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

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. 74-78-297

AMAX SPECIALITY METALS
PARKERSBURG, WEST VIRGINIA

JUNE 1976

I. TOXICITY DETERMINATION

Based upon a health hazard evaluation conducted by the National Institute for Occupational Safety and Health(NIOSH) on July 16-18, 1974, it has been determined that a dermatitis problem and a respiratory irritancy problem existed in conjunction with the company's refining of zirconium and hafnium. This determination is based upon: 1) medical interviews and cutaneous examination of exposed employees; 2) personal observations made by the NIOSH investigators; 3) review of medical records and studies; and 4) a review of available literature concerning the toxicity of the substances under consideration.

In November, 1974, zirconium operations were discontinued at Amax's Parkersburg facility due to the inability to purchase or manufacture economically crude zirconium tetrachloride. After notification in a letter dated May 19, 1975, that refining operations would be permanently discontinued, efforts to conduct an environmental evaluation were dropped and the determination report written based on medical findings alone.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this hazard evaluation determination are available upon request from the National Institute for Occupational Safety and Health, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. Copies have been sent to:

a) Amax Specialty Metals, Inc.
b) U.S. Department of Labor, Region III
c) Authorized Representative of Employees
d) NIOSH - Region III

For the purpose of informing approximately 150 "affected 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.

In lieu of "posting" this report, because the plant has been closed, the employer may furnish NIOSH with a list of the names and mailing addresses of the "affected employees" so that NIOSH can mail each individual a copy of the Determination Report.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S. Code 669(a)(6) authorizes the Secretary of Health, Education, and Welfare, following a written request by an employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentration as used or found. The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized union representative of the employees because some people in the plant had developed a hard to treat skin rash and a number of workers were found to have abnormal lung function tests.

HEALTH HAZARD EVALUATION

A. Plant Process

This plant produced nuclear reactor grade zirconium and hafnium from crude zirconium tetrachloride. To achieve the decided purity for reactor grade zirconium, a 2% hafnium content normally associated with zirconium must be reduced.[1] Bulk purchased crude zirconium tetrachloride, received in closed, impervious "rubber" bins, was put into aqueous solution and complexed with ammonium thiocyanate. The method of separation of hafnium and zirconium was a complex counter current liquid-liquid extraction. The crude tetrachloride solution was run through a number of multistory separation columns where the hafnium was preferentially extracted into methyl isobutyl ketone, while the zirconium was co-extracted in a backwash of dilute hydrochloric acid. The separated metals were precipitated from the respective solutions and calcined to the pure oxides. The hafnium oxide was stored. All subsequent operations discussed here could be run for either hafnium or zirconium; however, all further discussion of the process will consider only zirconium.

The high purity oxide was mixed with carbon and lactose to form pellets and chlorinated using chlorine gas resulting in a purified zirconium tetrachloride. The zirconium tetrachloride was then reduced in a furnace with magnesium chloride. Due to the extended reduction time involved, only one furnace was "dropped" and recharged per day. The reduction products were vacuum distilled to remove the leftover magnesium and magnesium chloride, leaving a porous zirconium metal (often referred to as zirconium sponge) which was crushed, sorted and packed for shipment. Slightly more frequently than yearly the zirconium was cleaned out of the equipment and the hafnium oxide reduced to hafnium metal in a "hafnium campaign" which lasted about a week. The equipment was again cleaned and the reduction of zirconium resumed.

At the time it was operating, the plant ran continuously. There were four rotating shifts, allowing each time period to be covered and one shift to be off. Except for one maintenance worker assigned to each of the rotating shifts, all maintenance workers worked the day shift, as did the utility workers and office staff. The pelletizing operation also ran only on the day shift. Table I details the work force.

The Company supplied and laundered uniforms. Each worker was issued two changes per week. For particularly dirty jobs coveralls were provided. Clothing was acid resistant. Leather gloves were used regularly, the average glove lasting about a month. During hafnium campaigns canvas gloves were used. Starting in early 1974 some gloves were cleaned and reused.

