NIOSH

TECHNICAL REPORT

ENVIRONMENTAL EXPOSURE TO AIRBORNE CONTAMINANTS IN THE ANTIMONY INDUSTRY

1975-1976

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

ENVIRONMENTAL EXPOSURE TO AIRBORNE CONTAMINANTS IN THE ANTIMONY INDUSTRY 1975 - 1976

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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Cincinnati, Ohio 45226

August 1979

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DHEW (NIOSH) Publication No. 79-140

ABSTRACT

A study of the antimony production industry in the United States was undertaken by the National Institute for Occupational Safety and Health (NIOSH) since a study by Cunningham and McCallum of Associated Lead Manufacturing, Ltd., disclosed 17 cases of respiratory cancer during the last 10 years among antimony production workers in England. The 1975 NIOSH study involved the monitoring of three major antimony producers, two of which roast imported antimony sulfide ore to produce antimony oxide (Plants B & C), while the other (Plant A), the only producer of antimony metal in the United States, produces antimony oxide by the oxidation of purified antimony metal. A follow-up study on Plant A was made in 1976 to collect breathing zone samples since these were not gathered in the preliminary survey.

The three plants showed antimony exposures above the current OSHA standard of 0.5 mg/m^3. The arsenic exposures although below the then current OSHA standard of 0.5 mg/m^3 exceeded in most instances the current OSHA standard of 0.010 mg/m^3.

Bagging operations appeared to be one of the larger air contamination sources in two of the plants. Controlling airborne antimony to 0.5 mg/m^3 may possibly reduce airborne arsenic to the OSHA standard.

CONTENTS

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of the following former and current NIOSH personnel who assisted in these surveys: Leo Blade, Hector Blejer, M.D., Bruce Etchinson, Stephen Gentry, Troy Marceleno, Gary White, and Ronald Young.

INTRODUCTION

The Division of Surveillance, Hazard Evaluations and Field Studies of the National Institute for Occupational Safety and Health initiated studies of antimony facilities after the results of a study done by Cunningham and McCallum of Associated Lead Manufacturing, Ltd., disclosed 17 cases of respiratory cancer among antimony oxide production workers in England during the last 10 years.[1] No such health survey had been made of antimony production workers in the United States; therefore, in 1975 an investigation was begun which included three major antimony producing facilities.

Antimony metal and oxide are the chief antimony products manufactured in the United States. With the exception of small quantities of antimony metal produced as a by-product from certain ore smelting operations, only one plant produces antimony metal. Antimony oxide however is produced in at least five or six plants with major production concentrated in the three plants selected for this study which operate essentially on a full time basis. The plants are designated in Table 1 as A, B, and C.

Table 1

Plants Surveyed

Plant	Product	Plant Population
A	Antimony metal & antimony oxide	120 (100 production workers)
B	Antimony oxide	130 (82 production workers)
C	Antimony oxide	60 (45 production workers)

Industrial hygiene surveys of the plants were begun in April 1975 and extended through March 1976. Epidemiological studies were initiated in 1974 at Plant A where employees were exposed primarily to antimony and low levels of arsenic and sulfur dioxide (SO_2). The retrospective mortality study on Plant A was abandoned when a review of the record systems indicated that a satisfactory cohort could not be traced.

Smelting

Antimony metal is produced in the United States, with minor exceptions, only at Plant A. It is recovered in a series of batch operations by reacting an antimony oxide ore with coke, iron oxide, and other fluxes in a blast furnace (singles furnace) to produce a metal of about 85% antimony content. This crude, molten metal from the singles furnace is further refined in a reverberatory furnace (doubles furnace) and then transferred to a starring furnace to produce antimony metal with as high as 99.8% purity.

Antimony Oxide Production

Antimony oxide is produced at all three plants studied. Plant A oxidizes antimony metal with air to form antimony oxide, which sublimes and passes first through coolers (where most of it is collected) and then through a fabric or baghouse collector where the remainder is collected. The antimony oxide is then bagged for shipment. Plants B and C roast antimony sulfide ore in rotary kiln-type furnaces to produce antimony oxide. This continuous process operates at about 2000°F and results in the sublimation of antimony oxide which condenses out in a series of coolers. The sulfur oxide formed by pyrometallurgical treatment of sulfide ore passes through an alkaline scrubber where it is removed. The antimony oxide is pneumatically conveyed to a refining furnace where the sublimation process is repeated and then transported via a screw conveyor to a packaging operation, where it is bagged and shipped.

