THE **CARBORUNDUM** COMPANY DOCKET NO. 40-5001

THE CARBORUNDUM METALS COMPANY DIVISION
P. O. BOX 22 · AKRON, NEW YORK

May 3, 1960

DOCKETED USAEC MAY 5 1960 Division of Licensing & Regulation Docket Office

Mr. J. C. Delaney
Chief, Nuclear Materials Section
Licensing Branch
Division of Licensing and Regulation
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Mr. Delaney:

We have your letter of April 27, 1960 and the temporary license which has been issued to allow us to continue with our evaluation program. We are naturally disappointed in not receiving a full term license at this time.

A few comments are thought to be in order on the dust control problem as associated with the carbiding of Nigerian ore. Prior to the initial run, and therefore before we had data upon which to act, very little was done to the carbide furnace and associated equipment. As data developed, much effort was expended to control the openings in the furnace hood. These efforts have been continuous and are still in effect, although we have made no carbide runs involving Nigerian ore since January 20. Since we have had data on the radioactive level of dust produced in this operation, a hood was designed and fabricated which has effected a considerable reduction in fume level from the car pulling operation, that is, where the carbide is removed from the shell. This is illustrated in the enclosed pictures.

Figure I is of the old system where the shell is lifted from the stationary base. Unreacted mix is shown falling away from the base with a build-up of a dust cloud. Figure 2 shows the operation at the same stage with the new hood being used. Little or no fume escapes from under the hood. Figure 3 shows one of the workmen raking old mix from the carbide pigs standing at the left. Note the high level of dust produced during this operation before the hood was installed. Figure 4 shows a close-up of this same operation with the hood in place. (Please note the air sample being taken during this operation.) You will note that little or no dust fume is escaping from the hood. These pictures are thought to be typical of the careful approach which is being used throughout all phases of the processing of this ore. You can be assured that all areas of concern will be worked over until we are confident that no radioactive hazard exists.

In reference to your other comment, the final radiation survey program which will be conducted in the carbide area has not been completely delineated as of this writing. The measurements which were recommended by Dr. Whipple in his March 10, 1960 report will be carried out during the next carbide run, after which Dr. Whipple will evolve what is thought to be necessary for the final established radiation survey program.

A/17

2/16/273

I am enclosing two copies of a memorandum report issued by Dr. Whipple and his associates on the radiological survey which was conducted during the chlorination of Nigerian ore. [We will be interested in your comments on this report.] You will note that under Section 8, "Conclusions and Recommendations", a tentative radiation survey program has been outlined. This is the program which will be used during future Nigerian ore chlorination runs or until further data indicates changes should be made.

Routine changes which will be introduced in the chlorination process will further reduce the radiation level in all areas. These changes will include better ventilation in critical areas, the use of closed hoppers for carbide feed to the chlorinators, and the use of larger size receivers which will be opened only once every two or three shifts.

Data so far obtained on the further processing of zirconium tetrachloride at Akron, where the liquid-liquid extraction step is currently being run, indicates that air concentrations are very low. As soon as this data is complete and evaluated a report will be issued.

[We would appreciate receiving several additional copies of the 10 CFR 20 regulations concerning radioactive hazards.]

Very truly yours,

THE CARBORUNDUM METALS COMPANY

D. R. Spink

D. R. Spink, Assistant to Manager
Technical Branch

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180

Enclosures

M E M O R A N D U M

April 20, 1960

TO: Dr. D. R. Spink
Carborundum Metals Co.
Akron, New York

FROM: R. J. Augustine, D. E. Barber and G. Hoyt Whipple
University of Michigan
Ann Arbor, Michigan

SUBJECT: Report of the Radiological Survey of the Chlorination Process, March 18 to April 7, 1960.

This report is divided into the following sections.

1. Introduction
2. Instrumentation
3. Air and Water Samples
4. Gamma Measurements
5. License Requirements
6. Transport of Zirconium Tetrachloride
7. Occupancy Factors
8. Conclusions and Recommendations
9. References

A/16

1. INTRODUCTION

The information provided herein is based on a visit to the Parkersburg plant on March 25, 1960 and subsequent sampling data provided by plant personnel.

The gamma spectrum of the $ZrCl_4$ sample (Fig. 1) obtained at the plant on March 25 proved to be very similar to that of the ore (8). Accordingly, sample data have been analyzed in the same manner described in our report on carbiding operations (1).

