CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361302 5

ORNL-2611
UC-25 – Metals, Ceramics, and Materials
TID-4500 (22nd ed.)

FIXATION OF FISSION PRODUCTS IN ALUMINUM NITRATE WASTES BY CERAMIC MASSES

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price: $0.75 Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-2611

Contract No. W-7405-eng-26

Metals and Ceramics Division

FIXATION OF FISSION PRODUCTS IN ALUMINUM NITRATE WASTES BY CERAMIC MASSES

Date Issued

SEP 27 1963

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0361302 5

FOREWARD

This report presents work performed during the period 1954–1958 by T. N. McVay, J. M. Kerr, R. L. Hamner, and M. P. Haydon on one phase of the waste disposal program of the Ceramics Laboratory of the Metals and Ceramics Division and supported by the Health Physics Division. After some delay in processing the manuscript on this research, the report was condensed and largely rewritten by Sigfred Peterson.

CONTENTS

Page

ABSTRACT ---------- 1

INTRODUCTION ---------- 1

EXPERIMENTAL METHODS AND MATERIALS ---------- 2

Synthetic Waste Solution ---------- 2

Materials Added to Waste Solution for the Fixation of Fission Products ---------- 2
Shales ---------- 3
Phosphate Tailings ---------- 4
Fly Ash ---------- 4
Cement Stack Dust ---------- 4
Limestone ---------- 4
Ball Clay ---------- 5
ARCO Basalt ---------- 5
Bentonites ---------- 5
Attapulgites ---------- 5
Porocel ---------- 6
Treated Clay Materials ---------- 6

Preparation of Sinters ---------- 6

Leaching ---------- 7

RESULTS AND THEIR INTERPRETATION ---------- 7

Selection of an Inexpensive Shale Formulation ---------- 8

Mineralogy of Mix No. 15 ---------- 9

Retention of Radioactivity ---------- 11
Low-Cost Clays ---------- 11
Attapulgites ---------- 13
Bentonites ---------- 16
Miscellaneous Minerals ---------- 16
Experiments with Higher Firing Temperatures and Activity Levels ---------- 16
Discussion ---------- 18

Reduction in Volume ---------- 19

Mechanics of Fixation ---------- 20

Solid-State Reaction Experiments ---------- 21
Strontium Nitrate-Clay Mixture ---------- 21
Cesium Nitrate-Clay Mixture ---------- 22
Cerium Oxide-Clay Mixture ---------- 22
Summary ---------- 22

SUMMARY AND CONCLUSIONS ---------- 22

FIXATION OF FISSION PRODUCTS IN ALUMINUM NITRATE WASTES BY CERAMIC MASSES

ABSTRACT

The retention of fission products by ceramics prepared by firing mixtures of natural clays with a synthetic aluminum nitrate waste solution was studied. Compositions based on Ottosee shale, tailings from washing phosphate rock, and attapulgites show promise for fixing fission products. Further development is required to establish adequate retention of cesium. A preliminary study has been made of the chemical and physical processes leading to fixation of fission products by these ceramics.

INTRODUCTION

The waste fission products separated during recovery of spent reactor fuels must be permanently immobilized to prevent radiological hazards to man and other living species. The present method of tank storage is generally considered inadequate because of high cost, space requirements, and uncertain long-term reliability. Many methods are under investigation for fixing the fission products in refractory solids. This report describes some experiments on fission-product retention by selected abundant natural clays fired with a synthetic waste to compact sinters. Emphasis was placed on the selection of materials that are inexpensive and readily available, that form gels with the waste solution, that retain the radioactivity after firing at relatively low temperatures, and that form sinters of low volume.

Experiments related to utilization of radioactive decay energy to sinter the ceramic masses are reported elsewhere.[1]

---

[1] J. R. Johnson, S. D. Fulkerson, T. N. McVay, and J. M. Warde, "Heat Experiments for Self-Fixation of Radioactive Wastes in Clay-Flux Mixtures," USAEC Report TID-7517 (Pt. Ib), pp. 339–51, 1956.

EXPERIMENTAL METHODS AND MATERIALS

Synthetic Waste Solution

All fission-product fixation tests were made using a synthetic waste solution of composition representative of effluents from the processing of aluminum-base reactor fuels. This solution was 1.6 M in $Al(NO_3)_3$, 0.16 M in HNO_3, and 0.02 M in H_2SO_4, and contained salts of the fission-product elements to give the following concentrations (mg/liter): Sr, 11.4; Y, 3.8; Zr, 31.2; Cs, 26.6; Ba, 9.4; La, 9.0; Ce, 26.4; Pr, 36.6. Radioisotopes added were obtained from the ORNL Isotopes Division. While most experiments used mixed fission products, some preliminary experiments used separated Cs^{137}, Ce^{144}, Sr^{90}, and Ru^{106}. There is some variation in the composition of mixed fission products obtained at different times; a typical analysis is given in Table 1.