There was an unmanned first aid room in the plant. Emergency medical care was obtained either at the doctor's office or the emergency room at St. Joseph's Hospital in Parkersburg. Regular medical care included: a pre-employment physical examination aimed particularly at heart, hernias, and kidney; a pre-employment chest x-ray; and a pre-employment audiogram (introduced in the last year the plant was in operation); planned yearly audiograms; and a periodic physical examination of all hourly employees every two years with ECGs on those over 40.

B. Evaluation Methods and Design

Due to the closure of this plant only an initial visit was made (July 16-18, 1974). A walk-through survey of the plant was followed by review of the OSHA Log, and a review of the records of all men on sick leave, on the disabled list, retired, or known to be dead. Sixty-seven workers were interviewed utilizing a standard non-directed questionnaire (Appendix A) which also asked for some work history. Physical examination was limited to inspection of skin lesions and auscultation of the chest when indicated. Additional medical information was obtained by talking to one of the physicians who had been treating the men and review of a dermatologic study conducted by Robert F. Bill, M.D., a year earlier at the request of the company. It was decided to talk to all the shift workers who were working (3 of the 4 shifts). Because of the number of workers involved, it was decided to interview only half of the maintenance staff. Table I details the work force and the sample interviewed. Table II gives average ages and length of service by departments. All workers interviewed were men.

Although no environmental samples were taken at the time of the initial visit, OSHA had sampled in the recent past and the reduction furnace area was under citation to correct an excessive level of hydrogen chloride.

C. Evaluation Criteria

1. Environmental

The primary source of environmental criteria considered in this report is the U.S. Department of Labor/OSHA in its Occupational Exposure Standards (29 CFR Part 1910.1000).

Substance	8-Hour Time Weighted Average Exposure Standard
Zirconium	5.0 mg/m^3 (a)
Hafnium	0.5 mg/m^3
Ammonia	50 ppm(b)
Chlorine	1 ppm
Hydrogen chloride	5 ppm
Methyl isobutyl ketone (MIBK)	100 ppm

(a) Denotes milligrams of substance per cubic meter of air.
(b) Denotes parts of substance per million parts of air.

2. Medical

The relationship between worker complaints and employment was deduced primarily from the histories as obtained from the workers, supplemented by other sources of medical information and personal observation.

Methyl isobutyl ketone[2] is narcotic and irritating to the eyes and nose. Repeated or prolonged skin contact can cause defatting of the skin and dermatitis. Ammonia,[3] chlorine gas,[4] and hydrogen chloride gas[5] are known irritants of the eyes, nose, throat and lungs. Solutions and high concentrations of the gases are irritating and destructive to the skin, particularly moist skin. Chlorine gas is a little less irritating locally than the other gases and so is more likely to be breathed in sufficient amounts to cause lung irritation.

Zirconium granulomas have received publicity recently regarding the use of zirconium complexes in aerosol antiperspirants. Sodium zirconium lactate and zirconium oxide can both cause epitheliod cell granulomas of the skin as a result of an allergic or hypersensitivity mechanism. Further, in a sensitized individual other zirconium complexes could also produce this effect. In the hearings conducted by the Food and Drug Administration[6] on the use of zirconium in antiperspirants, the concern was with granulomas in the lungs, although there are no reported cases of this having occurred.

All zirconium in commercial use except that used by the Atomic Energy Commission contains 2% hafnium.[7] It is extremely likely, therefore, that the zirconium granulomas reported in the literature were caused by a mixture of 98% zirconium and 2% hafnium. There is a possibility that hafnium and zirconium have different potentials for causing granulomas. Other than causing granulomas, zirconium has not been felt to be particularly toxic.[8] Less is known about hafnium but chemically it reacts similarly to zirconium. It is reported to be somewhat more toxic.[9]

D. Evaluation Results and Discussion

1. Environmental

Although no environmental evaluation was conducted by NIOSH some information was available from other agencies regarding environmental conditions present in the plant. Air samples collected by the U.S. Department of Labor/OSHA indicated that worker exposures to zirconium were within the present Federal limit of 5 mg/m^3. An evaluation for hydrogen chloride (HCl) also conducted by OSHA indicated excessive HCl exposures in the area of the reduction furnace. At the time of the NIOSH visit measures were being instituted to correct conditions cited by OSHA.

