LEACHING PROPERTIES AND CHEMICAL COMPOSITIONS OF CALCINES PRODUCED AT THE IDAHO CHEMICAL PROCESSING PLANT

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Since 1963, radioactive calcine has been routinely produced from highly radioactive liquid waste resulting from the reprocessing of nuclear fuel at the Idaho Chemical Processing Plant (ICPP). After production in the Waste Calcination Facility (WCF) the calcine is stored in stainless steel bins contained within concrete vaults. This method of storage was selected on the assumption that disposal at the ICPP would be permanent. It has now been decided that radioactive waste would not be permanently stored at ICPP and demonstrated that calcine is not suitable for long-term storage. Calcines stored at ICPP will be retrieved and converted to solid forms more suitable for long-term storage. Thus, before equipment and procedures could be developed for calcine retrieval a sample recovery program was performed to determine the properties of stored calcine.

Storage bins 3 and 7 in the Second Calcined Solids Storage Facility were selected as candidates for sampling.[1] Bin 3 was filled with aluminum fuel waste (alumina calcine) and Bin 7 was filled with zirconia fuel waste (zirconia calcine).[2,3] The samples from each bin were combined to give three composites for analysis. Thus, a composite of the deepest nine samples represented the material in the bottom third of each bin (3B and 7B), the composite of the middle ten samples represented the material in the middle third of each bin (3M and 7M), and the composite of the top nine samples represented the material in the top third of each bin (3T and 7T).

Based on the results of the analyses for physical properties it was concluded that the calcine can be pneumatically removed from the storage bins. These analyses

also indicate that the investigated physical properties of the retrieved calcine are not significantly different from those of product calcine.

Chemical Analyses

Tables I and II summarize the determinations of major chemical species in retrieved alumina and zirconia calcine composites. In most cases the ranges of values determined for the major constituents of retrieved zirconia calcine samples are similar to those determined for product zirconia calcine. The differences in ranges of values for major constituents in retrieved alumina calcine and those for WCF alumina calcine produced in the 2nd campaign reflect chemical changes in liquid wastes being calcined.

TABLE I. MAJOR CONSTITUENTS OF RETRIEVED ALUMINA CALCINE, WT%

Sample	Al	Na	NO_3
3T	35.53	3.1	6.87
3M	35.93	2.0	5.14
3B	39.75	1.7	5.70
WCF 2nd & 3rd Campaign Products	40-48	0.9-1.5	2.0

TABLE II. MAJOR CONSTITUENTS OF RETRIEVED ZIROCNIA CALCINE, WT%

Sample	Al	Ca	Zr	F
7T	7.53	25.49	16.87	20.1
7M	7.63	29.14	17.52	20.3
7B	7.62	27.86	17.74	21.1
WCF 4th Campaign Product	7.0-9.9	30.1-33.5	15.7-17.4	7.8-23.4

X-ray diffraction analyses were performed on both fines (<US Standard No. 140 mesh) and coarser (>US Standard No. 140 mesh) sample materials. The major crystalline and amorphous components are the same in all composites of retrieved calcines as are presente in alumina and zirconia product calcines. The minor components vary slightly, reflecting the presence of the bed startup material, dolomite, or in the case of alumina calcine, α-alumina.

Tables III and IV present the data obtained from the radiochemical determinations on the retrieved calcine samples. The fission products and their concentration in stored calcine depend on the fuel processed as well as on the age of the calcine. Thus, radionuclide content at the time of production is not readily available. The determination of transuranics are of importance to determine currently unknown quantities of these elements in stored calcine.

