NIOSH Survey Report.[1,2] In these studies, SO_2 concentrations ranging from 1.6 to 45 ppm (4-117 mg/m^3) were found in work areas of several copper smelters. No personal exposure or particulate sampling was done.

Plant and Present Process

The copper smelter at Garfield, Utah, is a large facility which employs about 1,250 workers and processes 2,100 metric tons of copper sulfide concentrates per day. A diagram of the smelter production area is shown in Fig 1.

The copper concentrates are batch smelted in a three step process. The concentrates are charged through the top of large reverberatory furnaces, 10 m wide x 5 m high x 33 m long, where they melt and form slag and molten copper sulfide — "matte." The molten matte is transferred by a 9 metric ton ladle to a cylindrical converter (4 m diameter x 11 m long). In the converter, air enriched with oxygen is blown through the matte, where the oxygen reacts with the copper sulfide to produce copper metal and sulfur dioxide gas. Most of the sulfur dioxide is captured by an overhead hood, from which it is conducted to one of several acid plants and converted to sulfuric acid. The copper is transferred from the converter to a refining furnace where residual oxygen is removed. Finally, the copper is cast into anodes, which are shipped to an electrolytic refinery at another location.

The truck maintenance shop, where the health study controls worked, is a single large building 49 m wide x 195 m long. In this shop, complete facilities are present for repairing mine haulage trucks, bulldozers, graders, and other heavy vehicles. Activities in the shop include welding (both arc and oxyacetylene), operating diesel engines for engine adjustments including tuning, electrical work and mechanical work of all types. The building had no mechanical ventilation system.

Methods and Materials

Stationary Area Samples. — Area measurements of SO_2 have been made in the Garfield smelter six times: 1940, 1959-1969, 1971, 1972, 1973 and 1974. In the 1940 survey by the U.S. Public Health Service, a conductometric method was employed to measure SO_2 continuously.[3] The survey results were probably artificially high (estimated 5-20%) because incoming particulate was not removed with a prefilter. After 1959, sequential samplers were used in surveys of the smelter by the Kennecott Copper Corp. to collect total dust and SO_2 in consecutive, round-the-clock, two-hour and eight-hour cumulative samples. In 1971, the West-Gaeke method was used by NIOSH for collection and analysis of SO_2 samples.[4] Surveys performed by NIOSH and the University of Utah after 1971 collected the prefiltered SO_2 in 0.5% (wt/wt) hydrogen peroxide with subsequent determination of the accumulated sulfate.[5] Continuous measurement of airborne SO_2 was made by Kennecott in 1974 with an electrochemical SO_2 sensor (Dynasciences Corp., Chatsworth, Calif.).

High volume samples with acid-washed glass fiber filters were also collected in the smelter during 1940, 1971 and 1972. In 1940, the samples were analyzed for total dust and copper.[3] In 1971, the samples were analyzed by atomic absorption spectroscopy for lead, zinc, cadmium, copper, molybdenum, and arsenic.[6] The percent of respirable particles in the total dust loading was measured in 1971 with a cyclone separator as a prefilter for a high volume sample. In 1972, size classified samples were collected with an Andersen cascade impactor.[7]

At the truck shop, consecutive two-hour samples were collected for SO_2, formaldehyde and acrolein. The latter two gases were collected in bi-sulphite solution and analyzed colorimetrically.[6] Short-term area samples were also collected for nitrogen dioxide,

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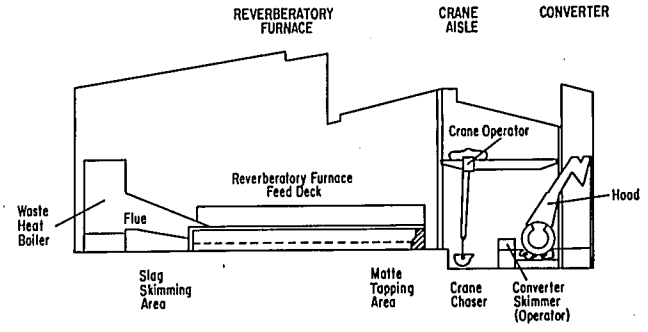

Fig 1. — Cross-section of the Garfield Smelter reverberatory furnace and converter buildings showing major work areas.

using the modified Griess-Saltzmann procedure published by the Intersociety Committee.[6]

Personal Samples. — All personal samples were taken by a special sampler during a full work shift, seven to eight hours in duration. Airborne contaminants were collected with a serial dust (5 μm pore, PVC membrane filter) and SO_2-sampling (0.5% wt/wt hydrogen peroxide in a midget impinger) train which sampled air at the worker's lapel when he was not using his chemical cartridge respirator.[8, 9] When the worker put on his respirator a switching device turned off the air pump and activated a timer that measured the cumulative time the respirator was worn.

