HEALTH HAZARD EVALUATION REPORT 71-27-59

HAZARD EVALUATION SERVICES BRANCH

DIVISION OF TECHNICAL SERVICES

Establishment : Penn Rare Metals Division
Kawecki Berylco Industries, Inc.
Revere, Pennsylvania

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

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PENN RARE METALS DIVISION
KAWECKI BERYLCO INDUSTRIES, INC.
REVERE, PENNSYLVANIA 18953

JULY 1973

I. SUMMARY DETERMINATION

A. 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 Penn Rare Metals, an employer, regarding exposure to cesium and rubidium compounds.

Cesium and rubidium metals and salts are extracted from pollucite (cesium aluminum silicate) and alkarb (crude rubidium carbonate). Cesium and rubidium salts are prepared from the respective hydroxides by reaction with the appropriate acid.

New industrial uses of cesium and rubidium compounds indicate a much larger demand for these compounds of unknown toxicity and prompted the employer to determine the inherent health hazards before engaging in large scale production. Management was also concerned with the possible toxic effects upon an expanded consumer population.

Little is known regarding the human response of exposures to cesium and rubidium metals or compounds. Physiological experiments indicate the exchangeability of cesium and rubidium for potassium in blood, plasma and tissue, but it cannot be assumed that compounds of these elements are completely nontoxic.

The hydroxides of all the alkali metals are strongly alkaline and extremely caustic. Cesium hydroxide, in theory, because of its position in the Group IA series of the periodic chart of elements, should be the strongest of all alkalis. Therefore, direct skin or eye contact must be avoided to prevent chemical burns. None of the various cesium or rubidium salts are known sensitizers. Lethal dose studies on animals with various halogen salts indicate a low order of oral toxicity. However, the hydroxides, as expected, are considerably more toxic when ingested and necropsy studies demonstrate hemorrhage and adhesions of abdominal organs characteristic of strongly caustic substances.

Air samples collected in the breathing zone of three operators at work on two different days indicate that exposure to both cesium and rubidium is minimal. Workers presently are exposed to less than one milligram of cesium per cubic meter of air when averaged over a period of eight hours. Exposure to rubidium is even less averaging one fifteenth that of cesium.

Medical evaluations of four employees, three of whom work full-time in the processing area, the fourth part-time, were conducted and biological specimens, blood and urine, collected. The samples were assayed for cesium, rubidium, sodium and potassium in the blood (erythrocytes and plasma) and urine. The latter two elements were studied because of their chemical and physiological similarity to the elements of primary interest.

Chronic toxicity data are not available, but review of the medical and toxicological literature suggest that both elements have very low degrees of toxicity.

The biological sample test results, while somewhat inconsistent, did not indicate a measurable up-take of these elements although some differences between the four subjects and the control group were noted. It is concluded that no evidence was found by clinical, biological and environmental studies that cesium and rubidium compounds as used or found constituted a hazard to the health of the employees.

Copies of this Summary Determination are available from the Hazard Evaluation Services Branch, NIOSH. Copies have been sent to:

a) Penn Rare Metals Division, Kawecki Berylco Industries, Inc.

b) U. S. Department of Labor - Region III

c) Occupational Health Program, Pennsylvania Department of Environmental Resources.

For purposes of informing "affected employees," the employer will promptly "post" the Summary Determination in a prominent place near where affected employees work for a period of 30 calendar days.

II. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 699 (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 concentration as used or found.

The National Institute for Occupational Safety and Health received such a request from an employer, Penn Rare Metals, Division of Kawecki Berylco Industries, Inc., relative to exposure to cesium and rubidium hydroxides in the production of the pure metals and compounds in the Revere, Pennsylvania processing plant.

This company specializes in the production of pure, rare metals and their compounds largely carbonates, hydroxides and halogen salts. Metals processed are cesium, rubidium, germanium, tellurium, columbium as well as high purity aluminum and ferro-nickel alloys. However, this report is concerned only with the production of cesium and rubidium metals and compounds as carried out in a building physically separated from the rest of the plant and with little or no interchange of labor between processing areas.