A comparison of Fig. 1 with the spectra obtained from ore samples provides an estimate of thorium activity in the $ZrCl_4$ assuming that the daughter products are in equilibrium with the thorium. Using the values provided by reference (2) and the comparison of the spectra, we estimate the percentage of thorium in the $ZrCl_4$ obtained from Kennecott ore to be from 0.6 to 1.2 percent. This is in surprisingly good agreement with your value of approximately 1% thorium based on chemical analysis of the $ZrCl_4$ from Kennecott ore (3). Similarly, estimates of percent thorium in $ZrCl_4$ from London Tin ore based on gamma spectra are 0.8% to 1.6%.

No information has been obtained as yet during bed residue pulling operations.

2. INSTRUMENTATION

Gamma radiation measurements were made with a Jordan ionization chamber meter owned by the company. There was an obvious rattle in the chamber of this instrument which resulted in erratic meter movements. It was returned to the manufacturer for repair following its use on March 25, 1960 to make the measurements tabulated in Table 2.

Malfunctioning of the NMC proportional counter made much of the data taken over the period of this report unusable. The number of samples tabulated in Table 1 is therefore small compared to the number actually taken.

3. AIR AND WATER SAMPLES

A summary of the sample data is given in Table 1. From the data it is clear that the operations of concern are the feeding of the chlorinator with carbide and the changing of the $ZrCl_4$ drums at the base of the condenser.

The activity in the plant sewer outfall at the river is puzzling in view of the activity found in the scrubber water effluent. However, the scrubber effluent value is based on only one sample and its average concentration may be higher than indicated. Furthermore, 100 ml water samples give relatively low count rates which may result in a higher percentage error. Higher volume (1000 ml) water samples should be taken.

No analysis has been made of river water samples since it is felt that they should be taken in a manner different from that which has thus far been used. Consideration must be given to the flow rate and current distributions in the river in order to know when and where to take samples which will be representative of the river. Samples should be taken sufficiently far down stream, in the main stream of the river, not at the bank, to take full advantage of mixing of the plant sewer outfall with river water. One needs also to be aware of potential settling basins in the river between the plant sewer outfall and sampling points. Samples taken upstream from the plant sewer outfall may be taken just above the outfall, provided there are no back eddies, in the main stream of the river.

Table 1.--Summary of Sample Data.

Location	Type of Sample	Operation	Average μc/ml	Highest μc/ml	Lowest μc/ml	No. of Samples	Average/MPC
3rd Floor	Air	Feeding Chlorinator "A"	9.9×10^{-10}	2.5×10^{-9}	3.9×10^{-11}	3	2.0
3rd Floor	Air	General	$< 2.6 \times 10^{-12}$	9.4×10^{-11}	$< 2.8 \times 10^{-13}$	11	< 0.05
2nd Floor	Air	Sponge Production	$< 1.6 \times 10^{-13}$	2.5×10^{-13}	$< 7.4 \times 10^{-14}$	6	< 0.003
2nd Floor	Air	General	$< 4.5 \times 10^{-12}$	2.5×10^{-11}	$< 2.4 \times 10^{-13}$	5	< 0.09
1st Floor	Air	General	2.1×10^{-12}	6.2×10^{-12}	2.8×10^{-13}	7	0.042
1st Floor	Air	$ZrCl_4$ Drum Pulling	2.4×10^{-10}	1.8×10^{-9}	4.5×10^{-13}	9	4.8
Outside Plant Fence	Air	General	$< 3.9 \times 10^{-13}$	1.8×10^{-12}	3.2×10^{-14}	7	0.23
Scrubber Effluent	Water	General	4.5×10^{-9}	4.5×10^{-9}	4.5×10^{-9}	1	0.09
Plant Effluent to River	Water	General	3.4×10^{-8}	8.2×10^{-8}	7.5×10^{-9}	6	0.68

The concentration of activity in the plant sewer outfall is what must be compared to the MPC however, and sampling there should be continued.

4. GAMMA MEASUREMENTS

Although some difficulty was encountered in obtaining the values given in Table 2 due to instrument malfunction, the values are believed to be reasonably reliable.

Table 2.--Gamma Measurements.