The quantity of SO_2 collected in the hydrogen peroxide was measured indirectly as sulfate.[10] The dust samples were weighed for total mass and analyzed, first, for hot-water-extractable sulfate by the same procedure as for the sulfur dioxide samples and, then, for acid-extractable copper by atomic absorption spectroscopy.[6] In 1974 hydrochloric acid extracts of the particulate were analyzed for metals by proton-induced x-ray fluorescence spectroscopy.[11] These extracts were also analyzed for sulfite and sulfate compounds by a thermometric titration.[12]

Group exposure levels were tested for significant differences by the Kruskal-Wallis one-way analysis of variance.[13] This is a nonparametric test which does not require normally distributed data. Contaminant concentrations were also tested for logrithmic normal distributions by D'Agostino's test of normality.[14]

Table 1. — Area Measurements of Sulfur Dioxide in the Garfield Copper Smelter.

Area Sampled	Mean SO_2 (mg/m³) 1940*	1959-69†	1971‡	1972‡	1973	1974
Reverberatory furnace area						
Furnace charging deck	29.4	75.4	25.0	16.8	—	—
Matte tapping area		22.3	21.6	31.5	4.1§	5.4§
Slag tapping area		4.4	8.6	2.0		
Converter area						
General	30.9					
Converter operator cab	—	1.2	—	1.9	—	—
Crane aisle	—	2.8	—	3.0	5.4	3.5
Anode plant	—	1.4	—	—	3.9	4.2
Acid plants	0.5-2.3	0.4	—	—	4.9	9.4

*U.S. Public Health Service data; the sampling locations and numbers of samples were not specified.[15]

†Kennecott Copper Corporation data.

‡NIOSH, Division of Technical Services data.

§The sampling point was between the two tapping areas.

Results

Smelter Area Measurements. — The SO_2 concentrations measured in various work areas of the smelter over the past 30 years are shown in Table 1. A number of important changes in the plant and plant processes have occurred which also affected the SO_2 levels.

The reverberatory furnace area generally had the highest SO_2 levels, and as a result, has been most extensively sampled. In 1969, local exhaust hooding was added over the matte tapping area to capture concentrated gases which had previously risen into the air space of the furnace feed deck. SO_2 measurements on the furnace charging deck for 1971 and after reflect these changes.

The converter area had generally the second highest levels of SO_2 in the plant. Its only significant change was the addition of a ninth converter in 1965-1966. The converters have always been hooded with the collected gases transmitted to an electrostatic precipitator and then either to the smokestack or to acid plants. The data in Table 1 indicate that there has been no substantial change in SO_2 levels in this area since circa 1959.

Overhead cranes operating in the converter crane aisle have had enclosed cabs since the late 1930's and have had air filtration systems with activated charcoal since 1947. Prior to 1947, cranemen used full-facepiece respirators with activated charcoal canisters to control exposure to SO_2 generated from the converters. SO_2 measurements made inside the crane cabs have indicated 0.5-6.7 ppm SO_2 levels since at least 1959 (unpublished Kennecott data).

The anode plant contains no sources of SO_2 in its operations. SO_2 levels have been relatively low (Table 1), coming primarily from adjacent converter operations.

The acid treatment portion of the smelter has been repeatedly enlarged since 1950. Table 1 shows that SO_2 levels are apparently higher in recently constructed portions than in older ones, although this may reflect changes in sampling technics and locations.

Extensive SO_2 measurements made in all areas of the smelter by NIOSH and the University of Utah during 1972-1974 showed considerable variability in airborne levels (Table 2). They were also skewed toward the higher concentrations.[2] The lowest SO_2 con-

Table 2. — Stationary Measurements of Sulfur Dioxide by Work Area: Summary of 1972-74 Data.

Work Location	n	Full-Shift Sulfur Dioxide Concentrations Mean (mg/m³)	S.D.	Maximum
Reverberatory furnace area				
Feed deck	15	16.8	15.3	47.0
Matte tap area	6	31.5	22.2	62.0
Slag tap area	9	2.0	0.9	4.0
Midway between slag and matte tap	142	1.1	0.8	17.1
Lunchroom	9	1.6	0.4	2.5
Converter area				
Converter operator cab	24	1.9	0.7*	6.7
Crane aisle	35	4.4	1.9	14.0
Converter walkway	130	6.2	3.6	12.0
Lunchroom	9	2.3	0.8	5.5
Anode plant				
Central area	100	3.9	1.8	7.3
Acid plants 6 and 7				
Ground level	53	5.4	3.6	10.6

centrations were found in the lunchrooms and midway between slag and matte tapping areas in the reverberatory furnace area.