Twenty people, including management personnel, are employed in the plant. Only three full time and one part time worker are employed in cesium and rubidium processing. The process is more fully described in Section IV A of this report.

III. BACKGROUND INFORMATION

A. Standards

Little is known concerning the human response to cesium and rubidium. Consequently, no standards for exposure exist. This fact prompted the request for Health Hazard Evaluation.

B. Physiologic Aspects

The physiologic similarity between potassium and its chemically similar relatives, rubidium and cesium, was first noted nearly a century ago. While the effects of cesium are like those of potassium in many respects, the similarity between rubidium and potassium is generally much closer. Numerous investigations have since confirmed this general pattern which has been demonstrated for a wide variety of biochemical and physiologic processes.

The distribution in the body of naturally occurring rubidium resembles that of potassium with both elements being found in relatively high concentrations in red cells, muscle, and viscera, with much less in bone and plasma. No data are apparently available on the distribution of cesium, but tracer doses of radioactive cessium demonstrate a similar pattern.

Animal feeding experiments with rubidium have demonstrated that rubidium and potassium are nearly interchangeable and rubidium is capable of substituting for potassium as an essential nutrient. Cesium can be also substituted for potassium but in a more limited way. For example, potassium depleted animals develop characteristic kidney, skeletal, and cardiac lesions, but the addition of rubidium or cesium to the diet will prevent or rapidly cure these changes.

Much early work has indicated that animal tissue are capable of accumulating large amounts of rubidium or cesium. In fact, muscle tissue may accumulate rubidium up to concentrations 20-60% higher than those of potassium. Similarly, rat skeletal muscle accumulates cesium in preference to potassium. Experiments have shown that in intact animals muscle tissue, red cells, and most viscera are capable of accumulating these ions against tissue-plasma concentration gradients equal to or greater than those existing for potassium. Both elements are excreted in the urine, probably via the same mechanism (tubular secretion) as potassium. The feces and sweat have also been shown to contain minute amounts of rubidium following test doses. In general, the renal clearance of rubidium is slightly less than potassium (85%) while that of cesium is approximately half that of potassium. Administered doses of cesium and rubidium are both excreted very slowly. Thus, ribidium has a biologic half-life of approximately 34 (21-50) days for plasma. In blood, rubidium establishes an equilibrium between red cells and plasma. Approximately one hour after an oral dose of rubidium red blood cell levels are three times plasma levels, but by 24 hours a final partition of 20.1 (cell/plasma) has occurred.

Nearly all the foregoing physiologic data supports the concept that there is slight preferential accumulation of both rubidium and cesium. Normal tissue and body fluid levels therefore can be expected to reflect largely dietary intake which should vary regionally with variations in soil concentrations, dietary habits, etc. Analysis of appropriate tissues (red blood cells) and body fluids (plasma, urine) should therefore be capable of easily identifying individuals who have experienced significant absorption from non-dietary sources in comparison with "normal" control specimens.

C. Toxicity

Despite the above data demonstrating the exchangeability of rubidium and cesium for potassium in physiologic experiments, it cannot be assumed that compounds of these elements are completely non-toxic. The hydroxides of all the alkali metals are strong alkalis and extremely caustic. In theory, CsOH should be the strongest of all alkalis. Therefore, direct skin or eye contact must be avoided to prevent chemical burns. None of the various rubidium or cesium salts are known to be sensitizers. LD_{50} studies on rats with various halogen salts all exceed 1 gm/kg indicating a low order or oral toxicity. As might be expected, the hydroxides are considerably more toxic when ingested and necropsy studies demonstrate hemorrhage and adhesions of the abdominal organs characteristic of strongly caustic substances.

Human response to cesium and rubidium compounds is still largely unknown and a matter of speculation. However, limited data and animal studies indicate a lower order of acute toxicity.