PLANT DESCRIPTIONS

Plant A was built in 1930; Plant B, in 1937; and Plant C, in 1951. The number of production workers was greatest in Plant A (about 100), since it utilized a batch process and much hand labor was used to sort and transport ore and slag. In Plants B and C, which utilized continuous processes with 82 and 45 production workers, respectively, less handling of ore and slag was required, since the antimony sulfide ore was already packaged in bags and could be easily slit open and dumped in the kiln. Unlike Plants A or C, Plant B had a plant-wide seniority system and also manufacture several other chemicals, most of which were inorganic. This meant that the employees of Plant B were exposed not only to airborne antimony but to other chemicals including soluble nickel, cadmium, and chromium.

Eleven of the plants surveyed provided adequate change room facilities such as showers and lockers. Work clothes generally were supplied. At Plant A clothing was laundered on the plant site. At Plants B and C work clothing was washed by a commercial laundry.

All plants had a medical program which included preplacement and periodic follow-up medical exams. Safety equipment was supplied at all plants. This generally included safety shoes, hard hats, and appropriate respiratory protective devices. Although Plant A was primarily an open air plant, all employees were encouraged to wear respirators continuously while in the production areas. In the other two plants which are under roof, respirators were generally required only on specific dusty operations such as bagging or dumping ore into the furnace feed hopper.

STUDY METHODS

Since antimony ores are composed essentially of either antimony oxide from Central America or antimony sulfide from Bolivia or Africa (analyses typical of these ores are listed in Appendix C), the resulting air contaminants present in the antimony plants are generally antimony, arsenic and sulfur dioxide. Arsenic is present in these ores in quantities as low as 0.05% in oxide ores and as high as 0.50% in sulfide ores. In the 1975 study, general area samples were collected in the three plants, and breathing zone samples were collected in Plants B and C. The 1976 follow-up study consisted of collecting breathing zone samples in Plant A. Portable sampling pumps were used for the collection of environmental samples for both arsenic and antimony. The pumps worn by each worker for the duration of his shift (6 to 7 hours) operated at 2.0 liters per minute (lpm) and collected dust on a 37 mm, 0.8 um pore-size mixed cellulose ester membrane filter. General area samples were also collected using the same equipment. Analyses for antimony were performed by atomic absorption spectroscopy.[2] Analyses for arsenic were performed by atomic absorption spectroscopy[2] for Plant B. At Plants A and C analysis consisted of conversion to arsine and detection by atomic absorption spectroscopy.[3]

RESULTS

Table 2 shows the range of the air concentration of antimony and arsenic in the three plants. Essentially no SO_2 was found in the plants except during upset furnace conditions at Plant A in the 1976 survey. Maintenance at Plant A had deteriorated since the 1975 survey when general area samples were collected and environmental contaminant levels were lower. Environmental sampling data collected at the three plants are listed in Appendix A; the process flow sheets in Appendix B; and analysis of ores and other pertinent data in Appendix C.

Table 2

Range of Antimony and Arsenic Samples

Type of Sample	GA	BZ	GA	BZ	GA	BZ
Number of Samples	12	50	4	5	8	4
Antimony mg/m^3	0.14-2.0	0.05-6.2	0.01-0.83	0.21-3.2	1.8-5.6	2.7-8.7
Arsenic mg/m^3	0.001-0.003	0.001-0.087	ND**	ND-0.039	0.002-0.016	0.016-0.056

*General Area Survey run in 1975, followed by BZ survey in 1976

**Non-detectable based on analytical method.

GA = General Area

BZ = Breathing Zone

DISCUSSION AND CONCLUSIONS

Examination of the environmental data from the three plants monitored indicates that all three plants showed significant exposure above the current OSHA standard of 0.5 mg/m^3 for antimony, while arsenic was below the then current OSHA standard of 0.5 mg/m^3, but greater than the present OSHA standard of 0.010 mg/m^3, and the NIOSH recommended standard of 0.002 mg/m^3.