Table 1. Typical Analysis of Mixed Fission Products

Isotope	Percent of Total	Disintegrations/min per 0.5 cc × 10^{-9}
Ce^{144}	15.3	0.806
Trivalent rare earths	49.3	2.600
Zr^{95}-Nb^{95}	12.3	0.650
Sr^{89}	18.9	1.000
Sr^{90}	1.9	0.100
Ru^{106}	1.3	0.080
Cs^{137}	0.6	0.030
Total	99.6	5.27

Materials Added to Waste Solution for the Fixation of Fission Products

The materials listed and described below were used in fixation experiments.

Shales

Shales are sedimentary rocks with a layer structure containing clays and other mineral debris such as quartz and calcite. The clay is usually illite.

Conasauga Shale. A weathered shale containing quartz, some limestone, and the clay mineral illite. This locally obtained shale was satisfactory, but it cannot be obtained in commercial quantities.

Shale from General Shale Company, Knoxville, Tennessee. A dense, unweathered shale; this material retained fission products unsatisfactorily.

Ottosee Shale. A weathered shale, similar to the Conasauga except that limestone is not present, was procured from the Volunteer Portland Cement Company, Knoxville, Tennessee. On the basis of x-ray diffraction, differential thermal analysis, and petrographic examination, the shale was identified as principally a mixture of quartz and illite. The illite was micaceous in very small plates and fibers, and consequently, it had a large surface-to-volume ratio. The chemical analysis of the shale is given in Table 2.

Table 2. Chemical Analyses of Ottosee Shale and Limestone

	Shale (%)	Limestone (%)
SiO_2[a]	68.8	8.21
Al_2O_3	12.7	1.23[b]
Fe_2O_3	7.61	--
TiO_2	0.82	--
CaO	--	46.10
MgO	1.03	3.03
Na_2O	0.18	--
K_2O	2.40	--
Ignition loss	7.31	39.40
	100.85	97.97

[a]Acid insoluble.

[b]R_2O_3.

Ordinarily, as-mined, moisture-containing shale is readily dry-screened to −16 mesh after grinding with conventional muller-type equipment. Dry-screening becomes more difficult when much smaller particle sizes are desired because the moist material cakes and blinds the screen openings. Therefore, to obtain −100 mesh material, it becomes necessary to dry the shale before grinding. This increases the processing cost. Preliminary experiments with both −100 and −16 mesh Ottosee shale showed that the coarser material retained fission products as effectively as the finer. Results given for the shale are for the coarser grade.

Phosphate Tailings

Phosphate tailings are slimes removed in the washing of phosphate rock. They contain clay and fine-grained collaphane, which is a cryptocrystalline carbonate-hydroxyl-fluorine apatite. The tailings have a high surface-to-volume ratio and fuse to a glass at a relatively low temperature. This material is obtained from phosphate washing plants in the form of a slurry that is very difficult to dewater.

Fly Ash

This is a finely divided coal ash obtained in the combustion of coal in a power plant. It did not prove satisfactory.

Cement Stack Dust

Cement stack dust is collected from the stacks of portland cement kilns.

Limestone

This is a Chicamauga limestone consisting primarily of calcite. Its chemical analysis is given in Table 2.

Ball Clay

This is a clay containing kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) as the main mineral, although ball clays may contain small amounts of bentonite, other clay minerals, and quartz. They are exceptionally fine grained and all of them contain organic matter.

ARCO Basalt

This is a fine-grained, basic, igneous rock produced by prehistoric lava flows.

Bentonites

These are exceptionally fine-grained clays derived from weathered and altered volcanic ash; some have the property of swelling greatly when wetted.

Hector Bentonite. A high magnesium montmorillonite (Hectorite) from California with substantial amounts of calcite and dolomite. The Hector bentonite was supplied by the Baroid Division of the National Lead Company.

M. H. Bentonite. A material similar to the Hector bentonite but containing less calcite and negligible amounts of dolomite.

Cerclay. A nonswelling Texas aluminum bentonite supplied by the Baroid Division of the National Lead Company.

Filtrol Montmorillonite. A beneficiated montmorillonite used for a fuller's earth.

Milwhite Bentonite. A Texas bentonite furnished by the Milwhite Company.

Attapulgites

Attapulgites are hydrated magnesium-aluminum silicate clays having crystals in the form of long hollow tubes that agglomerate into bundles, which may be broken up by high shear in water suspensions. The surface areas of these attapulgites are very large, as the particle size ranges from 0.077 to 2.5 μ. Unlike some other clays that gel in water (e.g.,

Wyoming bentonite), they have the important property of being able to form a gel or slurry in the presence of acids or salts.

Zeogel. An attapulgite furnished by the Baroid Division of the National Lead Company.

Attasorb and Permagel. Attapulgites procured from Minerals and Chemicals Corporation of America in several grades. Low volatile matter (LVM) Attasorb is an attapulgite which has been heated to a temperature at which part of the water of hydration is lost. Regular volatile matter (RVM) and high volatile matter (HVM) Attasorbs were also procured. Permagel is a refined, fine-grained attapulgite priced above 50¢/lb.

Porocel

Porocel is an activated bauxite from Minerals and Chemicals Corporation of America.