Location		Max. mr/hr.
55 gal. drums filled with $ZrCl_4$ (26 drums in all)		0.75
"A" Chlorinator:	1st floor	0.20
	2nd floor	0.15
	3rd floor	0.07
"A" Condenser:	1st floor	1.0
	2nd floor	0.50
	3rd floor	0.15
Sweepings,	2nd floor	0.10
NaOH Scrubber	2nd floor	0.20
H_2O Scrubber	2nd floor	0.20

Water accumulation from rainfall made it impractical to take measurements at the scrubber on the roof on March 25. The air concentrations and gamma levels observed inside the building made it seem unnecessary to make measurements at the scrubber on the roof.

The values presented in Table 2 indicate that there is no gamma radiation hazard associated with the chlorination process. Furthermore, the levels as of March 25, 1960 do not warrant film badge monitoring in this process. The extent to which the build up of bed residues will increase the gamma exposure remains to be determined.

5. LICENSE REQUIREMENTS

Contrary to expectation, the thorium content of the $ZrCl_4$ is not sufficiently low to exempt the $ZrCl_4$ from the licensing requirements of reference (4). The thorium content is about four times the exemption limit given by 10CFR40, Section 40.60 (f) which provides for exemption from the licensing requirement of "Rare earth metals and compounds, mixtures and products containing not more than 0.25% by weight thorium, uranium or any combination of these."

If a license for the $ZrCl_4$ is required under the provisions of 10CFR40 then compliance with the provisions of reference (5) is automatically required. This means that hazard evaluations similar to those accomplished at Parkersburg will have to be carried out at the Akron plant where the $ZrCl_4$ is to be handled.

6. TRANSPORT OF ZIRCONIUM TETRACHLORIDE

Interstate Commerce Commission Regulations govern the transport of radioactive materials by common and private carrier (6). The regulations which apply to motor freight are essentially the same as those which apply to rail freight save for the labelling of the vehicle.

At 1% thorium each pound of $ZrCl_4$ will contain approximately 1 μc of thorium (1). Since each 55 gal. drum holds approximately 300 lb. of $ZrCl_4$ (3) each 55 gal. will contain approximately 300 μc of thorium activity. Consequently, each drum is exempt from the labelling requirements of 10CFR20. If containers were used which held 500 lb. or more $ZrCl_4$ each container would have to be labelled in accordance with paragraph 20.203 (f).

A 55 gal. drum of $ZrCl_4$ does not meet the labelling exemption requirements of the ICC regulations (6) since each container must yield an exposure dose at its surface of not greater than 0.4 mr/hr. The drums must, therefore, be labelled with a Class D Poison label as described in paragraph 73.414 in the regulations (6). Mr. Chapman has already been provided with a copy of the required label and is aware of the need to have these printed locally. There is no commercial source for these labels.

Paragraph 73.394 of the regulations (6) provides that, "If the nature of the radioactive content cannot be appropriately designated by entering a single radioisotope or radioelement, it may be described as 'Chemical NOS' (i.e., chemical, not otherwise specified)." We suggest that this notation be used on the Class D poison labels used on $ZrCl_4$ drums.

The label also calls for the activity of the contents and the number of "Radiation Units" from the package. The activity will be equal to the number of pounds $ZrCl_4$ in μc units. For example, 300 lbs. of $ZrCl_4$ is 300 μc of activity. A "Radiation Unit" is 1 mr/hr. at one meter from the surface of the drum. This will have to be determined by actual measurement with the Jordan meter. Note that no more than 40 "Radiation Units" per truckload is permitted.

The truck must be labelled in accordance with provisions of para. 77.823 (a)(3) which states, "Every motor vehicle transporting any quantity of radioactive material, Class D poison, requiring red radioactive materials label must be marked or placarded 'DANGEROUS-RADIOACTIVE MATERIALS' on each side and rear with a placard or lettering in letters not less than 3 inches high on a contrasting background."

Labels must be removed from empty containers and the carrier or consigner of empty containers should be advised that the containers have contained radioactive materials.

The 55 gal. drum meets the packaging requirements provided it is filled such that there will be "no significant radioactive surface contamination of any part of the container" (6). From para. 74.566 (ref.6), which described permissible contamination limits for vehicles, "no significant radioactive surface contamination" is taken to mean less than 500 disintegrations per 100 sq. cm. surface area.

Accidents involving leakage of $ZrCl_4$ from the container must be reported promptly to the Bureau of Explosives (7).

It is emphasized that the foregoing statements apply to shipments by either private or common carrier unless exemption has been obtained in writing from the Bureau of Explosives (7).