Table 3

Current And Proposed Standards

	Concentration in Milligrams per Cubic Meter		PPM's
	Antimony	Arsenic	Sulfur Dioxide
Current OSHA Std.	0.5	0.010	5.0
Proposed OSHA Std.	--	--	2.0
NIOSH Recommended Std.	0.5	0.002	0.5
TLV-ACGIH	0.5	0.5*	5.0

*Notice of intended change: 0.005 mg/m^3 (1978 TLV's)

Sulfur dioxide, in general, appeared to be nondetectable in all three plants, except in the 1976 survey at Plant A where stibnite (Sb_2S_3) was used in the doubles furnace to scavenge oxygen from the metal. At that time there were upset conditions which showed intermittent short-term exposures as high as 25 ppm. Plants B and C were relatively free of SO_2 at the time of the survey and, though the presence of SO_2 could be detected, it was below 1 ppm, the sensitivity of the Drager tubes.

Plant A was in need of general maintenance to correct the fuming of furnaces and to improve the operation of the antimony oxide bagging machine. This plant is not presently in operation.

Plant B had air levels above the current standard for antimony in the feeding of antimony sulfide ore to the furnace. To correct this may require an alternative approach to feeding the ore into the furnace. Samples collected for arsenic during this survey were analyzed by a method of low sensitivity, which indicated that arsenic in the air was less than 0.035 mg/m^3.

Plant C showed levels of antimony and arsenic in air as high as 8.7 mg/m^3 and 0.056 mg/m^3 respectively. To reduce these levels the plant had two main problems which needed to be corrected; these were the feeding of antimony sulfide ore to the furnace, and repair or replacement of the antimony oxide bagging operation. Hopefully, such steps would reduce the antimony levels in the air to the OSHA standard of 0.5 mg/m^3 and the arsenic in air levels to the OSHA standard of 0.010 mg/m^3.

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2. National Institute for Occupational Safety and Health, Division of Laboratory and Criteria Development. General Procedure for Metals - Physical and Chemical Analysis Branch Analytical Method 173, in NIOSH Manual of Analytical Methods, HEW Publications No. (NIOSH) 75-121. Cincinnati: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH; 1974, pp. 173-1 to 173-10.

3. National Institute for Occupational Safety and Health, Division of Laboratory and Criteria Development. Arsenic in Urine and Air - Physical and Chemical Analysis Branch Analytical Method 138 in NIOSH Manual and Analytical Methods, HEW Publication No. (NIOSH) 75-121. Cincinnati: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH; 1974, pp. 139-1 to 139-6.

Appendix A. Sampling Results

Table A-1. Summary of Antimony Personal Samples by Operation at Plant A

Operation	No. of Samples	Range Low Mg/m3	Range High Mg/m3	Arithmetric Mean Mg/m3	Arithmetric Std. Err. Mg/m3	Geometric Mean Mg/m3	Geometric Std. Dev.	95% Confidence Limits Lower Mg/m3	95% Confidence Limits Upper Mg/m3
Oxide	6	0.09	3.1	2.2	0.45	1.5	3.99	0.35	6.4
Singles Furnace	4	0.41	1.8	1.3	0.31	1.1	1.98	0.37	3.2
Doubles Furnace	4	0.89	2.1	1.4	0.25	1.4	1.43	0.79	2.4
Maintenance	8	0.09	6.2	0.96	0.75	0.24	4.42	0.07	0.83
Laborers	22	0.09	4.9	1.3	0.22	0.86	2.83	0.54	1.4
Miscellaneous	6	0.05	3.7	1.1	0.55	0.56	4.14	0.13	2.5