2. Medical

Of the 67 workers interviewed, 91% indicated one or more complaints possibly associated with the work environment. By history, on questioning about ever having an occupationally related problem, major complaints were dermatitis - 47 (63%); irritation of eyes, nose, throat or sinuses - 20 (30%); and breathing problems - 13 (19%). Table III details these complaints.

(a) The dermatitis problem was noted through all sections of the plant, and appears to be a complex of several problems as described below.

(1) The bulk of the workers (31) complained of a rash which usually was said to itch. This characteristically came on first as little papules although some described vesiculation or blisters "like poison ivy;" it involved several parts of the body. Twelve complained of problems with their scalp particularly along the line of the hat band. In a few there was primary flakiness of the scalp. Nine complained of rash on unexposed parts of the body, sometimes characterized as heat rash. The groin area was most often involved (four of this latter group were maintenance workers).

If the dermatitis was extensive, the fumes were usually said to irritate the dermatitis. The skin conditions usually improved when the workers spent some time away from the plant. Often the less extensive dermatitis occurred only on occasion and was not troublesome much of the time.

(2) One worker in Separations and two current workers and one ex-worker in Sponge production complained of the fumes (primarily hydrogen chloride) irritating their faces when freshly shaved. Several wore beards to avoid shaving.

(3) One worker complained of general acne, one of acne localized to where his bakelite goggles rested and one of pimples on his legs.

(4) Six workers had complaints which either were one time occurrences, or involved some particular product or set of circumstances apparently unrelated to the major chemical process.

In March, 1973, Robert F. Bell, M.D., Acting Head of the Division of Industrial Medicine, University of Colorado Medical Center made a preliminary study of this problem. He had a preliminary questionnaire filled out on each employee with a 91% completion rate. Of the 110 questionnaires completed, 34 cases of dermatitis (31%) were identified and of these he was able to examine 17. Of these 34 cases, 24 (22% of 110 responding) appeared to him to be occupationally related. Maintenance Department and Sponge Department were worst with Sponge Handling and General Services and Laboratory showing almost no dermatitis. He believed about half of the Separations Department's dermatitis was not occupationally related. Separations had the highest rate for total dermatitis (52%).

Classifying the dermatitis he believed to be occupational:

12 were from chlorine or zircle (zirconium tetrachloride) burns
3 were from solvent exposure
2 were from Fiberglass exposure
1 was from ammonia exposure
1 was from zirconium oxide exposure
1 was possibly from zirconium metal exposure

More recently, some of the men had been seen by a local doctor. The skin testing in his reports is not readily interpretable as no concentrations are given and several of the reactions appear to have been primary irritation reactions at well above the irritancy threshold. Further, the testing with the zirconium tetrachloride suggests either the strength was changed or the material was allowed to react with moist air and degrade to zirconyl chloride ($ZrOCl_2$).

(b) History of symptoms of irritation of the eyes and upper respiratory tract were reported from three of the four production departments. Complaints were:

(1) Separations - seven out of 14 workers - the exposure here was primarily to a mixture of ammonia and solvents. Respirators were usually worn when the workers felt the "fumes" were really bad without them.

(2) Sponge Production - five out of 11 workers - symptoms were believed due to the fumes from the furnaces (primarily hydrogen chloride gas). Respirators were not always effective in preventing symptoms.

(3) Sponge Handling - four out of 12 workers - two of these workers believed their symptoms were due to emissions from the furnaces in sponge production. The other two related their symptoms to dust and dryness.

(4) Chlorination - The operators were not complaining of problems but stated that they kept their respirators handy in case of need.