TABLE III. RADIOACHEMICAL ANALYSIS OF RETRIEVED ALUMINA CALCINE

Sample	Sr^{90}* µg/g	γ-Scan* isotope	µg/g	Uranium mass µg/g	isotopic %		Transuranics nuclide	µg/g
3T	38.0	Co-60	0.093	59.83	234	5.0	Pu-238	0.10
		Cs-134	0.085		235	65.00	Pu-239	2.96
		Cs-137	73.5		236	6.7	Pu-240	0.32
		Eu-154	0.095		238	23.3	Pu-241	0.03
							Pu-242	0.01
							Np-237	5.2
							Am-241	0.09
3M	40.5	Cs-134	0.004	53.16	234	1.1	Pu-238	0.10
		Cs-137	73.5		235	69.4	Pu-239	2.98
		Eu-154	0.133		236	3.7	Pu-240	0.32
		Eu-155	0.0014		238	25.8	Pu-241	0.03
							Pu-242	0.01
							Np-237	5.9
							Am-241	0.09
3B	32.7	Cs-134	0.094	37.82	234	3.3	Pu-238	0.10
		Cs-137	60.0		235	67.1	Pu-239	2.33
		Eu-154	0.094		236	5.0	Pu-240	0.27
					238	24.2	Pu-241	0.02
							Pu-242	0.006
							Np-237	4.0
							Am-241	0.11

*Fission products determined on 9/15/78

TABLE IV. RADIOCHEMICAL ANALYSIS OF RETRIEVED ZIRCONIA CALCINE

Sample	Sr^{90}* μg/g	γ-Scan* isotope	γ-Scan* μg/g	Uranium mass μg/g	Uranium isotopic %		Transuranics nuclide	Transuranics μg/g
7T	13.2	Co-60	0.002	51.11	234	3.4	Pu-238	1.11
		Cs-134	0.027		235	68.9	Pu-239	3.89
		Cs-137	21.7		236	6.0	Pu-240	0.98
		Eu-154	0.137		238	21.7	Pu-241	0.26
		Eu-155	0.0006				Pu-242	0.13
							Np-237	1.3
							Am-241	0.32
7M	17.5	Co-60	0.003	13.20	234	6.8	Pu-238	.85
		Cs-134	0.040		235	59.8	Pu-239	3.38
		Cs-137	22.5		236	6.7	Pu-240	0.96
		Eu-154	0.185		238	26.7	Pu-241	0.29
		Eu-155	0.0009				Pu-242	0.17
		Sb-125	0.019				Np-237	1.1
							Am-241	0.24
7B	15.0	Co-60	0.001	23.36	234	3.9	Pu-238	1.00
		Cs-134	0.003		235	62.9	Pu-239	3.26
		Cs-137	22.4		236	6.5	Pu-240	0.87
		Eu-154	0.054		238	26.6	Pu-241	0.35
		Eu-155	0.0010				Pu-242	0.15
							Np-237	.93
							Am-241	0.15

* Fission products determined on 9/15/78

Leaching Studies

In two earlier studies the leaching of radionuclides and chemical species from alumina and zirconia calcines by distilled water was investigated.[4,5] These studies were undertaken to characterize the leachability of these calcines for comparison to other solid waste forms. Because product calcines are highly radioactive both studies were performed remotely.

Radioactive product alumina and zirconia calcine from the WCF was used for the radionuclide leaching experiments. At the start of the leaching tests, each gram of alumina calcine contained 26 mCi of cerium-144, 10.5 mCi of cesium-137, 7.6 mCi of strontium-90, 1.4 mCi of ruthenium-106, and lesser amounts of other fission products. The radionuclides present in the zirconia calcine included cesium-137 (2.1 mCi/g),

strontium-90 (1.5 mCi/g), ruthenium 106 (0.03 mCi/g), cerium-144 (1.0 mCi/g), and plutonium-239 (0.005 mCi/g). Nonradioactive alumina and zirconia calcine from experimental calciners was used to determine the leachability of chemical constituents.

A pyrex glass apparatus was used for the leaching studies. This apparatus consistad of a fritted glass filter to hold the calcine, a large reservoir to receive the leachate, and an air lift to recirculate the leaching solution from the reservoir back to the fritted glass funnel containing the calcine. Using this apparatus, distilled water was passed continuously through the calcine at a rate of about 100 mL per minute for time intervals varying from one to 620 hours. At the end of each leaching period all of the solution was siphoned from the equipment, an aliquot was removed for analysis, and fresh distilled water was added for the next run.

Test conditions for both experiments with alumina and zirconia calcine are given in Table V.