Treated Clay Materials

With the exception of E-223-57B the following were especially prepared materials obtained from Ralph Grim, Department of Geology, University of Illinois, Urbana, Illinois:

CPF-7A, CPF-28, and CPF-18. Acid-leached kaolins with surface areas of 443 m^2/g, 209 m^2/g, and 294 m^2/g, respectively.

E-197-55V. A fibrous silicate obtained by acid leaching attapulgite.

E-197-55X. A heat-treated bauxite.

E-223-57B. A highly adsorptive fine-grained aluminum silicate furnished by Minerals and Chemicals Corporation of America.

Preparation of Sinters

The proportions of clay minerals and waste solution were selected so as to obtain mixtures that would form either gels or thick slurries, to prevent segregation of solids after mixing and to keep the radioisotopes homogeneously distributed during drying. Limestone and other carbonates were included in certain compositions to aid gel formation.

Dolomite and cement stack dust were tried for this purpose and found unsatisfactory.

While a 250-ml portion of the tagged synthetic waste solution was agitated in a stainless steel milkshake cup by a Hamilton Beach mixer, the previously blended dry solids were added slowly. If gelation started, the mixing was continued until the gel was quite thick and would barely pour from the cup. The mixing time was often less than 5 min if limestone and soda ash were constituents. After thorough mixing, the batch was poured into a 600-ml beaker and placed on a hot plate for dehydration and evolution of some of the nitrogen oxides prior to firing.

Samples of the dried batch were fired in crucibles in an electric resistance muffle furnace and allowed to soak at the designated temperatures for 1 hr.

Leaching

The fired material was broken into small lumps; the pieces of sinter were weighed and placed in screw-cap bottles for leaching with 10 ml of water per gram of fired sinter. Tap water was used because of its similarity to the ground water in the Oak Ridge area. The fired ceramic mass was allowed to leach in a stagnant condition and the radioactivity of the lixivia was measured by standard GM counter techniques at intervals varying from one week to 6 months. It was impossible to make a satisfactory count of the fired material because of self-shielding.

RESULTS AND THEIR INTERPRETATION

At the start of this investigation, a ceiling cost of 15¢/gal of waste solution treated limited consideration to readily available low-cost materials. These include shales, phosphate tailings, and fly ash. Because the cost of liquid-waste storage at some installations exceeds $2.00/gal, materials of higher cost were also examined. These include attapulgite, ball clays, and several bentonites.

Selection of an Inexpensive Shale Formulation

Several compositions based on inexpensive clay sources were screened by evaluation of sintering characteristics on firing at 843, 898, and 954°C and preliminary determination of fission-product retention. On the basis of the results, a composition based on Ottosee shale was selected for more complete investigation as the one most nearly meeting the criteria imposed. This composition, designated Mix No. 15, contains 100 g Ottosee shale, 30 g soda ash, and 30 g limestone per 250 ml portion of synthetic waste solution. The selection of Composition No. 15 was based on low cost and availability, minimum weight and volume, stiff gel formation, and satisfactorily low firing temperature.

The low cost of the materials involved should make it possible to process the waste within the cost limit of 15¢/gal of radioactive waste. There is an abundance of shale and limestone in the East Tennessee area. Soda ash (Na_2CO_3) may be obtained readily in bulk quantities from chemical supply firms.

Mix No. 15 sinters to a relatively light, porous clinker, due to gas bubbles being entrapped during the decomposition of the carbonates. The bulk density varies with the firing temperature. The volume reduction from the original solution to the fired cake is only about 70%; this is not as favorable as obtained with compositions containing more expensive materials such as attapulgite.

Composition No. 15 has the desirable characteristic of forming a stiff gel. On heating, this gel breaks down to a slurry that remains sufficiently viscous to keep the particles more or less homogeneously suspended; the use of −16 mesh shale allows some large particles to settle out of suspension. The release of gas when the aluminum nitrate reacts with the soda ash and limestone causes the mix to become a foaming mass. With proper stirring, the foaming subsides and the mass gradually thickens due to gel formation and becomes stiff and spongy. If the mass is to be transferred to another container, it should be before the gel is completely formed. A container volume of several times the final cake volume is required because the escaping gases buoy

the mass upward. Substitution of hydrated lime for limestone to reduce the gas evolution was not successful because of poor gel formation. Several factors inhibit the formation of a gel or change its properties:

Temperature. Although the lower temperature limit of gel formation was not determined, it is known that a gel is not readily formed at very low temperatures. Upon heating to about 70°C, the gel breaks down to a slurry.

Speed of Mixing. The gel forms more slowly as the speed of mixing is decreased.

$CaCO_3$ Content. Mixes containing more limestone than specified gel almost instantaneously. Very quick gelling due to excess limestone results in a crumbly structure, which on firing does not form a massive, coherent clinker.

Mineralogy of Mix No. 15

A nonradioactive sample of Mix No. 15 was calcined at 900°C and analyzed; the analysis was also calculated from the analyses of raw materials. It was assumed that in the limestone all the insoluble material was SiO_2 and the R_2O_3 was alumina and that $Al(NO_3)_3$ solution decomposed to alumina. The calculated and measured chemical analyses are compared in Table 3.