During the walk-through survey some eye and nose irritation was noted by the NIOSH investigators in several areas of the plant. One was around the reduction furnaces in Sponge Production (the area under citation by OSHA). Exhaust ventilation was being installed at the time. Another area was in the vicinity of zirconium tetrachloride storage. The workers related that the zirconium tetrachloride was irritating both on breathing "fumes" and on skin contact. The NIOSH investigators were readily able to confirm that emanation from the zirconium tetrachloride irritated the eyes, nose and throat by taking the lid off a drum of the tetrachloride. The irritation is probably due to the zirconium tetrachloride's tendency to readily react with the moisture in the air to form zirconyl chloride ($ZrOCl_2$) and give off hydrogen chloride.[7]

(c) History of Breathing Problems - These are extremely hard to evaluate. Thirteen (19%) out of the 67 workers had complaints involving their breathing.

(1) Four workers had minimal symptoms. One was a two pack a day smoker who had accumulated about 36 pack-years of smoking. He complained of a feeling of lead weight about his waist first thing in the morning. This was worse in air conditioning. Another was an ex-smoker who said that quitting smoking cleared up his problems. One worker, another ex-smoker, had only a minimal cough

but complained that his breathing test showed he had 45% of normal breathing capacity. The fourth worker said the magnesium (chloride) in the dry room bothered his breathing some.

(2) Two workers had had myocardial infarctions in the past. Both had been two pack per day smokers. One who was on daily bronchodilators, said his pulmonary function tests were only 48% of normal, but had no particular symptoms. The other reported considerable problems on exposure to ammonia or chlorine gas, that he could not wear a respirator continuously, and that he had attacks of angina for which he took nitroglycerine. His difficulty breathing had been building up over the past three years, but did improve when away from the plant.

(3) Four workers complained of some shortness of breath. All were smokers or ex-smokers but not particularly heavy smokers.

(4) Three workers complained of difficulty when wearing a respirator - one had had a "bad" overexposure to chlorine gas in the past; one noticed this difficulty when shoveling hafnium oxide (dusty); and one complained if there was heavy exposure to chlorine gas and gave a history of black sputum when working in the now closed carbide department.

Three of the four workers with a history of minimal symptoms were in the Maintenance Unit. If we eliminate these workers with minimal symptoms from further consideration, the overall incidence of breathing problems would be 9 of 67 (13%) for the total group and four out of 17 (24%) for the Maintenance Unit.

Of the 10 men complaining of respiratory problems for whom a smoking history was obtained all were smokers or ex-smokers. It appears that when the men were being seen by one of the private doctors for dermatitis, most received routine pulmonary function tests. In all, seven men who had had pulmonary function testing were interviewed. The average Forced Vital Capacity (FVC) for these seven men was 79% of predicted, the average Forced Expiratory Volume in one second (FEV_1) was 82% of predicted, but the Maximum Voluntary Ventilation (MVV) was only 59% of predicted. Of these seven, two had no pulmonary complaints, an average FVC of 81%, average FEV_1 of 78% and an average MVV of 55%, and on the average had smoked an equivalent of 36 pack-years of cigarettes. Of the remaining five, on one a smoking history is lacking (FVC 99% of predicted, FEV_1 95% and MVV 61%). Of the other four, all were or had been at least 1 pack per day smokers. The one with worst functions (FVC 56%, FEV_1 63%, MVV 48%) had a myocardial infarction

three years before this study, stopped his 2 pack per day smoking for about 8 months, but was again smoking one pack per day. The other three had an average FVC of 79%, FEV_1 of 94% and MVV of 57% of predicted.

According to Breathing by Areud Bouhuys[10] the MVV is not a particularly useful test except for following an individual in therapy. Also, recent articles on pulmonary function standards have not made reference to it.

Because pulmonary functioning is affected by age, sex, race, and height, it is the usual practice to predict the individual's functions using formulas (or tables developed from these formulas) which allow for these factors. The actual values are then compared to the predicted values. For FVC and FEV_1 it is generally accepted that anything over 80% of the predicted value is normal. For other tests, the extent of normal variation from the predicted value is not well established, but is large. Cigarette smoking is a well known cause of decreased pulmonary functioning.