Table A-2. Summary of Arsenic Personal Samples by Operation at Plant A

Operation	No. of Samples	Range Low Mg/m^3	Range High Mg/m^3	Arithmetric Mean Mg/m^3	Arithmetric Std. Err. Mg/m^3	Geometric Mean Mg/m^3	Geometric Std. Dev.	95% Confidence Limits Lower Mg/m^3	95% Confidence Limits Upper Mg/m^3
Oxide	6	0.008	0.16	0.045	0.023	0.027	2.72	0.010	0.078
Singles Furnace	4	0.005	0.013	0.009	0.002	0.008	1.50	0.004	0.016
Doubles Furnace	4	0.002	0.010	0.006	0.002	0.004	2.10	0.001	0.015
Maintenance	8	0.001	0.017	0.003	0.002	0.002	2.61	0.001	0.004
Laborers	22	0.001	0.041	0.010	0.002	0.006	2.88	0.004	0.010
Miscellaneous	6	0.001	0.047	0.011	0.007	0.004	3.89	0.001	0.019

Table A-3

Results of Personal Sampling for
Antimony and Arsenic at Plant A
March 1976

Operation and Job	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)
Oxide				
Furnace operator	445	0.89	0.090	0.008
Furnace operator	464	0.93	3.0	0.022
Furnace operator	460	0.92	3.1	0.037
Furnace Operator	471	0.94	2.0	0.017
Packer	457	0.91	2.6	0.16
Packer	470	0.94	2.6	0.025
Singles Furnace				
Tapper	505	1.01	1.6	0.005
Tapper	480	0.96	1.2	0.008
Tapper	466	0.93	0.41	0.010
Conveyor operator	460	0.92	1.8	0.013
Doubles Furnace				
Furnace operator	401	0.80	1.3	0.002
Furnace operator	456	0.91	0.89	0.003
Furnace operator	437	0.87	2.1	0.010
Furnace helper	455	0.91	1.5	0.007
Maintenance				
Blacksmith	431	0.86	0.15	0.001
Maint. man-shop	480	0.96	0.11	0.001
Mechanic	447	0.89	0.09	0.001
Mechanic shop	440	0.89	0.09	0.001
Maint. welder	447	0.89	0.09	0.002
Bricklayer	458	0.92	0.70	0.002
Bricklayer	470	0.94	6.3	0.017
Bricklayer	442	0.88	0.20	0.002
Laborers				
Laborer	440	0.88	0.09	0.001
Laborer	448	0.90	1.6	0.013
Laborer	451	0.90	1.9	0.009
Laborer	477	0.95	0.95	0.002
Laborer	485	0.97	1.3	0.041
Laborer	482	0.96	0.39	0.004
Laborer	457	0.91	1.6	0.013
Laborer	466	0.93	0.67	0.005

Table A-3
(Continued)

Operation and Job	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)
Laborer	487	0.97	1.1	0.005
Laborer	454	0.91	1.6	0.009
Laborer away from yard most of day	456	0.91	0.23	0.003
Laborer	468	0.94	0.98	0.007
Laborer	461	0.92	0.12	0.001
Laborer	427	0.85	0.14	0.001
Laborer	454	0.91	1.9	0.010
Laborer	458	0.92	2.0	0.029
Laborer	453	0.91	1.2	0.008
Laborer	443	0.89	0.47	0.002
Laborer	439	0.88	1.6	0.011
Laborer	411	0.88	4.9	0.025
Laborer	459	0.92	1.5	0.009
Laborer	450	0.90	1.2	0.004
Miscellaneous				
Sweeper-yard	458	0.92	3.7	0.047
Fork lift operator	464	0.93	0.58	0.002
Gardener	443	0.89	0.04	0.001
Scale operator	459	0.92	1.3	0.009
Warehouse operator	455	0.91	0.46	0.003
Warehouse operator	452	0.90	0.50	0.003
Current OSHA Standard			0.5	0.010

Table A-4

Results of Area Samples for
Antimony and Arsenic at Plant A
April 1975

Location	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)
Blast furnace	454	0.91	0.11	0.007
Slag tapping-blast furn.	454	0.91	0.26	0.001
Slag tapping-blast furn.	455	0.91	1.1	0.002
Doubling furnace #2	451	0.90	1.1	0.003
Starring furnace #1	458	0.92	1.1	0.003
Starring furnace #2	457	0.91	0.52	0.002
Casting area	453	0.91	2.0	0.004
Warehouse	451	0.90	0.61	0.002
Burner end of #1 starring furnace	437	0.87	1.2	0.003
Oxide furnace	436	0.87	0.14	0.001
Charge scale	417	0.83	0.36	0.001
Change room	432	0.86	0.54	0.001