Table 3. Composition of Sinter from Mix No. 15

	Calculated Analysis (%)	Measured Analysis (%)
SiO_2	47.8	51.1
Al_2O_3	22.5	21.9
Fe_2O_3	5.1	4.95
TiO_2	0.5	0.56
MgO	1.3	1.13
CaO	9.2	8.65
Total Alkali	13.5	10.26

A composition such as the above is essentially a five-component phase system consisting of SiO_2, Al_2O_3, Fe_2O_3, CaO, and alkalis. Consequently, the crystallization of compounds from such a composition would be complex; it would be possible under equilibrium conditions to have as many as five coexisting crystalline phases. Also, it is possible — even probable — that as the temperature is increased phases would be formed at lower temperatures and then disappear at higher temperatures. For instance, quartz goes into solution as the firing temperature is increased.

However, there are some limitations as to the crystalline compounds that can be formed, as this mixture would be classified as moderately basic. For example, the formation of anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$, nephelite $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, and gehlenite $2CaO \cdot Al_2O_3 \cdot SiO_2$ would be possible. On the other hand, it would be unlikely that silicates with a much greater tenor of silica would be produced on firing. Glass would certainly be formed, but glass is unstable and would completely crystallize if the mix were held within the proper temperature range for a sufficient length of time.

Thoroughly dried nonradioactive Mix No. 15 was ground in a pebble jar mill to ensure homogeneity. A differential thermal analysis showed that practically all volatiles were removed at 750°C. Approximately 20-g samples were heated at about 5°C/min to temperatures ranging from 200 to 1100°C and then held for 2 hr within ±5°C of the desired temperature. These calcined samples were examined with a petrographic microscope and by x-ray diffraction techniques.

The petrographic and x-ray results for these samples showed the phases present from 200–500°C to be illite, quartz, and sodium nitrate. There was a trace of sodium nitrate present in a sample heated at 550°C; none was detected above this temperature. Although the usual decomposition temperature of $NaNO_3$ is 380°C, the duration of heating at 400–500°C was not sufficient to decompose the nitrate. Highly birefringent material persisted in samples heated up to about 800°C, indicating that the structure of illite persisted at temperatures above which it lost its chemically combined water.

In the material calcined at 750°C for 2 hr there were narrow rims of glass around the quartz crystals. At lower temperatures glass was not observed. With further increase in temperature, the formation of glass increased and the quartz went into solution at an increasingly rapid rate until there was only a trace in the sample calcined at 1100°C.

The x-ray spectrometer patterns showed that nephelite first appeared at 750°C, the amount increasing as the temperature was raised to 1100°C. The petrographic examination of the sample fired at 1100°C showed a phase present in very minute, needle-like crystals, too small to be positively identified. Also, the x-ray pattern showed several peaks, which were not positively identified but may have been due to pyroxene.

Additional samples were kept at temperature for 24 hr. Samples held at 600°C, but not at 550°C, showed reaction rims around the quartz grains in the sample. There are indications of the formation of a melilite mineral and anorthite as low as 850°C. In addition, several unidentified x-ray lines appeared as the firing temperature of the samples increased from 750 to 900°C. It is interesting to note that in samples fired in this temperature range new crystalline phases appeared coincident with an increase in the amount of glass. Nephelite was not as easily detected by x-ray diffraction in the sample that had been held at 1100°C for 24 hr as in the sample heated 2 hr. The minute, needle-like crystals that were present in the sample fired for 2 hr at 1100°C had disappeared on heating for 24 hr.

Retention of Radioactivity

Low-Cost Clays

Results of preliminary screening experiments, evaluation of sintering characteristics, and other considerations already given limited the low-cost clay materials that were investigated to any extent to Ottosee shale and phosphate tailings. The compositions of selected mixes based on these materials and selected fission-product retention measurements on resulting sinters are presented in Tables 4 and 5. Compositions were selected according to the criteria already described.

The retention of fission products by sinters based on phosphate tailings is summarized in Table 4. Tested with mixed fission products, all compositions showed complete retention as far as could be determined at the activity levels used. However, tested with pure cesium activity the mixes with carbonate additives showed poor retention, which improved with increasing firing temperature and amount of clay per volume of waste. The one composition without carbonates was not tested with cesium, but it was tested with sufficiently high levels of mixed fission products that very poor cesium retention should have been detected despite the low content of cesium activity in the mixture.

Table 4. Retention of Fission Products by Sinters of Phosphate Tailings

Mix No.	Weight of Components (g)[a] Soda Ash	Limestone	Phosphate Tailings	Firing Temperature (°C)	Fission Product	Leaching Time (mo)	Leached (%)
9	30	30	200	454–954	Sr^{90}	3.5	< 1
				426–982	Cs^{137}	1	10
				426–982	Mixed	1	< 1
8	30	30	100	426–982	Cs^{137}	1	≥ 20
				538–982	Mixed	1	< 0.7
30	30	30	50	538	Cs^{137}	1	100
				982	Cs^{137}	1	1
				638–982	Mixed	1	< 0.4
36			50	538–982	Mixed	1	< 0.3
				1000–1200	Mixed	1	< 0.03

[a]Per 250 ml portion of synthetic waste solution.