Chronic toxicity data are not available, but review of the medical and toxicological literature suggest that both elements have very low degrees of toxicity.

IV. HEALTH HAZARD EVALUATION

A. Initial Visit

1. An initial observational, environmental and medical evaluation survey of the Penn Rare Metals Division of the Kawecki Berylco Industries, Inc., Revere, Pennsylvania was conducted on October 21, 1972 by NIOSH personnel Albert A. Maier, Kenyon Rupnik and James B. Lucas, M.D. The functions of the National Institute for Occupational Safety and Health and its relation to Section 20(a)(6) of the Occupational Safety and Health Act of 1970 were explained to Messrs. [redacted], Jr., Plant Manager and [redacted], Administrative Manager. The National Surveillance Part I Questionnaire Form was completed with their assistance.

2. Cesium is extracted from the ore, pollucite, a cesium aluminum silicate (Cs_2O. Al_2O . $4SiO_2$). Ore is received in truck load lots of 4 or 5 tons every two years. It is then ground to 200 mesh size, then digested in sulfuric acid to form Cs-Al sulfate. The cesium aluminum sulfate is purified by fractional crystallization after which sodium hydroxide is added to adjust the pH, followed by ammoniation with NH3 gas. Barium hydroxide is added after filtration to form cesium hydroxide which is then concentrated. The hydroxide is used as raw material for the salts which are prepared by the reaction with the appropriate acid.

3. Rubidium is extracted from Alkarb--a mixture of alkaline metal carbonates--a by product of lithium production. It is reacted with tartaric acid then separated as the tartrate. The tartrate is then burned off in a small electric oven leaving the pure carbonate from which the pure metal and salts are prepared.

4. Acid reduction is carried out in a one story cinder block building approximately 32' x 42' in seven open, heated and agitated tanks holding 250-300 gallons. Six filter crocks are located near the tanks. All tanks are under a canopy hood which provides fairly good ventilation.

5. Purified salt production is carried out in a separate room from the raw production area. This room which occupies one end of the building approximately 28' x 32' is essentially a chemistry laboratory. Here are found laboratory benches, ovens, one ventilated laboratory hood and the usual laboratory equipment. Various acids are used to convert the hydroxides to the desired salts; the iodide being the most commonly produced.

6. Employee exposure during ore extraction is minimal. There is no reason for operators to work near the tanks and the tanks are ventilated. The operators devote most of their time adjusting pH, making titrimetric calculations and performing other process control procedures.

7. Salt purification is simple and relatively non-hazardous. Salts are washed, filtered and evaporated to dryness in laboratory glassware after which it is placed in ovens for complete dehydration. It is then dumped into fiber drums and removed to the storeroom. Most evaporating is done under a laboratory fume hood. Dust respirators and gloves are worn while handling the dried salts.

B. Environmental Evaluation

1. Sampling Methods: Four personal air samples were collected on October 31, 1972 and eight on January 9, 1973 which were analyzed in the Cincinnati laboratory for cesium and rubidium. These breathing zone samples were collected in midget impingers containing 15 milliliters of 5% nitric acid solution. They were obtained by attaching the holster containing the impingers to the collar of the operator and by the use of tygon tubing connected to the vacuum pump attached to the waist by a belt. Air was sampled at a rate of two liters per minute for at least 25 minutes to a maximum of 2 hours.

2. Analytical Methods: A suitable aliquot was analyzed in the Cincinnati laboratory by atomic absorption spectrophotometry using a nitrous oxide - acetylene flame.

3. Results: The concentration of cesium varied from a minimum of 0.07 to a maximum of 0.7 mg/M^3. However, only two samples were above 0.2 mg/M3. Rubidium compounds were lower and ranged from 0.004 to 0.04 mg/M^3. Results are found in Table IV.

