U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45202

HEALTH HAZARD EVALUATION DETERMINATION REPORT NO. 73-164-169

ANACONDA COMPANY
ANACONDA, MONTANA
JANUARY 1975

I. TOXICITY DETERMINATION

Based upon information obtained during a survey conducted in the Converter Department on January 15-17, 1974 it has been determined that no significant health hazard exists to employees in most of the job categories from exposure to the fume or dust of copper, lead, zinc, and cadmium. A potential hazard does exist from exposure to airborne lead for the job categories of ore handler and skull breaker.

If the airborne arsenic concentrations observed are truly indicative of employee exposure there exists a potential for arsenic-induced cancers. However, it should be noted that the dose-response relationship of arsenic-induced cancer is not clearly defined and the potential for such cancers is extremely difficult to assess.

Evidence exists that an irritant toxic effect is present in the exposed group of workers. This is concluded because 78-80% of these workers complained of eye, nose and throat irritation and 47-60% of lower respiratory tract irritation. Control subjects from a nearby office reported much less symptomatology. The most likely cause of the symptoms found in workers studied is sulfur dioxide, a primary mucous membrane irritant which has been found in high levels in other copper smelters.

These determinations were based on environmental and biological measurements, conditions of use, employee interviews and medical examinations, and available literature on the toxicity of substances investigated.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are available upon request from the Hazard Evaluation Services Branch, NIOSH, U.S. Post Office Building, Room 508, 5th and Walnut Streets, Cincinnati, Ohio 45202. Copies have been sent to:

a) Anaconda Company, Anaconda, Montana
b) Authorized Representative of Employees
c) U.S. Department of Labor - Region VIII
d) NIOSH - Region VIII

For the purposes of informing the Converter Department employees the employer will promptly "post" the Determination Report in a prominent place(s) near where exposed employees work for a period of 30 calendar days.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of the employees of the Converter Department of the Anaconda Company's copper smelter in Anaconda, Montana regarding exposure to metal fumes and dusts. No request was made for an evaluation of exposure to sulfur dioxide, a gas routinely found in irritating airborne concentrations in copper smelters. As a consequence, no measurements of sulfur dioxide were attempted.

IV. HEALTH HAZARD EVALUATION

A. Conditions of Use

It is difficult to describe the operation of the Converter Department in regard to its effects on employee exposure because all the operations in the smelter contribute to the exposure of each employee and no one operation is truly physically isolated. It is best to describe the entire smelting procedure and to identify that part which concerns the Converter Department.

The sulfide ore treated at Anaconda consists basically of a mixture of copper and iron sulfides, valuable trace elements, and a siliceous gangue of little economic value. Some of the common trace elements are: arsenic, lead, zinc, cadmium, selenium, molybdenum, gold, and silver.

The copper ore is not treated directly but is subjected to a flotation process which produces a concentrate. Copper concentrate is the raw material supplied to the smelter. Smelting is essentially the application of sufficient heat to the concentrate to cause by fusion the conversion of the gangue into a nearly valueless slag and at the same time to concentrate the copper and other valuable constituents of the ore into a high grade material. The general term "smelting" may be considered to cover the successive operations of reverberatory smelting, converting, and fire refining.

At Anaconda old roasters are operated at several hundred degrees Fahrenheit and used as dryers to control the water content of the concentrate. The concentrate is then melted in a reverberatory furnace at a temperature of about 2800°F. Although the reverberatory furnace is primarily a melting furnace, some concentration of the copper is effected. Addition of a siliceous flux aids in concentrating the iron into slag which is skimmed from the surface of the bath. The copper remains as "matte", essentially a mixture of copper sulfide and iron sulfide in varying proportions. All of the sulfur originally in the concentrate in excess of these compounds is expelled in the off-gas as sulfur dioxide. Much of this gas leaks into the smelter building.

The matte is transferred from the reverberatory furnaces to one of six converter furnaces where most of the remaining iron and sulfur are removed by oxidation. The transfer is accomplished by tapping a hole in the reverberatory furnace allowing the matte to flow into a large ladle. The ladle is then lifted up to the converter furnace spout by an overhead crane and poured into the furnace. (The crane operators, converter furnace operators, crane aisle employees, and converter furnace maintenance personnel are all employed in the Converter Department.) Oxidation is accomplished by blowing streams of air through the molten mass. Again a siliceous flux is added to aid in forming an iron oxide slag which is returned to the reverberatory furnace for reprocessing. Further blowing after removal of the slag produces "blister copper" which is about 98% pure. The blister copper is transferred using the overhead cranes and ladles to a gas fired, fire refining furnace where copper oxides are reduced to metallic copper forming "anode copper" of 99+% purity. The anode copper is poured into anodes on a casting wheel.