(d) Review of sick leave and ex-workers. Review of sick leave showed that five workers were on sick leave and one on total and permanent disability. This latter was a maintenance worker, had had a heart condition and reportedly had had a couple of bad overexposures to chlorine gas. Of the five workers on temporary sick leave, four were from the Maintenance Unit. There was no consistancy to the causes of illness.

Of those no longer working for the company, there had been one retiree since 1968. Four long-term workers had quit to work elsewhere, one reportedly because of a dermatitis problem caused by the solvents.

Six workers were known to be dead. Three were said to be from leukema. One was a young man who worked only about a year in the Sponge Handling Unit. Of the other two, one was in the Production area and the other was not in the Production area. One worker was said to have lung cancer, and another cancer of an unspecified site. The last worker had an unspecified lung problem. Again, there was no consistancy to the causes.

E. Conclusions

There was a dermatitis problem at the time of this evaluation. This is based on medical history obtained both from the workers and review of other medical studies. Additionally, some of the workers had active lesions at the time of the NIOSH visit. It is not firmly established whether this represented zirconium

granulomas (or hafnium granulomas), or direct irritancy, or both. It appears that the hydrogen chloride levels in the atmosphere at least aggravated other skin lesions and that zirconium tetrachloride was irritating on contact with moist skin.

The atmosphere, particularly in the vicinity of the reduction furnaces and in the zirconium tetrachloride storage area was irritating to the eyes, nose and moist skin. This is based on medical histories and direct observation by the NIOSH investigators.

The majority of the pulmonary problems other than irritancy were probably not job-related. This is suggested by the normal or near normal FVC's and FEV_1's, the smoking histories and the other medical histories.

V. RECOMMENDATIONS

As the plant is no longer in operation, no environmental recommendations are appropriate.

Medically it is suggested that workers with alleged breathing problems seek further elucidation of their pulmonary function studies.

Other problems, if job-related, have probably already cleared up and require no further follow-up.

VI. REFERENCES

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VII. AUTHORSHIP AND ACKNOWLEDGEMENTS

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TABLE I
CHARACTERIZATION OF WORK FORCE

Amax Specialty Metals
Parkersburg, W.Va.
July 16-18, 1974

A. Shift Workers
(There were four shifts scheduled so that 3 shifts cover the 24 hours of the day and one shift is completely off on any given day.)

	TOTAL WORKERS INTERVIEWED		TYPICAL SHIFT		TOTAL WORK FORCE	
Separations Unit						
Feed Makeup Operator	3		1			
Feed Makeup Assist.	1					
Filter Operator	3		1			
Filter Assistant	3		1			
Tower Operator	2		1			
Tower Assistant	3		1			
Total		14		5		
Chlorination-Briquetting Unit						
Chlorination Operators		6		3		
Sponge Production Unit						
Sponge Prod. Operators	6		2			
Sponge Prod. Assist.	5		2			
Total		11		4		
Sponge Handling Unit						
Sponge Handling Operators	9		3			
Sponge Handling Assist.	3		2			
Total		12		5		
Maintenance Unit						
Shift Mechanic		2		1		
Total Shift Workers		45		18		72

B. Day Shift Workers

Chlorination-Briq. Unit						
Pelletizing Operators		2			2	
General Services						
Storeroom Clerks		2			2	
Maintenance Unit						
Mechanical	8			9		
Facility(Carpentry)	2			2		
Inst. Electricians	1			4		
Painters	1			3		
Welders	3			5		
Total		15			23	
Utility (Cleanup)						
Utility Workers		3			4	
Total Day Shift		22				31
Total Production and Main.		67				103
Laboratory & Office						11
Supervisory & Professional						28
				Total Work Force		142