Continuous measurements of SO_2 concentration in high-exposure work locations of the smelter were made to determine the short term variations in the SO_2 concentration. During a three hour period in 1974, in the matte tapping area, the visually estimated time weighted average was approximately 30 mg/m³. There were nine one-minute periods exceeding 130 mg/m³ and three brief "puffs" approached 520 mg/m³. Qualitatively similar variations in SO_2 concentrations were obtained near other point emission sources in the work environment.

Measurements of particulate concentrations and their composition performed in the reverberatory furnace area in 1940 found copper concentrations to be less than 0.5 mg/m³ (no average reported).[15] Several area samples taken between 1971 and 1974 contained highly variable total particulate levels. The average dust concentrations varied from a high of 2.03 mg/m³ in the crane aisle to a low of 0.41 mg/m³ in the north acid plants. The concentration distributions were skewed toward the larger values.

In 1971 and 1974, measurements were made of several metals in the total airborne particulate. In the reverberatory furnace area during 1971, airborne lead concentrations averaged 0.04 mg/m³, zinc averaged 0.03 mg/m³, and cadmium averaged 0.0015 mg/m³. There was no detectable molybdenum (less than 0.03 mg/m³). Airborne arsenic concentrations averaged 0.0075 mg/m³ and copper concentrations averaged 0.32 mg/m³. Very similar results were obtained in reverberatory furnace area measurements made in 1974. In 1974, the highest airborne metal levels were found in the converter area samples which showed 0.24 mg/m³ copper, 0.089 mg/m³ zinc, 0.014 mg/m³ lead, 0.009 mg/m³ arsenic and trace amounts of selenium. Airborne metal levels in other parts of the smelter were substantially lower than the reverberatory furnace and converter areas.

Sulfate composition of airborne smelter particulate matter was measured in 1973-1974. The dust was comprised of an average 15-30% hot-water-soluble sulfate in the respirable size range (less than 7 μm diameter). The hot-water-soluble sulfate was composed of sulfate compounds (H_2SO_4 or metal sulfates or both), sulfite compounds (absorbed SO_2 or metal sulfites or both), and sulfide compounds (predominantly iron and copper sulfides).[16] In the reverberatory furnace area, sulfate compounds averaged 0.111 mg/m³ and sulfites averaged .046 mg/m³; slightly higher, but similar levels were found in the converter area. The sulfate compounds in all areas of the smelter were found predominantly (approximately 80%) in the respirable fractions, whereas the sulfite compounds were uniformly spread over all particle sizes.[16]

Table 3. — Average Personal Sulfur Dioxide and Dust Exposures and Respirator Use by Job Category and Work Location for 1973-1974.

Job Category and Work Location	SO2 (mg/m³)	Respirator Usage (hr/shift)	Total Dust (mg/m³)	Sulfate* (mg/m³)	Copper (mg/m³)
Reverberatory furnace area					
Furnace feeder	3.5	1.0	0.97	0.11	0.023
Matte tapper	3.0	0.4	0.97	0.13	0.018
Slag skimmer	3.0	0.5	0.86	0.091	0.016
Laborer	2.7	1.1	1.05	0.082	0.018
Converter area					
Converter operator	2.6	0.5	0.61	0.088	0.022
Crane chaser	2.6	1.0	0.98	0.095	0.026
Craneman	2.6	0.6	0.90	0.093	0.019
Reverb and converter					
Supervisors	2.6	0.4	0.67	0.069	0.016
Maintenance	1.7	0.5	0.78	0.063	0.020
Anode plant general	2.5	0.2	0.74	0.064	0.021
Acid plants general	4.2	0.2	0.71	0.069	0.008
Unspecified smelter areas	2.1	0.9	0.93	0.070	0.016

*Hot-water-extractable sulfate.

Smelter Personal Exposure Measurements. — No personal air samples were collected in the smelter prior to 1973. Table 3 shows the average personal measurements of SO_2 exposure and respirator use over 1973-1974. Acid plant workers had the highest SO_2 time weighted average concentration of 4.2 mg/m³ (1.6 ppm). Other smelter job categories had similar SO_2 exposures averaging approximately 3.0 mg/m³ (1.2 ppm). Personal exposure levels were generally lower than the full-shift SO_2 measurements from the workplace area samplers. Large variability of exposure was found within all job categories and between test years. As a result, the only statistically significant differences ($p < 0.05$) in SO_2 exposure were between job or work area categories with the highest and lowest time weighted average concentrations. For example, acid plant workers had significantly more SO_2 exposure than reverberatory furnace and converter maintenance workers. All personal SO_2 measurements as a group had a logrithmic-normal distribution.