B. Evaluation Design and Methods

1. Medical

Fifty-four workers in the Converter Department and twenty office workers from the Accounting Department serving as controls were administered a questionnaire. Specific questions were asked about work and smoking history, upper and lower respiratory tract irritation, eye irritation, skin irritation, and symptoms of heavy metal intoxication such as, nausea and vomiting, changes in hair and finger nails, loss of appetite, weakness, and tremor of extremities.

A short physical exam including examination of nasal septum for perforation, finger nails for striae (Mees' lines), gums (lead lines) was included.

At the same time approximately 10 cc of whole blood was taken from each subject and kept in a lead-free vacutainer. This blood was later analyzed spectrophotometrically for lead and copper content. A spot sample of urine was collected in plain plastic bottles with EDTA added and was analyzed for arsenic content by atomic absorption.

2. Environmental

Employee exposure to airborne copper, lead, zinc, cadmium, and arsenic was determined by collecting air samples on 0.8 µm pore size membrane filters using personal air sampling pumps and sequential air samplers.

Three of the five sequential samplers were located in skimmer shacks, one in a crane cab, and another in the punching aisle. Selected filters were anlayzed for arsenic, the remaining filters were analyzed for the trace metals.

Two personal samplers were worn by each employee for approximately 8 hours. The filter on one of the samplers was preceeded by a miniature cyclone to obtain a respirable sample. Some of the elements and compounds evaluated have standards and Threshold Limit Values applicable to the fume and the use of cyclones was an attempt to exclude that fraction of the aerosol containing fume. Selected pairs of filters were analyzed for arsenic.

All filter analysis was performed at the Western Area Occupational Health Laboratory in Salt Lake City. The filters were digested in acid and concentrations determined utilizing atomic absorption spectrophotometry.

C. Evaluation Criteria

1. Environmental

The criteria for evaluating the atmospheric environment was partly selected from five sources:

(a) For copper and zinc oxide: The Occupational Health Standards promulgated by the U.S. Department of Labor, Federal Register, October 18, 1973, Title 29, Chapter XVII, Sub-Part G, Tables G-1 and G-2 for 8-hour time-weighted average exposures;

(b) For cadmium and cadmium oxide: Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1973, published by The American Council of Governmental Industrial Hygienists (ACGIH);

Table 1. Environmental Evaluation Criteria

Source	Compound	Standard or Limit mg/m³
NIOSH	Arsenic	Not Detectable by a given method (0.002 mg/m^3)
OSHA (Table G-1)	Cu fume	0.1 mg/m^3
OSHA (Table G-1)	Cu dusts and mists	1.0 mg/m^3
NIOSH	Pb inorganic (as Pb)	0.15 mg/m^3
OSHA (Table G-1)	ZnO fume	5 mg/m^3
ACGIH	Cd (metal dust & soluble salts)	0.2 mg/m^3
ACGIH	CdO fume (as Cd)	0.1 mg/m^3
	intended change	0.05 mg/m^3

(c) For inorganic lead: National Institute for Occupational Safety and Health's (NIOSH) criteria for a recommended standard in "Occupational Exposure to Inorganic Lead";

(d) For inorganic arsenic: National Institute for Occupational Safety and Health's (NIOSH) criteria for a recommended standard in "Occupational Exposure to Inorganic Arsenic", and also;

(e) Memo from Associate Director, National Institute for Occupational Safety and Health to Assistant Secretary of Labor, Occupational Safety and Health Administration (OSHA), dated November 8, 1974 modifying reference (d) with attachments titled "Evaluation of New Evidence" and "Recommendations for an Inorganic Arsenic Standard."