Compositions based on phosphate tailings were not tested more extensively, since the cost advantage of this material would probably be lost when the drying and shipping of large quantities are considered. In addition, formulations without limestone did not form a gel with the synthetic waste solution.

Fission-product retention by sinters of Ottosee shale is summarized in Table 5. Again it is seen that, within the limit imposed by the low level of activity used, the mixed fission products appear to be retained, although most compositions do not retain cesium completely. Composition No. 5 retained cesium, although the activity level tested was quite low. Strontium was retained by the sinters in the standard leaching test but not in a single test with simulated sea water.

A Geiger counter held in the path of escaping gases from the furnace during firing of Mix No. 15 tagged with Ru^{106} gave evidence of radioactive volatiles. Counting of samples from the sinter, however, established that only part of the ruthenium was volatilized. Little or no activity was released to the lixivium during leaching of shale sinters tagged with ruthenium at relatively low levels.

The activity leached from sinters did not vary with contact time over the range from one to four months.

Attapulgites

Several formulations of attapulgites with synthetic waste solution were tested at mixed-fission-product activity levels sufficient to detect 0.5% leaching. From the results summarized in Table 6, it is clear that the retention is improved with increasing amount of clay. The LVM Attasorb and the Permagel seem less effective than the other attapulgites tested. An aluminum silicate additive appeared beneficial in Mix No. 113 but not at a lower concentration in Mix No. 120. The retention is generally improved by increasing the firing temperature; an additional demonstration of this will be presented later.

Of the attapulgite formulations listed in Table 6, the only ones tested for cesium retention were based on Zeogel. After firing Mixes Nos. 83 and 85 at temperatures from 426 to 800°C, cesium was not detected at the 0.5% level in one-month leaches. However, the leaner mix, No. 84, after firing to 800°C showed 4% of the cesium leached but none leached after firing to 426 or 638°C. This would indicate that firing to higher temperatures, which improves retention of radioisotopes making up the mixed fission products, would impair retention of cesium. The results

Table 5. Retention of Fission Products by Sinters of Ottosee Shale

Mix No.	Weight of Components (g)[a] Soda Ash	Lime-stone	Ottosee Shale	Firing Temperature (°C)	Fission Product	Leaching Time (mo)	Leached (%)
5	30	30	200	843–954	Ru,Cs,Ce	3	< 5
				566–732	Mixed	2	< 1
				732	Sr	2	< 0.1
				454–934	Sr	3.5	< 1
16	30	30	150	566–954	Sr	3.5	< 1
15	30	30	100	843–954	Ru,Ce	3	< 3
				843	Cs	3	12
				954	Cs	3	7
				566–954	Sr	3.5	< 1
				566–732	Mixed	4	< 0.5
26		60	200	732–954	Sr	1	< 0.5
				732	Cs	0.5	3
				843	Cs	0.5	2
				954	Cs	0.5	1
27		60	100	843–954	Sr	1.5	< 0.3
				566	Sr	1.5	6
				566–943	Cs	1.5	2–10
				566	Mixed	1.5	0.5
25			200[b]	454–732	Sr	2	< 0.7
				454,566	Sr	1[c]	8,3
23	30	30	200[d]	566–732	Sr	2	< 1
24			260[b,d]	454–566	Sr	2	< 1

[a]Per 250 ml waste solution.

[b]Plus 250 ml water.

[c]Leached with simulated sea water.

[d]Plus 20 g activated alumina.

Table 6. Retention of Mixed Fission Products by Attapulgites

Mix No.	Solids Added to 250 ml Synthetic Waste Solution
Formulations from which 0.5% mixed fission products could not be detected in a one-month leach after firing at 426 to 800°C:	
83	100 g Zeogel
85	50 g Zeogel plus 25 g Ottosee shale
97	200 g RVM Attasorb −30 +60 mesh
98	100 g RVM Attasorb −30 +60 mesh
103	100 g LVM Attasorb
105	25 g RVM Attasorb −200 mesh plus 35 g LVM Attasorb
106	100 g RVM Attasorb −200 mesh
110	100 g HVM Attasorb
Formulations from which 0.5% mixed fission products could not be detected in a one-month leach after firing at 638 to 800°C, but from which measurable radioactivity could be leached after firing at 426°C:	
84	50 g Zeogel
99	50 g RVM Attasorb −30 +60 mesh plus 25 g LVM Attasorb
100	100 g Permagel
101	50 g Permagel
102	35 g Permagel plus 25 g LVM Attasorb
108	25 g Permagel plus 25 g RVM Attasorb −200 mesh
113	35 g RVM Attasorb −200 mesh plus 15 g E-223-57B
126	25 g E-197-55V
Formulations from which mixed fission products were detectably leached in one month after firing at 426 to 800°C:	
104	50 g LVM Attasorb
107	50 g RVM Attasorb −200 mesh
111	50 g HVM Attasorb
119	30 g RVM Attasorb
120	30 g RVM Attasorb plus 3 g aluminum silicate

with Mix No. 85 show that a lean attapulgite mix can be improved by adding shale, and that attapulgite-shale combinations deserve further study.

