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STABILITY STUDIES OF HIGHLY RADIOACTIVE ALUMINA CALCINE
DURING HIGH TEMPERATURE STORAGE

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IN NUCLEAR SCIENCE ABSTRACTS

M. W. Wilding and D. W. Rhodes

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A B S T R A C T

Stability of highly radioactive alumina calcine from the Waste Calcining Facility was studied in a temperature range from 600°C to 1200°C. Strontium-90 and cerium-144 were not volatile. Cesium-137, ruthenium-106, boron, mercury, and nitrate were volatile to some degree over this temperature range. The alumina produced in the WCF was amorphous but converted to alpha alumina at 800°C and higher temperatures.

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I. SUMMARY

Laboratory studies were made of the stability of highly radioactive alumina calcine from the Waste Calcining Facility (WCF) in a temperature range from 600°C to 1200°C in 24-hour tests and at 800°C for one year. Volatility measurements were made, and the distribution of the volatile components along a temperature profile was determined after a 14-day heating period.

Strontium-90 and cerium-144 did not volatilize at temperatures up to 1200°C, which is in agreement with earlier data obtained with non-radioactive materials(1). Volatilization of cesium-137 and ruthenium-106 was first detectable at 800°C, and that of boron at 1000°C; mercury and nitrate were volatile at 600°C, and since this was the lowest temperature used, they probably also volatilize at lower temperatures. X-ray diffraction patterns of the calcine showed that the amorphous alumina produced in the WCF converted to alpha alumina (the stable, high-temperature, acid-insoluble form of alumina) above 1000°C in the 24-hour tests, with increasing alpha formation as the temperature was increased. Gamma alumina was the only crystalline component detected in the 24-hour test at 800°C, but in the one-year experiment at 800°C the major crystalline component was alpha alumina indicating that although the transition is slow at this temperature, alpha alumina is the final crystalline end product(2).

Storage of the alumina calcine at temperatures under 400°C -- as was done with the initial WCF solids storage bins -- now appears to be unnecessarily conservative. On the basis of the results obtained in this study, second-generation storage bins are being designed for maximum (centerline) temperatures of 700°C, and further studies are expected to show that this temperature limitation can be significantly increased in the future.

II. INTRODUCTION

Highly radioactive calcine produced in the WCF at the Idaho Chemical Processing Plant (ICPP) has to date been stored in stainless steel bins designed to prevent the centerline temperature from exceeding 400°C ^(3,4). This temperature is also the calcination temperature, so waste constituents that are volatile at 400°C presumably have been volatilized prior to storage. However, if a centerline temperature appreciably higher than 400°C can be tolerated, a significant saving can be made in the cost of storage bin construction.

The desirability of using a centerline temperature greater than 400°C in the storage bins for the WCF calcine necessitated an investigation of the volatility and migration of the fission products and other minor constituents in the calcine. The calcine currently in storage was produced from highly radioactive waste solutions resulting from the reprocessing of aluminum-uranium alloy fuel elements. The solid calcine is a mixture of alumina, fission product oxides or nitrates, small amounts of undecomposed aluminum and sodium nitrates and small quantities of mercury, boron, and water.

III. WASTE COMPOSITION

The radioactive and non-radioactive composition of the calcine varies with the age and chemical composition of the precursor liquid waste. The calcine used in this experiment was produced from waste stored in tank WM-187 with an approximate age after discharge from the reactor of 6.5 years. A batch of this calcine was collected in a remote sampler, transferred to a stainless steel container, and mixed thoroughly to assure homogeneity of the calcine for the experimental work. Table I shows the results of an analysis of this material for radioactive and non-radioactive minor constituents.