7. OCCUPANCY FACTORS

If the $ZrCl_4$ drum under the condenser must be changed 6 times per shift and each change takes a maximum of 5 minutes, men will be exposed to the high air concentrations produced by this operation a maximum of 30 minutes per day (3). Such a situation should allow application of an occupancy factor of 0.5/8 to the Avg/MPC value given in Table 1. Exposures in the long run will, therefore, be well below the MPC even without consideration being given to the protection provided by the chemical cartridge respirators worn during this operation.

A similar argument applies to the operation of feeding the chlorinator with carbide. Since this operation is accomplished usually only once per shift and takes a maximum of 10 minutes (3) the factor

(1/6)/8 is applicable to the Avg/MPC value given in Table 1 for this operation, which reduces that value well below one.

8. <u>CONCLUSIONS AND RECOMMENDATIONS</u>

a) Air concentrations are sufficiently low to warrant a reduction in the air sampling schedule. The following schedule is recommended.

1) One air sample every 24 hours during chlorinator loading operations.
2) One air sample every 24 hours during $ZrCl_4$ drum changing operations.
3) One air sample every 48 hours from off the plant property, preferably down wind of the stack. When the continuous samplers are set up and in operation, use of the high volume air samples for off site air sample collection may be discontinued. The use of the continuous samplers will provide two samples every 24 hours.
4) Two air samples during any "bed pulling" operation.
5) One water sample from the plant sewer outfall at the river every 48 hours. The time of day at which the sample is taken should be varied from sample to sample.
6) One water sample from the chlorination scrubber every 48 hours.

b) Higher volume water samples should be taken. Each water sample should have a volume of at least 1000 ml.

c) Gamma measurements indicate that film badge monitoring, during the chlorination process is unnecessary.

d) If it is desired that water samples be taken from the river, samples should be taken in the main stream of the river and at least tw: miles down stream of the plant effluent.

e) To insure that operations with the $ZrCl_4$ at the Akron plant comply with the provisions of 10CFR20 a hazard evaluation should be accomplished there similar to that performed at the Parkersburg plant.

f) High air concentrations during the $ZrCl_4$ drum pulling operation suggest that the outside of the drums will very likely be contaminated. Pieces of filter paper should be rubbed lightly over 100 cm^2 of the drum, outside surface and the resultant "smear" counted in the NMC counter, with the voltage set at the beta plateau level, to determine the dpm/100 cm^2. Greater than 500 dpm per 100 cm^2 (approximately 250 cpm on your instrument) will require either cleaning of the outside of the drums or modification of the drum filling and changing method to reduce surface contamination. If contamination above this level is found the latter course would probably be the better of the two inasmuch as it would also very likely reduce air concentrations during the drum changing operations.

g) The use of protective clothing and respirators should be continued for $ZrCl_4$ drum pulling and chlorinator loading operations until such time as method modification provides lower air concentrations during these operations. This will probably also be true of the bed residue pulling operation.

h) All things considered the chlorination process at the present time does not constitute a radiological hazard to either plant personnel or the public outside the plant provided the few precautions mentioned herein are followed.

i) This report does not cover all operations involved in the chlorination process. Data from the bed residue pulling operation remains to be collected and analyzed.

R. J. Augustine

Donald E. Barber

G. Hoyt Whipple

9. **REFERENCES**

1. Memo dated March 10, 1960 to D. R. Spink from R. J. Augustine, D. E. Barber and G. Hoyt Whipple; Subject: "Report of Radiological Survey of the Operations at the Parkersburg Plant, January 6 to February 19, 1960."
2. Memo dated November 16, 1959 from D. R. Spink to L. B. Hoskins; Subject: "Handling, Storage and Processing of Nigerian Ore at Parkersburg."
3. Telephone conversation, D. R. Spink and D. E. Barber, April 18, 1960.
4. Title 10, Code of Federal Regulations, Part 40, "Control of Source Material" as amended January 1, 1954.
5. Title 10, Code of Federal Regulations, Part 20, "Standards for Protection Against Radiation," Federal Register, Vol. 22, No. 19, January 29, 1957.
6. "Handbook of Federal Regulations Applying to Transportation of Radioactive Materials," AEC Division of Construction and Supply Traffic Management Section, July 1955 (Available from U. S. Government Printing Office, Washington 25, D. C.).
7. Bureau of Explosives, 30 Vesey Street, New York 7, New York.
8. Memo dated March 21, 1960, to D. R. Spink from R. J. Augustine and G. Hoyt Whipple; Subject: "Gamma Spectrum Analysis."