Bentonites

The retention of fission products by bentonite sinters is summarized in Table 7. These compositions in general do not appear satisfactory. Cesium is leached from sinters fired at the highest temperatures, except for compositions containing the larger quantities of Cerclay, Texas, and Filtrol bentonites without additives. The only one of these tested showed poor retention of mixed fission products. The addition of shale or phosphate tailings to the bentonites showed no significant effect on cesium retention. Cesium retention was impaired by the addition of soda ash and limestone.

Miscellaneous Minerals

A few experiments with various special minerals failed to find satisfactory formulations. Compositions based on the bauxite, Porocel, did not retain either cesium or the fission-product mixture. This mixture was also not retained by a sinter of the aluminum silicate designated as E-223-57B. Formulations based on ARCO basalt and Tennessee ball clay, the latter with carbonate additives, retained fission products from the mixture, but not cesium. Other kaolin formulations are considered below.

Experiments with Higher Firing Temperatures and Activity Levels

Selected compositions were tagged with sufficient mixed-fission-product activity to detect leaching of the order of 0.05% and fired at temperatures up to 1200°C. The retention of fission products by these sinters is given in Table 8. In general, increasing the firing temperature increases the retention of fission products. Certain of the special clays and the attapulgites, particularly the acid-leached attapulgite E-197-55V, show promise. The inexpensive clays, Ottosee

Table 7. Retention of Fission Products by Sinters Based on Bentonites

Mix No.	Solids per 250 ml Waste: Bentonite (g)	Bentonite Type	Additives (g)	Retention of Fission Products[a] (1-mo leach): Mixed	Cs
47	100	Hector		L	L
48	50	Hector		L	L
53	100	Cerclay		L	R
54	50	Cerclay		L	L
59	25 25	Cerclay Filtrol			rL
63	200	Texas			R
64	100	Texas			R
65	50	Texas			rL
67	200	Filtrol			R
68	100	Filtrol			rL
77	100	MH			rL
78	50	MH			rL
55	50	Cerclay	25 Ottosee shale	L	rL
76	50	MH	100 Ottosee shale		rL
49	50	Hector	25 Phosphate tailings	1R	L
70	100	Filtrol	50 Phosphate tailings		rL
71	75	Texas	75 Phosphate tailings		rL
74	50	MH	100 Phosphate tailings		rL
75	25	MH	75 Phosphate tailings		rL
79	50	MH	25 Phosphate tailings	1R	rL
60	200	Texas	30 Soda ash 30 Limestone		1R
61	100	Texas	30 Soda ash 30 Limestone		L
62	50	Texas	30 Soda ash 30 Limestone		L
66	150	Filtrol	30 Soda ash 30 Limestone		L
69	100	Filtrol	30 Soda ash 30 Limestone	1R	
73	75 25	Texas MH	30 Soda ash 30 Limestone	1R	

[a]L = 0.5% or more leached from sinters fired at 428 to 800 or 870°C.
R = activity retained by all sinters.
1R = activity leached only from sinter fired at 428°C.
rL = activity leached only from sinter fired at 800 or 870°C.

Table 8. Retention of Mixed Fission Products by Sinters Fired at an Extended Temperature Range

Mix No.	Clay Used Per 250 ml Waste Solution (g)	Mixed Fission Products (%) Leached in 1 mo from Sinters Fired at: 426 °C	638 °C	800 °C	1000 °C	1200 °C
15	100 Ottosee shale[a]	0.10	0.08	< 0.05	0.07	< 0.05
36	50 Phosphate tailings	0.25	< 0.03	0.03	< 0.03	< 0.03
125	25 E-197-55X (bauxite)	0.94	0.19	0.04	0.04	0.07
122	25 CPF-7A	0.80	0.21	0.05	0.02	0.02
128	50 CPF-7A	1.0	0.08	0.03	< 0.03	< 0.03
129	50 CPF-28	2.4	0.05	0.05	< 0.03	< 0.03
130	50 CPF-18	1.1	0.10	< 0.03	0.05	0.04
130	50 CPF-18	0.45	0.23	0.15	< 0.03	0.03
104	50 LVM Attasorb	2.7	1.1	0.78	0.13	< 0.05
107	50 RVM Attasorb −200 mesh	2.3	0.61	1.3	0.11	0.08
111	50 HVM Attasorb	2.0	0.70	1.7	0.11	< 0.05
101	50 Permagel	1.6	0.16	< 0.05	0.20	0.05
126	25 E-197-55V	1.4	0.13	0.07	< 0.02	< 0.02

[a]Plus 30 g each soda ash and limestone.

shale and phosphate tailings, show fission-product retention properties as good as or better than the more expensive clays.