4. Conclusions: Air samples indicate that exposure to cesium compounds was quite low and rubidium exposure was negligible. However, it was found the greatest exposure does not occur while working in the main processing area, but occurred in the laboratory where the final purification, i.e., re-crystallization, drying, and packaging take place. Several operations, principally re-crystallization, are not routinely performed under the laboratory hood. Obviously, the exposure could be reduced and virtually eliminated by using the hood, which is adequate if the window is closed since the average velocity of 75 feet per minute was obtained across the entire six-foot opening when the window was opened 14-1/2inches. Another hood and make-up air supply for the laboratory would be feasible.

C. Medical Evaluation

1. Procedure: All four employees with exposure to cesium-rubidium production and salt manufacture were examined and interviewed. All were totally asymptomatic and exhibited no obvious relevant abnormalities. There was no history of ill health or mental aberrations. One individual had noted eye and nasal irritation when a vial breaks and the metal oxidizes in the air. A second individual had noted occasional skin burns due to direct contact with CsOH.

Blood and urine specimens were obtained from these four workers and from four similarly aged men for control purposes. These specimens were returned to Cincinnati and analyzed for Cs, Rb, Na, and K. Separate analyses were carried out on the plasma and red blood cell components of the blood. It was felt that should appreciable absorption be occurring, it should be demonstrable by these studies.

2. Results and Discussion: The data from these assays is presented in Tables I, II and III. This data must be interpreted in the light of the small numbers involved, the lack of published values for cesium in biologic fluids, differing methods of assay, and the well known large biologic individual variation in urinary excretion. For statistical purposes, subject means and variances were compared with those for the control groups using Student's t test (one tailed).

Table I data pertains to erythrocyte levels which correspond to the intracellular milieu. Cesium levels were actually higher in the control group than in the exposed subjects, although not significantly (P=.67). Rubidium levels were significantly higher (P=.00035) than in the controls suggesting absorption and accumulation. However, the subject levels are closer to the normal values reported in the literature (4.18 ± .62 and 5.32 ug/gm) than the controls and the differences may be due to regional dietary variation. In any event, the levels are far below those at which significant physiologic alterations might be expected since at least 50% of intracellular potassium can be safely replaced by rubidium. Neither the sodium or potassium values differed significantly between the two groups with P values of .61 and .95 being found, respectively. The potassium mean value is considerably below those reported in the literature (3.62, 3.70 and 3.84) and the sodium level considerable above the .20-.27mg. sodium levels previously reported. Also contrary to previous reports, tissue (erythrocyte) levels for cesium exceed rubidium in absolute amounts.

While there is considerable range in the cesium plasma levels (Table II) and particularly among the exposed worker group, no significant difference was found (P=.079). The worker with the highest value for plasma cesium reported that he spent only 50% of his time in the Cs-Rb work areas. Plasma rubidium levels do not differ between the groups (P=.14) but the means are considerably above those in the literature (.16 and .53-1.80), a difference perhaps due to analytic methods of dietary intake. Plasma sodium does not vary between the groups (P=.85) and corresponds fairly well to the "Normal" values in the literature (2.83 and 3.06-3.29). Potassium levels do vary between the groups (P=.009), being significantly less in the exposed population This suggests that cesium or rubidium may be displacing plasma potassium especially since the levels of these ions are higher, although not significantly higher, in the exposed group. The values for potassium are also noted to be generally lower than previously reported (.13-.19,.16±.016, and .10).

It is well established that rubidium (and pre umably cesium) compartmentalize between serum and red blood cells after equilibrium is reached. The reported ratio is 20:1 (cells/plasma). Our data reveals a nearly equal distribution (4.45:3.38). While this is a slight preponderance intracellularly, this data is substantially inconsistent with previous studies. The inconsistency is even more marked for cesium where the plasma levels are nearly double erythrocyte levels. As was noted with the erythrocyte levels, the absolute amounts of cesium exceed that of rubidium, an unanticipated result, since rubidium is the far more common element in biologic materials.