TABLE II
EMPLOYEES INTERVIEWED BY AGE AND LENGTH OF SERVICE

Amax Specialty Metals
Parkersburg, W.Va.
July 16-18, 1974

	TOTAL	SEPARATION	CHLORINA-TION	SPONGE PRODUCTION	SPONGE HANDLING	MAINTEN.	OTHER
Age:							
Average	37.4	31.9	34.8	33.5	40.0	45.0	33.2
Median	35	33.5	31.5	33	40.5	42	30
Range	20-63	20-48	27-54	26-48	26-55	27-63	25-54
Years with Company:							
Average	8.2	5.9	8.6	6.1	8.1	12.0	5.4
Median	8	5.25	9	7	8	14	7
Range	1 1/2m-	1 1/2m-	4m-17y	3m-17y	1y-17y	4y-18y	2y-8y
Total Seen	67	14	8	11	12	17	5

TABLE III
REPORTED SYMPTOMATOLOGY

Amax Specialty Metals
Parkersburg, W.Va.
July 16-18, 1974

SYMPTOMS	TOTAL		SEPARATION		CHLORINA-TION		SPONGE PRODUCTION		SPONGE HANDLING		MAINTEN.		OTHER	
	#	%	#	%	#	%	#	%	#	%	#	%	#	%
A. Possible Job related:														
Dermatitis	42	63	10	71	2	25	6	55	7	58	14	82	3	60
Irritation of upper respiratory tract	20	30	7	50	2	25	5	45	4	33	1	6	1	20
Breathing Problems	13	19	0	0	0	0	1	9	2	17	7	41	3	60
Cough	5	7	1	7	0	0	2	18	0	0	1	6	1	20
Hearing Problems	2	3	1	7	0	0	0	0	1	8	0	0	0	0
Chest Pains	3	4	0	0	0	0	2	18	0	0	0	0	1	20
Heart Problems	3	4	0	0	0	0	0	0	0	0	1	6	2	40
Hypertension	6	9	1	7	0	0	0	0	2	17	1	6	2	40
Dizziness	3	4	0	0	0	0	0	0	2	17	1	6	0	0
Abdominal Complaints	8	12	0	0	0	0	3	27	2	17	3	18	0	0
Other	9	13	3	21	1	12	1	9	1	8	3	18	0	0
Total With Possible Job-Related Problems	56	84	13	93	5	62	10	91	9	75	15	88	4	80
B. Non-Job Related Problems	13	19	2	14	0	0	0	0	5	42	4	24	2	20
C. Total With No Complaints	6	9	1	7	3	38	1	9	1	8	0	0	0	0
TOTAL SEEN	67		14		8		11		12		17		5	

APPENDIX A

RHHE No. _____
Date _____

HEALTH HAZARD EVALUATION INITIAL SURVEY
EMPLOYEE INTERVIEW
(Confidential)

1. Ask the workers being interviewed if they have any health problems. If they say no, obtain only their name, job title, age and sex. If they say yes, fill out the complete form.

2. Employee Name _____
(First) (Middle) (Last)
Job Title _____ Shift _____
Description of Work Duties _____
Address _____
(Street) (City/State/Zip Code)
Age_____ Sex _____ Telephone _____

3. Occupational Work History (Include Present Job):

Company	Job Description	Dates Start	Dates End

4. Do you have any health problems at work or you feel might be related to your work? If so, list symptoms, describe how and when they occur, when they go away, and how long you have had them? What do you think they are caused by:

_____
_____
_____
_____

5. Do you have any other health problems? If so, list symptoms, describe how and when they occur, when they go away, and how long you have had them. What do you think they are caused by?

_____
_____
_____

6. Attempt to find out about workers who are absent because of sickness and have been discharged or transferred to other areas for health reasons, and workers who are deceased. For these workers attempt to find out diagnoses, symptoms, when they became ill and suspected relationship to work, if any. Suggested sources: (a) other workers, (b) union officials, (e) company officials (optional), (d) personnel records (personnel turnover, transfers, etc.) and (e) OSHA records, (f) plant medical personnel.
*Use reverse side for additional space if needed.