IV. EXPERIMENTAL EQUIPMENT

A high temperature (1800°C maximum) combustion tube furnace was used to heat the calcine in these experiments. The heating section itself was an impervious alumina sheath 1-inch ID and 17 inches long with a built-in thermocouple for automatic temperature control. The WCF calcine samples were placed in one of two alumina tubes shown in Figure 1; the tubes were then inserted into the furnace and heated. Tube A was used for simple volatility tests at various temperatures while tube B was used for migration tests. Both tubes (A and B) were 7/8-inch OD and 18 inches long with flat bottoms. Tube A had four 1/8-inch holes spaced equidistant around the tube and up 1/8-inch from the bottom and a 1/4-inch hole centered in the bottom, while tube B was a solid tube without air holes. Smaller (3/8-inch OD) alumina tubes, 6-inches or 1 1/2-inches long respectively, were fitted inside the large tubes to hold

Table I

MINOR CONSTITUENTS IN WCF CALCINE

<u>Radioactive</u>	<u>Non-Radioactive</u>	<u>December 1964 Concentration</u>
Ce ¹⁴⁴		5.49×10^{10} d/min-g
Cs ¹³⁷		2.31×10^{10} d/min-g
Cs ¹³⁴		1.40×10^9 d/min-g
Ru ¹⁰⁶		3.03×10^9 d/min-g
Sr ⁹⁰		1.79×10^{10} d/min-g
	B	1.3 mg/g
	Hg	20 mg/g
	HNO ₃	~ 50 mg/g

the radioactive calcine. In a separate small combustion tube furnace, a sample of calcine was heated for one year to measure the long-term effect of heating.

V. VOLATILITY AND MIGRATION EXPERIMENTS

A temperature profile for subsequent experiments was established by filling tube B with non-radioactive alumina calcine and taking readings by placing a thermocouple at various positions in the heated column. Two types of experiments were then conducted: the first was designed to measure the loss of minor constituents (volatility) from a small sample at a given temperature; the second was to determine the extent of migration of these minor constituents through calcine along a temperature profile.

Fig. 1 Alumina tubes used in high temperature furnace

1. Volatility Measurements

In the volatility experiments, two grams of WCF calcine were placed in the small alumina sample tube (Figure 1-A). A thermocouple was inserted into the center of the sample, and the tube was then lowered into the long tube and placed so that the sample was in the hottest position in the furnace. A slight vacuum was pulled on the tube to create a mild flow of air past the sample, thence out through two caustic scrubbers (4.0M NaOH) connected in series. Individual samples were heated at 600°, 700°, 800°, 900°, 1000°, 1100°, and 1200°C for 24 hours. In the one-year volatility study, WCF calcine was placed in a small alumina sample tube similar to the one shown in Figure 1-B, but in this test there was no air flow past the sample and no scrubbers were used. This sample was maintained continuously at 800°C. The solid calcine in both experiments was analyzed before and after heating. In the 24-hour tests, the alumina tubes were washed with hot 4.0M nitric acid after heating; the results of analyses of these washes and of the scrubbing solutions, as well as a correction factor to account for residual activity on the alumina tube, were used to obtain a material balance.

2. Migration Measurements

In the migration experiment, two grams of WCF calcine were placed in the small alumina tube (Figure 1-B). A thermocouple was placed in the calcine, and the tube containing the calcine and thermocouple was placed in the bottom of the long alumina tube. Sixteen inches of non-radioactive calcine similar in composition to the WCF alumina calcine product were then added to cover the radioactive sample. The tubes were open to the atmosphere during heating. The radioactive calcine, which was positioned in the hottest zone of the furnace, was maintained at 800°C for fourteen days. Figure 1-B shows the temperature profile that existed during this experiment. After heating, samples of the originally non-radioactive calcine were removed pneumatically from the tubes in one-inch layers, and transferred to sample bottles for analysis.

VI. RESULTS

The percent volatility of the minor constituents that had detectable volatility at temperatures from 600° to 1200°C during 24-hour, 6-month, and 12-month heating periods is shown in Figures 2, 3, and 4. The distribution of the minor constituents that migrated into the non-radioactive calcine column during the fourteen-day experiment and were detected at various levels along the temperature profile in the calcine are shown in Figure 5. Volatility measurements were made only on the radioactive and non-radioactive constituents that might appreciably affect the storage of calcined alumina. The results of the different experiments are in reasonably good agreement and are summarized in the following numerical listing.