2. Medical

a. Lead

According to Patty, between 70-80 micrograms per hundred ml of blood are indicative of non-harmful absorption and between 80-150 micrograms per hundred ml of blood of dangerous absorption.[1]

b. Copper

Normal copper levels have been reported to average 120 micrograms per hundred (114 micrograms/gram) of whole blood in man.[2]

c. Arsenic

Average urinary excretion in controls has been reported as 0.13 mg of arsenic per liter and 0.82 mg per liter in workers. Excretion of as much as 45 mg of arsenic per liter without evidence of systemic poisoning has also been reported.[3]

D. Evaluation Results

1. Medical

No significant exposure to the elements studied - lead, copper, and arsenic - was found in this study either by biological tests or from physical signs and symptoms. However, a vast majority of workers studied (78-80%) complained of eye, nose, and throat irritation and a large portion of workers (47-60%) complained of lower respiratory tract irritation. These findings can be attributed to the work environment since control subjects working in an office nearby reported much less symptomatology. The most likely cause of the symptoms found in workers studied is sulfur dioxide, a primary mucous membrane irritant which has been found in high levels in other copper smelters.

a. Questionnaires

Fifty-four exposed workers (53 male, 1 female), all caucasian, were interviewed. Their ages ranged from 20 to 60 years (average age 38) and their work experience ranged from 3 weeks to 37 years (average = 11.8 years). Sixty-five percent were regular smokers the remainder smoking less than 5 cigarettes a day were considered to be non-smokers. Symptomatology reported by both the smoking group and the non-smoking group was essentially the same; Table 2.

Twenty controls (18 male, 2 female), all caucasian, were also given the same questionnaire. Their age ranged from 21 to 59 (average age 41). Their work experience ranged from 4 months to 39 years (average = 14 years). Fifty-five percent were regular smokers by the same criteria as the reduction workers. Table 3.

b. Physical Examination

No specific signs relating to heavy metal toxicity such as changes in skin, hair, finger nails, gums, or tremor or weakness were found in any subject.

c. Lead Bioassay

Total blood lead levels in workers ranged from 11 to 51 micrograms per hundred milliliters of blood (average = 23 µg), controls that ranged from 10 to 28 micrograms per hundred milliliters of blood (average = 15 µg).

d. Copper Bioassay

Total blood copper levels in workers ranged from 67-113 (average - 88 µg) and controls ranged from 53-148 micrograms per hundred ml (average = 84 µg).

e. Arsenic Bioassay

Urinary arsenic levels ranged from less than .002 mg per liter to .1 mg per liter in both workers (average = .034) and controls (average = 0.29). Arsenic toxicity diagnosed by physical signs such as skin changes, presence of a nasalseptal perforation and neurological changes such as weakness and tremor in extremities was not observed.

Table 2. Results of Converter Department Employees Questionnaires

WORKERS (n=54)		
CONDITION	SMOKERS (n=35)	NON-SMOKERS (n=19)
Eye, nose, throat irritation	80% (28)	73% (14)
Chest tightness shortness of breath	60% (21)	47% (9)
Skin irritation	17% (6)	11% (2)

Table 3. Results of Accounting Department Employees Questionnaires

CONTROLS (n=20)		
CONDITION	SMOKERS (n=11)	NON-SMOKERS (n=9)
Eye, nose, throat irritation	18% (2)	11% (1)
Chest tightness shortness of breath	27% (3)	11% (1)
Skin irritation	0% (0)	0% (0)

2. Environmental

a. Personal Samples

The results of the personal sampling effort are shown in Tables 4 and 5. Table 4 gives average for various job categories. The values for zinc oxide were calculated from total zinc determinations assuming that all of the zinc present was in the oxide form. It is recognized that this assumption results in higher values for zinc oxide than actually existed but the error is probably small since the vapor pressure for zinc (boiling point = 907°C) at the furnace operations is quite high.

The data in Table 5 indicates that whereas about 25-50% of arsenic, cadmium, lead and zinc dust was non-respirable, nearly 94% of the copper dust was included in the non-respirable portion. This phenomenon does not appear unusual if the melting and boiling points of the elements involved are examined (Table 6). It is obvious that within the temperature range at which copper is smelted (about 1300-1500°C) that arsenic fume would be readily formed; cadmium, and zinc, would boil; a high vapor pressure of lead would exist; and the vapor pressure of the copper would be relatively low. Most of the copper collected in the converter department area probably was copper sulfide dust from other areas of the smelter. The airborne arsenic certainly didn't originate in the converter area.

New information regarding the potential for induced cancers resulting from exposure to arsenic compounds required the National Institute for Occupational Safety and Health (NIOSH) to reevaluate its recommendations in the inorganic arsenic criteria document. The decision was made that there should be "no detectable occupational exposure to arsenic compounds" based upon a specific sampling and analytical method. The method can detect environmental arsenic levels of 2 $\mu gm/m^3$ or greater. Exposure to environmental arsenic at this or higher concentrations presumably presents a risk of arsenic-induced cancers. All of the arsenic measurements made during this survey exceeded this value.