Discussion

Of the various minerals tested for retention of fission products, the only ones showing promise are Ottosee shale, phosphate tailings, and attapulgites. The first two of these have the advantage of low cost, the third of better volume reduction (to be discussed later).

The effectiveness of this method of fixing radioactive wastes appears to be limited by the retention of cesium, which as an alkali metal is more

difficult to convert to insoluble form. Most of the formulations tested with cesium showed greater leaching of cesium from sinters fired at 800 or 870°C than from those fired at lower temperatures. On the other hand, increasing the firing temperature favored retention of other fission products. Shale formulations showed poor cesium retention, but improvement with increased firing temperature. The few experiments with cesium on attapulgites show some promise. It may be that a superior sinter would involve a combination of shale and attapulgite.

The phosphate tailings show poor cesium retention, but the only formulations tested with cesium contained carbonate additives, which have been shown in other systems to impair cesium retention. Other fission products are retained well by sinters based on phosphate tailings, so tests of cesium retention by this material without carbonates would be in order. It may also be that a combination of this material with another clay, perhaps an attapulgite, will give a suitable sinter.

In many cases, where there was a difference in proportions of the solid materials and the waste solution for the same firing temperatures, the activity of the lixivia was greater as the clay content was reduced. Although the clay content varied in different mixtures, the amount of alumina resulting from the denitration of the aluminum nitrate solution was constant. As alumina has a very high melting point, the compositions with the higher clay content should be less refractory than those with a lower content of the same clay. The refractoriness could influence the retention of the radioactivity in the sinter, as the presence of alumina in most compositions would decrease the amount of glass. Consequently, a more detailed study is needed to determine the relation of the clay content to the retention of radioisotopes.

Reduction in Volume

It is important to compare the volume of the fired ceramic mass to the volume of the original waste solution. The volume of the sintered material will depend primarily on the sintering temperature and on the

amount of clay added to a given volume of solution. Clays shrink on firing and the porosity decreases until a minimum volume of sinter or glass is formed, which for a given amount of clay depends upon time-temperature relationships.

The bulk density of a mixture using 50 g of attapulgite and 250 ml of waste solution, after firing at 638°C, was 2.1 g/cc. The weight of the sintered cake was 67.7 g and the volume was 32.2 ml, 13% of the volume of the original waste solution. This is considerably greater volume reduction than was noted with Mix No. 15 fired at the same temperature, which had about 30% of the volume of the original solution.

The surface area of the sinter should be sufficiently large that heat from decay of very high-level wastes would be sufficiently dissipated by radiation to avoid melting of the sinter.

Mechanics of Fixation

The mixtures of simulated waste solution with minerals were dried and then fired at various temperatures to immobilize the radioisotopes. Upon firing, sintering takes place with or without some glass formation. At sufficiently elevated temperatures all clays melt and become glass, and the temperature of glass formation depends primarily on the chemical composition of the clay. The actual weight of the fission products present is so small they do not affect the melting point of the materials used.

There are several ways whereby such isotopes may be fixed: base exchange, solid-state reactions, and glass formation. For the aluminum nitrate waste solution of this study, very little if any base exchange of the radioisotopes would be expected because most, if not all, of the base exchange sites on the surface of the adsorber would be filled with aluminum. In mixtures of ceramic materials and the aluminum nitrate solution, fixation most probably takes place by solid-state reactions at low temperatures and by glass formation at higher temperatures.

Solid-State Reaction Experiments

Cesium, strontium, and the rare earths are known to occur in several silicate minerals as well as some synthetic refractory silicates. If these silicates could be formed by simple syntheses, it is very likely their formation would aid in the retention of fission-product isotopes of these elements. This was tested by examination of the reactions occurring on firing mixtures of Florida kaolin with cesium nitrate, with strontium nitrate, and with cerium dioxide.

Florida kaolin was used in these experiments as it is a rather pure clay which has a formula near $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Also, the clay was selected rather than a mixture of alumina and silica because it was expected to react more rapidly with basic oxides. One-mole portions of the Florida kaolin (258 g) were ground in pebble mills with one or two moles of $CsNO_3$, one mole of $Sr(NO_3)_2$, or one mole of CeO_2. The $CsNO_3$- and $Sr(NO_3)_2$-clay compositions were ground with absolute alcohol in which these nitrates have a low solubility. The CeO_2-clay mixture was ground in water.

After firing at various temperatures in the range 700 to 1600°C, samples of the different mixtures were studied by petrographic methods and by x-ray diffraction. The results follow:

Strontium Nitrate-Clay Mixture

The x-ray diffraction pattern showed indications of compound formation in all samples in amounts increasing with increased firing temperatures. The x-ray data showed that there were some d values for one of these compounds in fairly close agreement with values for the calcium and barium feldspars, anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$, and celsian $BaO \cdot Al_2O_3 \cdot 2SiO_2$. Petrographic examination showed $SrO \cdot Al_2O_3 \cdot 2SiO_2$ (ref 2) in the compacts fired at both 1300 and 1600°C for 2 hr, associated with different unknown compounds at the two temperatures. The unidentified phase in the sample fired at 1600°C was isotropic (n = 1.640).