TABLE V. TEST CONDITIONS FOR LEACHING ALUMINA AND ZIRCONIA CALCINE SAMPLES

Calcine Sample Wt.	20 grams
Leachate	Distilled H_2O
Leachate Volume	500 mL
Leachate Flow	100 mL/min
Leachate Temperature	25°C

Because of their relatively high concentrations in the calcines the leaching characteristics of fission products cesium and strontium was of major importance in these studies. For both calcines cesium and strontium were leached at rapid initial rates with that for cesium being more than twice the rate for strontium (Figures 1 and 2). With time, however, the leaching rates of cesium and strontium from both calcines became about equal. After 2000 hours about 95 percent of the cesium and 33 percent of the strontium leached from the alumina calcine. In this same time nearly 60 percent of the cesium and 33 percent of the strontium leached from the zirconia calcine. Leaching rates of cerium and ruthenium fission products

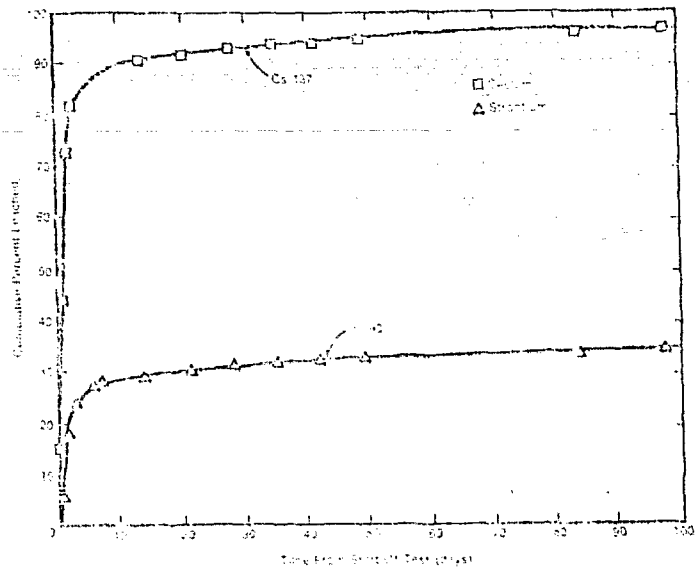

FIGURE 1. TOTAL PERCENT OF CESIUM AND STRONTIUM LEACHED FROM ALUMINA CALCINE WITH DISTILLED WATER AT 25°C

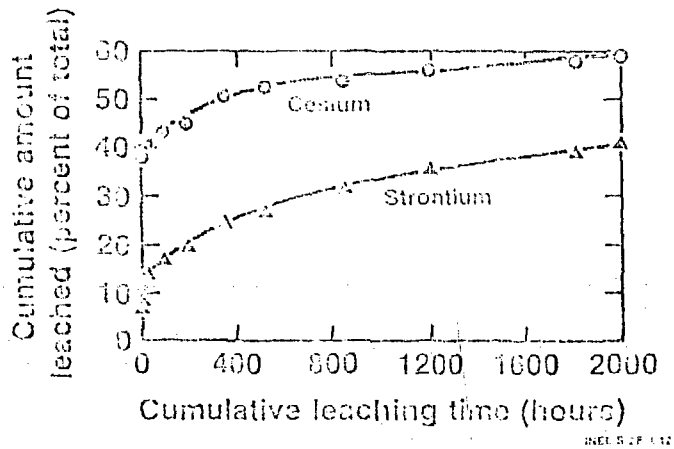

FIGURE 2. LEACHING OF CESIUM AND STRONTIUM FROM ZIRCONIA WITH DISTILLED WATER AT 25°C

from alumina calcine were as low as that for aluminum, and from zirconia calcine too low to be accuractely measured. After 1800 hours of continuous leaching only 0.1 percent of the total plutonium in the zirconia calcine had been removed and the rate of removal had become extremely slow (Figure 3).