Copper dust exposures, with two notable exceptions, were found to be low. The average gross concentration was 0.52 mg/m^3 of copper. The two exceptions (3.30 and 2.55 mg/m^3) involved jobs where higher than usual exposure to dust would be expected. Because of the form of the material and the manner in which it is handled it is likely that the particles generated would be relatively large, a fact borne out when the gross and respirable fraction samples are compared. Also, not only is most of the copper dust in these samples not respirable but most of the copper in the material at issue (ore and skull) is in the form of copper sulfides not copper salts for which the original Threshold Limit Value of 1.0 mg/m^3 was established. It is the opinion of this investigator in considering the above reasons that the two high copper dust values do not represent toxic exposure levels. The associated relatively high levels of lead, however, do indicate a potential health hazard.

There is little evidence to suggest that there was much copper fume in this smelter during the time of the investigation. Fume would constitute about 6% of the total airborne copper if the assumption is made that the entire respirable fraction was fume (a very improbable situation). The average for the respirable samples was 0.03 mg/m^3 with only one sample exceeding the Occupational Safety and Health Administration Standard of 0.1 mg/m^3 for copper fume. As noted above it is highly doubtful that the entire respirable fraction consisted only of fume and therefore, it is improbable that the standard for fume was exceeded even in this single instance.

b. Area Sequential Sampling

The sequential sampling results are presented in Table 7. The values for zinc oxide were calculated as in section (a) above.

V. REFERENCES

1. Patty, F.A.: Industrial Hygiene and Toxicology. 2nd Edition, Volume I, p. 162, New York.

2. Patty, F.A.: Industrial Hygiene and Toxicology, 2nd Edition, Volume 1, p. 1036, New York.

3. Toxicity of Industrial Metals. Browning Ethyl; London 1961.

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Table 4. Personal Sampling Results

Job Title	No. of Workers Sampled	Type of Sample R=respirable G=gross	Averages of 8-Hour Samples in mg/m^3					
			Cd	Cu	Pb	Zn	ZnO	As
Craneman	5	G	0.002	0.06	0.02	0.07	0.09	
"	"	R	0.002	0.02	0.02	0.07	0.09	
"	4	G						0.03
"	"	R						0.02
Puncher	4	G	0.006	0.28	0.07	0.27	0.34	
"	"	R	0.006	0.02	0.06	0.26	0.32	
"	3	G						0.05
"	"	R						0.07
Skimmer	8	G	0.004	0.24	0.05	0.09	0.11	
"	"	R	0.002	0.02	0.03	0.06	0.07	
"	6	G						0.07
"	"	R						0.05
Ladle Chaser	4	G	0.004	0.74	0.04	0.12	0.15	
"	"	R	0.004	0.03	0.04	0.18	0.22	
"	2	G						0.08
"	"	R						0.05
Ore Handler	1	G	0.015	2.55	0.24	0.90	1.12	
"	"	R	0.004	0.11	0.07	0.27	0.34	
Skull Breaker	1	G	0.023	3.30	0.23	0.47	0.58	
"	"	R	0.003	0.08	0.03	0.08	0.10	
Cat Operator	1	G	0.002	0.28	0.01	0.06	0.07	
"	"	R	0.002	0.03	0.01	0.04	0.05	
Utility Man	1	R	0.001	0.01	<0.01	0.02	0.02	

Table 5. Analysis of Respirability of Arsenic and Metals

	As	Cd	Pb	Zn	Cu
Average Ratio of Total Amount Collected to the Respirable Fraction	1.33	2.02	1.92	1.68	16.5
Average Percent Respirable	75.2	49.5	52.1	59.5	6.1

Table 6. Melting and Boiling Points

Element	Melting Point (°C)	Boiling Point (°C)
Arsenic	Sublimates	--
Cadmium	321	767
Lead	327	1620
Zinc	419	907
Copper	1083	2310

Table 7. Sequential Sampling Results

	Averages Over Total Sampling Time in mg/m^3					
Location	Cd	Cu	Pb	Zn	ZnO	As
Crane Cab - No. 2	0.003	0.06	0.05	0.27	0.34	0.02
Puncher Aisle (Behind No. 2 Converter)	0.004	0.25	0.08	0.31	0.38	0.05
Skimmer Shack No. 5	0.003	0.33	0.03	0.08	0.10	0.06
Skimmer Shack No. 3	0.005	0.26	0.09	0.38	0.47	0.13
Skimmer Shack No. 1	0.006	0.34	0.12	0.08	0.10	0.10