---

[2]Optical data for this compound are reported in National Research Council, "Data on Chemicals for Ceramic Use," (National Research Council Bulletin No. 118) Revised edition, University of Pittsburgh, 1949.

The formation of a strontium compound at temperatures as low as 700°C suggests a reason for the relative ease of fixation of Sr^{90}.

Cesium Nitrate-Clay Mixture

X-ray diffraction patterns showed no evidence of cesium compounds being formed by firing the equimolar $CsNO_3$-clay mixture at any temperature. In the 2:1 molar $CsNO_3$-clay composition fired at 900°C, there were indications of an unidentified compound, and the x-ray lines were more prominent in samples fired at higher temperatures. An isotropic phase in samples of both these mixtures fired at 900°C was probably glass. If so, the temperature was above that for solid-state reactions. Also, mullite ($3Al_2O_3 \cdot 2SiO_2$) was present in both samples fired at 1100°C and above.

Cerium Oxide-Clay Mixture

Cerium oxide was used as an example of rare earths present in fission products. Neither x-ray nor petrographic data showed any evidence of compound formation between cerium oxide and clay at any temperature within the limits of this study. Both cerium oxide and mullite were identified by x-ray diffraction in samples fired at 1100 and 1300°C.

Summary

On the basis of the solid-state reaction studies, it appears that cesium, when well retained, is fixed in a glass and possibly as a compound formed at 900°C. Strontium can be immobilized in compounds by solid-state reactions at temperatures as low as 700°C. Since no reaction was observed between kaolin and CeO_2, no information was obtained concerning the mechanism of fixation of cerium, which is a representative of the rare earths that constitute a substantial fraction of the mixed fission products.

SUMMARY AND CONCLUSIONS

Retention of fission products was demonstrated in several sinters prepared by firing selected clays with a synthetic aluminum nitrate waste solution. Sinters based on the relatively cheap Ottosee shale, tailings from washing of phosphate rock, and certain attapulgites retained fission

products when leached by water. Other formulations based on bentonites, bauxites, a basalt, a ball clay, kaolins, and aluminum silicate did not appear satisfactory. Ruthenium was partially volatilized during firing of a shale-base sinter. Further investigation is needed to demonstrate adequate cesium retention by sinters of the type studied. It appears that combinations of shale and attapulgite would merit further study.

Clay sinters appear to fix cesium in glass that forms at 900°C and above, while strontium undergoes solid reactions with the clay at 700°C. Firing mixtures of cesium nitrate with pure kaolin in the range 700 to 1600°C gave no crystalline cesium compounds, but glass formation was evident at 900°C. Strontium nitrate gave crystalline reaction products, including a feldspar, with kaolin at all temperatures in this range. In the same temperature range, cerium dioxide did not react with kaolin. The shale formulation that retained fission products was examined by x rays and petrographic techniques after firing in the range 200 to 1100°C. A number of crystalline products and glass were found.

Sinters that were based on attapulgite and shale and retained fission products had volumes 13 and 30%, respectively, of the original waste solution.

Fission-product retention by clay sinters was improved by increasing the firing temperature at least to 1200°C. Cesium retention was not investigated at such high temperatures, but poorer cesium retention was often observed at the highest temperatures tested (800–870°C) than at lower temperatures, probably because of a breakdown of the hydrated clay structure in this range. Cesium would be expected to be fixed better at higher temperatures as glass formation is favored.

ORNL-2611

UC-25 – Metals, Ceramics, and Materials
TID-4500 (22nd Ed.)

INTERNAL DISTRIBUTION

1. Biology Library
2–3. Central Research Library
4. Reactor Division Library
5–6. ORNL - Y-12 Technical Library, Document Reference Section
7–26. Laboratory Records
27. Laboratory Records, ORNL RC
28. ORNL Patent Office
29. P. S. Baker
30. W. J. Boegly, Jr.
31. W. E. Clark
32. F. L. Culler
33. J. E. Cunningham
34. J. H Frye, Jr.
35. H. W. Godbee
36–40. M. R. Hill
41. T. S. Kress
42. R. H. Lafferty, Jr.
43. H. G. MacPherson
44. S. Peterson
45. J. J. Pinajian
46. E. G. Struxness
47. J. A. Swartout
48. M. E. Whatley
49. W. C. Yee
50. A. A. Burr (consultant)
51. J. R. Johnson (consultant)
52. C. S. Smith (consultant)
53. R. Smoluchowski (consultant)

EXTERNAL DISTRIBUTION

54–55. David F. Cope, AEC-ORO
56. D. E. Baker, GE Hanford
57. Ersel Evans, GE Hanford
58. J. L. Gregg, Cornell University
59. C. M. Adams, Jr., MIT
60. J. Simmons, AEC, Washington
61. E. E. Stansbury, University of Tennessee
62. Donald K. Stevens, AEC, Washington
63–647. Given distribution as shown in TID-4500 (22th ed.) under Metals, Ceramics, and Materials category (75 copies – OTS)