Table A-5

Results of Personal Sampling for
Antimony and Arsenic in Plant B
June 1975

Job	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)
Furnace operator	355	0.71	1.2	0.039
Furnace operator	385	0.77	3.2	<0.035
Packager	380	0.76	0.21	<0.035
Packager	370	0.74	0.78	<0.035
Process operator	380	0.76	1.2	<0.035

Table A-6

Results of Area Samples for Antimony, Arsenic, and Nickel at Plant B
June 1975

Location	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)	Nickel Concentration (Mg/m^3)
Locker room	375	0.75	0.28	<0.035	--
Nickel sulfate facility	355	0.71	0.01	<0.035	0.018
Bagging operation	300	0.60	0.43	<0.035	--
Bagging operation	300	0.60	0.83	<0.035	--

Table A-7

Results of Personal Sampling For Antimony and Arsenic at Plant C
June 1975

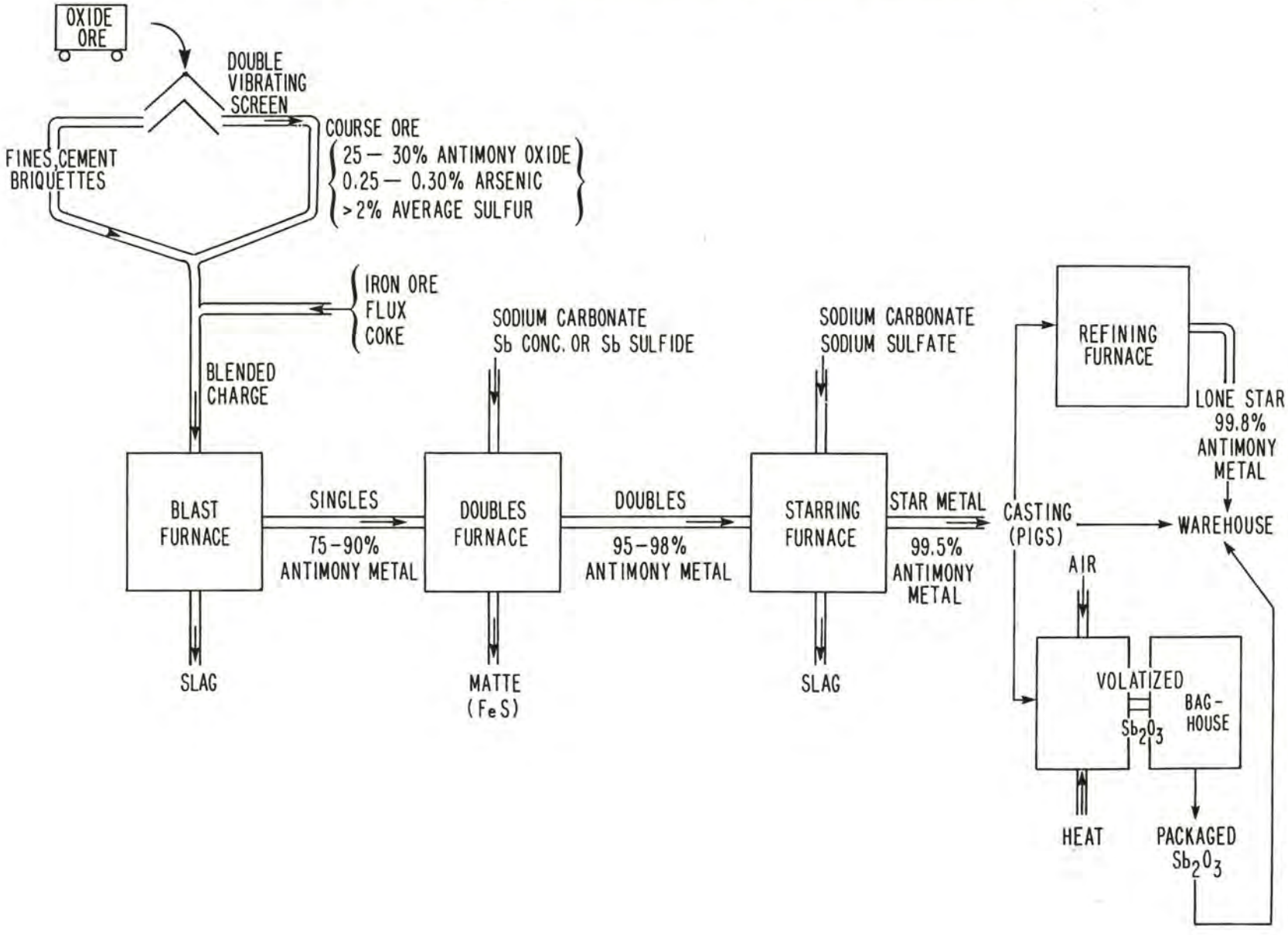
Job	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)
Operator	420	0.84	2.7	0.017
Operator-miscellaneous	420	0.84	5.0	0.027
Bagging	420	0.84	8.7	0.056
Ore Dumper (wore hood) sampler not under hood	420	0.84	4.5	0.016