Respirator usage varied considerably between job categories and work areas. The largest amount, approximately 1.0 hour per shift, was observed in the reverberatory furnace laborers, crane chasers, and unspecified smelter workers. Acid and anode plant workers' usage of respirators averaged less than 30 minutes per shift. There was no clear relationship between respirator usage and SO_2 exposure as measured by either personal exposure or general area samples. It should be noted that the personal exposure samples for SO_2 do *not* include SO_2 levels occurring while the subject was wearing his respirator. This technic probably underestimates exposures as would be determined by the sampling procedure specified by OSHA regulations.

Personal samplers were also used to measure exposure to respirable particulate matter and some of its constituents. Data for respirable dust, hot-water-extractable sulfate, and copper are also shown in Table 3. While the average respirable particulate exposures differed considerably according to job classifications and work areas, the large variability within categories and the changes from year to year obscured any differences between jobs or work areas. None of the differences were statistically significant (Kruskal-Wallis, $p > 0.1$), except copper exposures which were significantly higher ($p < 0.05$) for anode workers when compared to acid plant workers.

Comparison of smelter work area and personal exposure samples show that, in general, work area measurements in high-exposure jobs overestimated actual worker exposures. For example, in 1973, reverberatory furnace feeders' personal exposure data showed a time weighted average SO_2 concentration of 3.5 mg/m³, whereas the charging deck area samples averaged 16.8 mg/m³ during an eight-hour work shift. However, workers only spend approximately two hours per shift on the charge deck and they averaged 0.95 hours per shift of respirator usage while on the feed deck.

Tests were performed in 1975 to evaluate the *in-use* SO_2 protection provided by the chemical cartridge respirators used by the smelter workers. These tests showed that the respirators used since 1971 removed an average of 94% of the SO_2 in the workroom air (a range of 56-99% removal).[17] From about 1940 up to 1971, a cloth respirator composed of a cloth bag impregnated

Table 4. — Workplace Area and Personal Monitor Measurements of Air Contaminants at the Truck Shop During 1973-74.

	Full-Shift Concentrations		
	n	Mean	S.D.
Workplace area measurements			
Sulfur dioxide (mg/m³)	30	0.3*	0.2
Nitrogen dioxide (ppm)	14	0.014	0.004
Acrolein (ppm)	66	0.002	0.004
Formaldehyde (ppm)	52	0.012	0.016
Total dust (mg/m³)	125	0.61	0.60
Personal monitor samples			
Nitrogen dioxide (ppm)	137	0.067	0.065
Respirable dust (mg/m³)	149	2.2	3.0
Sulfate (mg/m³)	80	0.096†	0.19
Copper (mg/m³)	80	0.019	0.039

*The limit of detection for SO2 was < 0.2 mg/m³. Another 61 samples had no detectable SO2 in them

†Sulfate was measured as total hot-water-extractable sulfate.

Table 5. — Comparison of Airborne Concentrations of Respirable Dust and Selected Metals from Truck Shop and Smelter Worker Personal Monitor Samples for November 1974.

	Truck Shop (n = 45)		Smelter (n = 139)	
	Mean (mg/m³)	S.D.	Mean (mg/m³)	S.D.
Respirable dust	1.86	1.58	1.30	1.24
Sulfate compounds*	0.110	0.087	0.066	0.077
Sulfite compounds*	0.003	0.007	0.020	0.025
Copper†	0.008	0.008	0.029	0.026
Arsenic	0.002	0.002	0.007	0.007
Lead	0.005	0.008	0.018	0.016
Manganese	0.038	0.043	0.031	0.025
Zinc	0.18	0.30	0.045	0.039

*Sulfate and sulfite compounds were measured in hydrochloric acid extractions of the particulate by the method of Eatough, et al.[14]

†Copper levels measured over 1973-74 averaged 0.019 mg/m³ at the truck shop and 0.018 mg/m³ at the smelter.

with a glycerine-calcium carbonate mixture was used. Laboratory tests performed by Holaday showed they removed 95% of incoming SO_2.[18] In general, respirators have been used by workers to control SO_2 exposures only as deemed needed by the workers and not on a continuous basis.