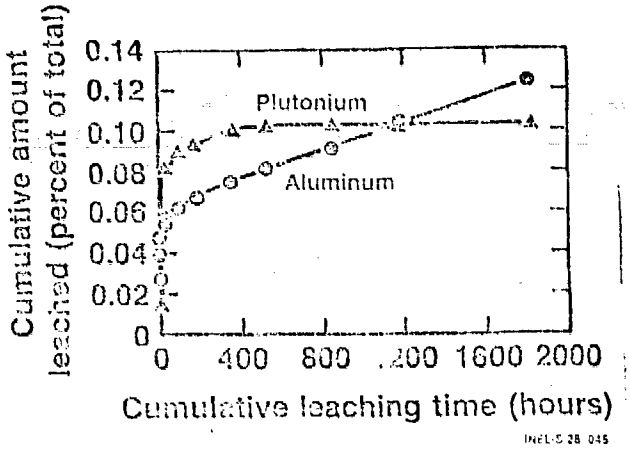

FIGURE 3. LEACHING OF ALUMINUM AND PLUTONIUM ZIRCONIA CALCINE WITH DISTILLED WATER AT 25°C

In the experiments with alumina calcine the loss of aluminum was measured of calcine dissolution. At 25°C the leaching rate of aluminum dropped from an initial rate of about 0.12 percent per day to 1.5×10^{-4} percent per day after 7 weeks (Figure 4).

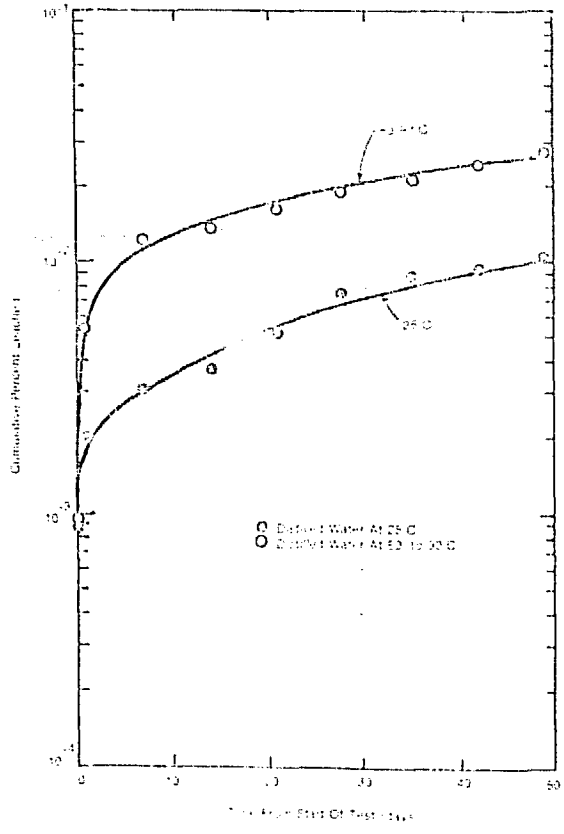

FIGURE 4. EFFECT OF TEMPERATURE UPON AMOUNT OF ALUMINUM LEACHED FROM ALUMINA CALCINE WITH DISTILLED WATER

Leaching results from the zirconia calcine experiments indicate that aluminum is very resistant to leaching as only 0.12 percent of the amount present had been leached in the first 1800 hours. The calcium compounds were considerably more leachable than aluminum compounds. About 3 percent dissolved in the first 1800 hours. Less than one percent of the fluoride was leached and about fifty percent of the nitrate was leached in 1800 hours.

Conclusions

No significant chemical differences were determined between retrieved and fresh calcine based on chemical and spectrochemical analyses. Little can be derived from the amounts of the radioisotopes present in the retrieved calcine samples other than the ratios of strontium-90 to cesium-137 are typical of aged fission product. The variations in concentrations of radionuclides within the composite samples of each bin also reflects the differences in compositions of waste solutions calcined.

In general the leaching characteristics of both calcines by distilled water are similar. In both materials the radionuclides of cesium and strontium were selectively leached at significant rates, although cesium leached much more completely from the alumina calcine than from the zirconia calcine. Cesium and strontium are probably contained in both calcines as nitrate salts and also as fluoride salts in zirconia calcine, all of which are at least slightly soluble in water. Radionuclides of cerium, ruthenium, and plutonium in both calcines were highly resistant to leaching and leached at rates similar to or less than those of the matrix elements. These elements exist as polyvalent metal ions in the waste solutions before calcination and they probably form insoluble oxides and fluorides in the calcine.

The relatively slow leaching of nitrate ion from zirconia calcine and radiocesium from both calcines suggests that the calcine matrix in some manner prevents complete or immediate contact of the soluble ions with water. Whether radiostrontium forms

slightly soluble fluoride salts or forms nitrate salts which are "protected" in the same manner as radiocesium is unknown. Nevertheless, selective leaching of cesium and strontium is retarded in some manner by the calcine matrix.

References

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