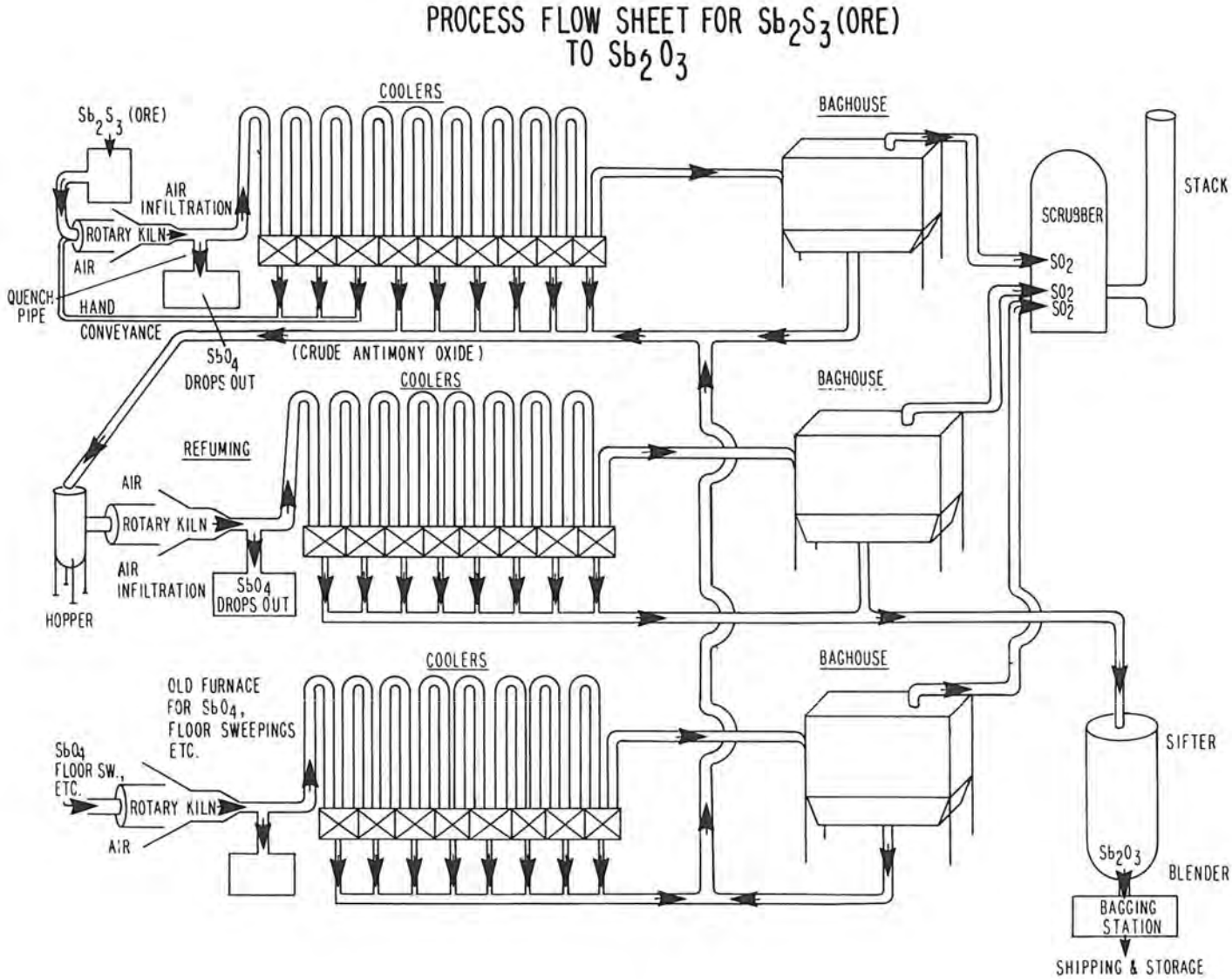
Table A-8

Results of Area Sampling for
Antimony and Arsenic in Plant C
June 1975

Location	Sample Time (min.)	Sample Volume (m^3)	Antimony Concentration (Mg/m^3)	Arsenic Concentration (Mg/m^3)
Top of coolers	400	0.80	5.6	0.006
At bagging station	405	0.81	2.3	0.014
At ore hopper	405	0.81	2.8	0.009
Ore feed, 2nd level	410	0.82	1.8	0.002
Above bagging operation	340	0.78	2.6	0.016
At control panel	390	0.78	1.9	0.010
At operator's desk	400	0.80	2.9	0.015
Feed oxide - outdoors	405	0.81	5.3	0.006

APPENDIX B. ANTIMONY METAL AND OXIDE PROCESSING FLOW SHEET




PROCESS FLOW SHEET FOR Sb_2S_3(ORE) TO Sb_2O_3
COOLERS
BAGHOUSE
Sb_2S_3 (ORE)
AIR INFILTRATION
ROTARY KILN
AIR
QUENCH PIPE
HAND CONVEYANCE
SbO_4 DROPS OUT
(CRUDE ANTIMONY OXIDE)
SCRUBBER
STACK
SO_2
SO_2
SO_2
COOLERS
BAGHOUSE
REFUMING
AIR
ROTARY KILN
AIR INFILTRATION
SbO_4 DROPS OUT
HOPPER
COOLERS
BAGHOUSE
OLD FURNACE FOR SbO_4, FLOOR SWEEPINGS ETC.
SbO_4 FLOOR SW., ETC.
ROTARY KILN
AIR
SIFTER
Sb_2O_3
BLENDER
BAGGING STATION
