195

IN-1322

10-29-69

1056

MASTER

IN-1322

September 1969

unclass
Hahn 10/30/69

POST-CALCINATION TREATMENT POSSIBILITIES FOR
CALCINE FROM FLUIDIZED BED CALCINATION

D. W. Rhodes

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

P3075

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U. S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

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, express 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.

IN-1322
Issued: September 1969
Waste Disposal and Processing
TID-4500

POST-CALCINATION TREATMENT POSSIBILITIES FOR CALCINE FROM FLUIDIZED BED CALCINATION

By

D. W. Rhodes

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.

IDAHO NUCLEAR CORPORATION
A Jointly Owned Subsidiary of
AEROJET GENERAL CORPORATION
ALLIED CHEMICAL CORPORATION
PHILLIPS PETROLEUM COMPANY

U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

ABSTRACT

The dry, granular calcine that is produced by fluidized bed calcination of highly radioactive waste in the Waste Calcining Facility at the Idaho Chemical Processing Plant is a versatile material that can be recovered readily from storage and treated to modify some of its properties if desired. Methods are discussed that have been investigated, together with other methods that have been considered but not yet tried, to modify the leachability, thermal conductivity, and physical dispersability of calcine.

SUMMARY

Highly radioactive calcine from the Waste Calcining Facility is stored in underground stainless steel bins at the Idaho Chemical Processing Plant; however, this dry, granular material can be retrieved for additional treatment if desired. Methods to modify the leachability, thermal conductivity, and dispersability of the calcine have been tried in bench-scale experiments and many other approaches have been considered. These methods include: (1) coating the calcine particles, (2) imbedding them in a solid matrix, (3) fusing with additives to form a glass, (4) canning in a secondary container, and (5) removal of radionuclides. While none of these methods is currently planned for implementation at the Idaho Chemical Processing Plant, they may prove desirable for fluidized bed calcination processes installed at other locations.

CONTENTS

	Page
ABSTRACT	ii
SUMMARY	iii
I. INTRODUCTION	1
II. PROPERTIES OF CALCINE	2
III. MODIFICATION OF CALCINE PARTICLES	4
1. Coating on Calcine Particles	4
2. Investment in Matrices	4
2.1 Metals	5
2.2 Salts	6
2.3 Asphalt	7
2.4 Plastics	7
2.5 Concrete	8
2.6 Grout	9
3. Change of Physical Form	10
3.1 Formation of a Homogeneous Glass	10
3.2 Formation of a Glass with Excess Calcine	10
3.3 Glass Making Chemicals Added to Calciner Feed	11
4. Canning	11
5. Removal or Fixation of Fission Products	12
5.1 Leaching of Fission Products	12
5.2 Volatilization of Fission Products	12
IV. DISCUSSION AND CONCLUSIONS	13
V. REFERENCES	15

FIGURES

	Page
1. Calcined Alumina Particles Coated with Aluminum	4
2. Calcined Alumina Particles Coated with Steel	4
3. Calcined Alumina Particles Imbedded in an Aluminum Matrix	5
4. Calcined Alumina Particles Imbedded in a Tin-Lead Matrix	5
5. Calcined Alumina Particles Imbedded in a Plastic Matrix . . .	8
6. Alumina-Phosphate Glass Prepared from Non-Radioactive WCF Calcine	10

TABLES

I. Composition and Properties of Alumina Calcine	2
II. Composition and Properties of Zirconia Calcine	3
III. Wettability of Calcined Alumina with Various Materials	6
IV. Possible Methods of Modifying Properties of WCF Calcine	13

POST-CALCINATION TREATMENT POSSIBILITIES FOR CALCINE FROM FLUIDIZED BED CALCINATION

I. INTRODUCTION

Highly radioactive wastes from the chemical reprocessing of nuclear fuels at the Idaho Chemical Processing Plant (ICPP) are routinely converted to granular solids in the Waste Calcining Facility (WCF)^(1,2). Although the WCF has been used only to calcine high-level aluminum nitrate and fluoride-containing wastes, simulated stainless steel-nitrate and sodium-containing aluminum nitrate wastes have been calcined during development studies at the ICPP. Based on extensive development work performed at the ICPP, it is believed that essentially all wastes, including those from commercial aqueous-fuel reprocessing in the United States, can be processed in a fluidized bed calciner by using the proper chemical additives and suitable operating techniques.