Inspection of Table III reveals two sets of values for each of subjects 1-4. The second set (in parenthesis) are the results obtained from a second urine collection made January 9, 1973. This was felt to be necessary since inspection of the original data revealed a very wide range of values for both cesium and rubidium among the subjects when compared with the control mean and range. This suggested possible laboratory error, calculation error or contamination. While the range on the repeat specimens is much smaller, the values differ substantially from the controls. This would seem to be due to a lack of reproducibility in the laboratory procedure. In any event, the repeat values are much lower than in the controls suggesting a lack of excessive absorption. Nearly all the rubidium values far exceed those reported in the literature.

The levels of both sodium and potassium are highly variable in the urine of normal subjects and largely reflect the loss of these ions resulting from dietary intake in excess of metabolic needs. While some small loss of sodium is obligatory this situation is rarely met within normal subjects receiving ordinary diets. Both sodium (P=.002) and potassium (P=.045) were significantly less in the original subject urines than in the controls. Values on the repeat specimens while still lower than the controls were not significantly so. The values tended to be lower than for reported "normals" for sodium (5-15) while the potassium values for the subjects, both original and repeat, resembled the "normal" of 1.91± .58 mg/ml. Control potassium levels were well above this "normal" level.

3. Summary: Four employees with variable exposure to cesium and rubidium metals and salts were interviewed and examined to ascertain any health problems associated with their exposure to these substances. Biologic samples were obtained to assess possible absorption of these substances. These tests included assays for cesium, rubidium, sodium, and potassium performed upon erthyrocytes, plasma, and urine. The latter two elements were studied because of their chemical and physiologic similarity to the elements of primary interest.

4. Conclusions: No evidence suggesting a medical hazard was encountered during the course of the investigation. Reviews of the medical and toxicological literature suggest that both elements have very low degrees of toxicity. While chronic toxicity data are not available, it seems unlikely that such exposure would be deleterious for man barring exceedingly high prolonged levels of exposure. Biologic sampling did not indicate definite measurable absorption of either cesium or rubidium although differences between subjects and control groups were occasionally noted. These differences are markedly inconsistent and do not conform to patterns which would suggest absorption or the likelihood of altered physiologic composition.

D. Conclusion

It has been determined by environmental and medical evaluations that exposure to the substances cesium and rubidium and their salts is minor and all exposed employees were asymptomatic. Assays to assess the possible absorption of these substances were made of erythrocytes, plasma and urine with negative results. Hence, it is our determination that the employees show no ill effects from exposure to these substances in their working environment.

V. RECOMMENDATIONS

This health hazard evaluation proved that present conditions are satifactory to prevent overexposure to cesium, rubidium and their compounds. Since expansion and modernization or rehabilitation of plant facilities is contemplated, several recommendations are being made to further reduce exposure of personnel.

1. Provide another laboratory hood and/or rehabilitate the existing hood. Facilities should be of sufficient capacity to permit all boiling, evaporation or drying to be done under a laboratory hood having a face velocity of 100 feet per minute. Tempered make-up air to replace the air exhausted by the hood(s) is strongly recommended.

2. The present canopy hood(s) are poorly designed. Details for efficient canopy hoods may be found in "Industrial Ventilation" - a manual of recommended practice, 11th edition or later by American Conference of Governmental Industrial Hygienists, Committee on Industrial Ventilation, P.O. Box 543, Lansing, Michigan 48902.

   a. Consideration should be given to enclosing the back of the tanks (and perhaps even two sides - leaving the front open) if the use of the canopy hood is continued.

   b. Tempered make-up air to replace the air removed by the exhaust ventilation system should be installed.

3. The use of closed vessels on reactors which are heated, agitated and pressurized (positive or negative) should be considered. A closed system would streamline the operation, reduce the corrosive action of acid and other aqueous vapors and virtually eliminate exposure of employees to hazardous substances.

4. Effluent discharged to the atmosphere should be scrubbed or cleaned to remove the contaminants prior to discharge.

5. The use of approved dust respirators and impervious gloves should be continued while transferring the dried salts from the drying oven to storage containers. Respirators, face shields, aprons, and gloves should be available and worn during any exposure to acids, bases, ammonia and acetic acid vapors.