SHIPPING & STORAGE

APPENDIX C

Table C-1

Typical Analyses of Antimony Ores at Plant A

Type of Ore	% Sb	% S	% As	% Pb
Guatemalan	51.2	14.0	0.072	0.286
Bolivian	59.6	18.5	0.126	0.396
Mexican	31.6	0.46	0.054	0.136
Honduran	40.3	0.44	0.072	0.110

The unanalyzed portions of the ores consist mainly of silicates, calcium and iron oxides, plus some trace metals.

Table C-2

Typical Analysis of Antimony
Ore at Plants B and C

ANTIMONY CONCENTRATES	TYPICAL VALUES
Antimony	59.5%
Sulfur	25.6
SiO_2	4.0
Calcium	0.2
Magnesium	2.0
Iron	1.5
Aluminum	0.2
Lead	0.1
Nickel	0.2
Copper	0.1
Arsenic	0.3
Selenium	<1 part per million

ANTIMONY OXIDE	
Antimony trioxide	99.2%
Antimony tetraoxide	0.3
Copper	0.0001
Nickel	0.001
Iron	0.0003
Lead	0.06
Arsenic	0.3
Sulfate	0.01
SiO_2	0.02
Selenium	<1 part per million

The values for the antimony concentrates are based on the last 10 lots of concentrate. The typical values for antimony oxide are based on analytical work completed since December 1972.

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