Truck Shop Employee Exposure Measurements. — The shop workers, who repair large diesel ore trucks, were selected as a control group for the smelter workers because their sulfur dioxide exposure was presumed to be low (less than 0.2 mg/m³). Worker exposure to selected air contaminants as measured during 1973-1974 is summarized in Table 4. An industrial hygiene survey was performed in 1969 by the state of Utah which indicated workplace conditions similar to those seen in 1973-1974. There have been no major modifications affecting environmental conditions since the truck shop was constructed in 1963, so the exposures have probably remained about the same over the past 14 years.

Workplace area measurements of air contaminants at the truck shop were much lower than the personal exposure measurements of NO_2 and dust (Table 4). Personal samples taken on the shop workers showed respirable dust levels of 2.21 mg/m³. Air contaminant levels in the truck shop tended to be much higher during the winter, because the huge access doors were often shut to maintain a reasonable work area temperature, and closing the doors radically reduced the building ventilation.

Table 5 is a comparison of the airborne concentrations of respirable dust and selected metals for the truck shop and smelter workers as determined in November, 1974. Major differences were evident, except between total respirable dust, copper, and manganese levels. The respirable dust results suggest that the shop workers had a wider range of annual variability in workplace exposures than do the smelter workers. Smelter workers were determined to have had significantly higher exposure to sulfite, arsenic, and lead ($p < 0.05$). Sulfite in smelter particulate was probably composed of both adsorbed SO_2 and sulfite compounds, such as iron sulfite. The amount of adsorbed SO_2 was probably relatively small — at most 0.04 mg/m³ — when compared to the amount of SO_2 gas (approximately 3.0 mg/m³). Shop workers had significantly higher exposure to zinc and benzene-soluble compounds. Based on the source, the particulate at the shop was probably a sooty exhaust aerosol, while the smelter particulate was primarily inorganic.

Discussion and Conclusions

Measurements of SO_2 concentrations in smelter work areas have shown that SO_2 levels can be quite high (>13 mg/m³) near localized SO_2 emission sources. However, workers apparently did not spend a full work shift in these areas; they stood away from the emissions, wore respirators, or used fans to lower their personal exposure when necessary. Recent personal exposure samples show that workers regulate their exposures so that, on the average, their time weighted SO_2 exposures are between 0.8 and 10.0 mg/m³. A further result of this self-protective activity was the lack of significant differences in SO_2 exposure between job classification and work area categories. The measurements suggest that most of the workers' chronic exposure has been the result of a generalized SO_2 level pervading the production areas of the smelter.

Historical SO_2 measurements (Table 1) indicate there have been no substantial changes in workplace area SO_2 concentrations with one possible exception, the reverberatory furnace charge deck. However, personal exposure samples indicate the furnace feeders usually also self-regulate their SO_2 exposures by the means noted above, such that their actual exposures are similar to other smelter workers. Hence, historical data on SO_2 exposure and current respirator usage patterns suggest that the time weighted average SO_2 exposure for smelter workers has probably been in the range of 1 to 5 mg/m³ over the past 34 years.

A comparison of the smelter and truck shop (control) workers' exposure to SO_2 and respirable particulate matter reveals that the smelter workers probably have had at least a tenfold greater chronic exposure to SO_2 than the controls. Smelter workers were also determined to be exposed to higher concentrations of respirable sulfite (including adsorbed SO_2), arsenic, and lead aerosol than the controls. Neither the arsenic nor lead exposures were considered substantial; that is, they were well below any levels currently associated with pulmonary effects. Shop workers, because of their exposure to diesel exhaust particulate and NO_2, are not a "no exposure" control group, but rather, a "low SO_2 exposure" control group. In conclusion, the smelter workers were determined to have had substantially more exposure to SO_2 and sulfite aerosol than the controls, but do not significantly differ from them in their exposure to total respirable particulate matter or hot-water-extractable sulfates. None of the other substances

present in the particulates appear to be present in sufficient amount to have any effects on pulmonary function.

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South Bronx Hospital Profitable

As a so-called "proprietary" hospital, Prospect Hospital is supposed to make money. Still, Dr. Freedman's feat isn't a mean one whether measured by other proprietary hospitals or nonprofit institutions. And at a time when hospitals everywhere are being severely squeezed by escalating costs, it is instructive to take a look at a medical facility that wins praise from the largely poverty-stricken community it serves and yet is able to turn a profit without charitable contributions.

The formula is simple. Instead of trying to be all things to all people, 168-bed Prospect Hospital elects to concentrate on the routine medical procedures — appendectomies, say, or hernia operations — that comprise 95% of an average general hospital's activities. It has no maternity department because maternity departments are money losers. Its emergency room isn't equipped to deal with every kind of casualty.

— From "Hospital In Slum Turns a Profit by Providing Basic Care for the Poor" by Stanley H. Slom, in *The Wall Street Journal*, October 21, 1977.