TABLE I

ERYTHROCYTE LEVELS

SUBJECT NO.	Cs ug/gm	Rb ug/gm	Na mg/gm	K mg/gm
1	6.80	4.73	1.98	2.82
2	6.94	5.04	0.97	2.19
3	6.63	4.87	1.10	2.98
4	6.59	5.14	1.29	2.14
Average	6.74	4.95	1.34	2.53
CONTROLS NO.				
5	6.92	3.88	1.23	1.73
6	6.29	3.61	1.43	2.13
7	9.00	4.02	1.12	1.90
8	6.00	4.23	1.28	2.35
Average	7.05	3.94	1.27	2.03
Reported Values		4.18±.62	.20	3.70
		5.32	.27	3.84
				3.62
Probability of Difference Between Groups	.6686	.00035	.6126	.9531

TABLE II

PLASMA LEVELS

SUBJECT NO.	Cs ug/gm	Rb ug/gm	Na mg/gm	K mg/gm
1	20.33	3.80	2.63	1.04
2	13.42	3.13	2.80	0.90
3	10.98	3.25	2.56	1.01
4	14.38	4.16	2.51	1.10
Average	14.78	3.59	2.63	1.01
CONTROLS NO.				
5	10.65	3.26	2.01	1.10
6	11.46	3.71	2.38	1.27
7	13.02	3.26	2.76	1.22
8	10.68	2.47	2.56	1.17
Average	11.45	3.18	2.54	1.19
Reported Values		0.16 .53-1.80	3.06-3.29 2.83	.13-.19 .16±.016 .10
Probability of Difference Between Groups	.0789	.1447	.34	.0093

TABLE III

URINE LEVELS

SUBJECT NO.	Cs ug/ml	Rb ug/ml	Na mg/ml	K mg/ml
1	4.39 (2.7)*	1.39 (2.6)*	0.70 ().77)*	1.08 (1.81)*
2	162.74 (5.2)	298.18 (5.3)	0.41 (3.03)	0.36 (3.04)
3	6.43 (5.7)	1.57 (7.0)	2.07 (3.70)	1.66 (3.91)
4	1.36 (7.0)	71.87 (8.4)	3.66 (2.70)	4.44 (3.04)
Average	43.73 (5.15)	93.25 (5.53)	1.71 (2.55)	1.89 (2.95)
CONTROLS NO.				
5	12.62	54.27	6.18	3.42
6	17.43	47.41	5.52	3.58
7	16.97	40.30	4.72	3.70
8	17.85	57.34	5.07	4.20
Average	16.22	49.83	5.3725	3.73
Reported Values		1.52±0.55	5-15	1910ug/ml±580
Probability of Difference Between Groups (original analysis)			.00198	.0445

* Results of second specimen collection.

Table IV

Personal Air Samples

No.	Date	Location		Cs mg/M^3	Rb mg/M^3
1	10/31/72	Lab. & Process	-RR	0.14	0.038
2	10/31/72	Laboratory	-GS	0.17	0.008
3	10/31/72	Process Dept.	-CS	0.083	0.025
4	10/31/72	Laboratory	-GS	0.18	0.004
5	1/9/73	Process Dept.	-CS	0.10	0.008
6	1/9/73	Lab. & Process	-RR	0.661	0.010
7	1/9/73	Laboratory	-GS	0.069	0.011
8	1/9/73	Process Dept.	-CS	0.230	0.006
9	1/9/73	Laboratory	-GS	0.068	0.012
10	1/9/73	Lab. & Process	-RR	0.195	0.008
11	1/9/73	Laboratory	-GS	0.072	0.017
12	1/9/73	Process Dept.	-CS	0.16	0.013
			Average	0.177	0.013
				Range	
			Min.	0.068	0.004
			Max.	0.661	0.038