Fig. 2 Volatility of mercury and boron from WCF alumina calcine in a 24-hour test

Fig. 3 Volatility of cesium from WCF alumina calcine during 24-hour heating

Fig. 4 Volatility of cesium and ruthenium at 800°C from WCF alumina calcine

Fig. 5 Distribution of constituents volatilized at 800°C and condensed in an alumina-filled column with a decreasing temperature profile

1. Cerium-144 did not volatilize from WCF calcine at any of the temperatures studied (600°-1200°C).
2. Cesium-137 appeared to be slightly volatile at 800°C and became increasingly more volatile as the temperature increased (Figure 3); however, the volatilized cesium condensed prior to reaching the 600°C zone (Figure 5). Approximately 85 percent of the cesium volatilized at 800°C in one year (Figure 4), indicating that, while cesium is only slowly volatile at this temperature, nearly all the cesium migrates at a sustained temperature of 800°C.
3. Ruthenium-106 appeared to be only slightly volatile (< 1 percent) after two weeks of heating at 800°C; it condensed in the 650°C to 400°C zone (Figure 5). In the one-year experiment at 800°C, approximately 99 percent of the ruthenium volatilized (Figure 4). Apparently the reaction which produced volatile ruthenium has a low rate constant, but given sufficient time, migration from an 800°C or higher temperature to a colder zone will continue until essentially complete transfer occurs.
4. Strontium-90 did not volatilize from WCF calcine at any of the temperatures studied.
5. Boron volatilization was first detected at about 1000°C. The one-year and the 24-hour experiments at 800°C did not indicate significant volatility.
6. Mercury was volatile at 600°C in all experiments, becoming increasingly more volatile as the temperature increased, and condensing in the zone below 600°C (Figures 2 and 5).
7. Nitrate was essentially all volatilized at about 600°C. The amount of residual nitrate in the calcine increased as the temperature decreased from 600°C to 100°C in the non-radioactive material used in the fourteen-day test. Some volatilization of nitrate undoubtedly occurred at all temperatures above the calcination temperature (400°C).
8. X-ray diffraction analysis of the heated calcine indicated that the originally amorphous alumina was converted to the crystalline species beta, gamma, or alpha alumina⁽²⁾ during heating. Gamma alumina was the major crystalline constituent after 24 hours of heating at 700°, 800°, and 900°C. At 1000°C there was a minor amount of alpha alumina present, and at 1100°C and 1200°C approximately 15 percent beta alumina and over 50 percent alpha alumina were present. In the long-term experiment, in which the calcine was maintained at 800°C for 12 months, approximately 50 percent of the alumina was in the alpha form.

VII. CONCLUSIONS

Strontium and cerium do not volatilize from calcined wastes stored at temperatures up to 1200°C. Cesium and ruthenium, however, will migrate from a hot zone (800°C or higher) to a colder zone. Since the migration of any heat generating radioactive fission products to colder zones flattens the temperature profile of the stored calcine and lowers the centerline temperature, this will eventually result in a stable situation. A cold zone always exists at the outer edge of each bin due to cooling by air flow with either forced or natural convection. The design of the new WCF solid storage bins limits the initial centerline temperature to 700°C, and hence only moderate long-term migration of cesium-137 and ruthenium-106 is expected. Further studies are expected to show that even this centerline temperature can be increased significantly in the future.

Mercury and nitrate will migrate from the 700°C zone to a colder zone; however, the ultimate distribution and chemical form of these minor constituents along a temperature profile during long-term storage has not been established. Additional experiments are planned to study this problem. In addition, amorphous alumina stored at 800°C (and possibly at lower temperatures) for a long time will convert to the alpha crystalline form; this may increase slightly the thermal conductivity of the stored calcine, as indicated by an extrapolation of experimental data by Kelly⁽⁵⁾ and may also increase the absolute density of the calcined alumina product^(6,7).

New storage bins have been designed and are currently under construction for storing calcined product at a centerline temperature of 700°C⁽⁸⁾. The experimental data obtained in this study were used as a basis for the design and indicate that storage of solid product at this temperature will not create any problems because of migration of fission products.

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