The solids produced by calcining the ICPP wastes are porous, nearly spherical granules that are transported pneumatically to underground, stainless steel storage bins. Although leaching experiments^(3,4) have shown that significant amounts of the long-lived radioisotopes, Cs-137 and Sr-90, are leached from these calcines if they are contacted by water, the double physical barrier system (consisting of stainless bins inside concrete bins) used at the ICPP and the heat generated within the calcine itself by fission product decay, effectively prevent any water from contacting the calcine, thus assuring indefinite safe storage.

The dry, relatively inert calcine is an extremely versatile waste product, however, that can be removed from storage relatively easily and treated to modify some of its important properties. For example, methods have been developed to reduce greatly its leachability or increase its heat transfer properties or both, and many additional methods to accomplish these changes appear to be feasible, but have not been attempted. This report describes some of these possible post-calcination treatments for the product from a fluidized bed calciner.

II. PROPERTIES OF CALCINE

The high-level radioactive wastes produced at the ICPP result from the aqueous chemical reprocessing of aluminum-uranium alloy fuels and zirconium-uranium alloy fuels. In addition to aluminum and zirconium, these wastes contain nitric acid from the aluminum fuel dissolution and hydrofluoric acid from dissolution of the zirconium fuel. Calcium nitrate is added to the fluoride-containing waste just prior to calcination to produce calcium fluoride in the calcine product thus preventing volatilization of the fluoride. The chemical and physical properties of the two types of calcine produced in the WCF are given in Tables I and II.

TABLE I
COMPOSITION AND PROPERTIES OF ALUMINA CALCINE

	<u>wt%</u>
Aluminum as Al_2O_3	88-89
Sodium as Na_2O	1.3-2.0
Nitrogen as N_2O_5	4.0
Mercury as HgO	2.9
H_2O	2.0
Gross fission product oxides	0.6
Heat generation (watts/g)	$(1.9-5.2) \times 10^{-4}$
Bulk density, g/cc	1.0-1.2
Mass median particle diameter, mm	0.56-0.70

TABLE II
COMPOSITION^(a) AND PROPERTIES OF ZIRCONIA CALCINE

	<u>wt%</u>
Zirconium as ZrO_2	21.3
Calcium as CaF_2	54.2
Aluminum as Al_2O_3	21.8
Nitrogen as N_2O_5	1.9
H_2O	0.6
Gross Fission Product Oxides	0.2
Heat generation, watts/g	$(0.7-1.3) \times 10^{-4}$
Bulk density, g/cc	1.7
Mass median particle diameter, mm	0.6-0.8

^(a) Analysis of a single sample

III. MODIFICATION OF CALCINE PARTICLES

1. COATING ON CALCINE PARTICLES

If each individual particle of calcine were coated with a durable and impervious coating, this coating would prevent the fission products from being leached if the calcine particles were ever contacted by water. Preliminary bench-scale studies⁽⁵⁾ showed that aluminum or steel could be sprayed onto the calcine particles in a fluidized bed to form such a protective coating. The technique used consisted of feeding a stream of metal powder into an oxy-acetylene flame where it melted immediately and was sprayed by the hot gases from the flame into a bed of alumina fluidized by air. Cross sections of samples of the alumina calcine particles coated with steel and aluminum are shown in Figures 1 and 2.

Recent experiments⁽⁶⁾ in the ceramics industry demonstrated that a unique combination of alumina and titania could be plasma flame sprayed to deposit an unusually dense coating on various metals without using a sealer. The coating had excellent wear resistance, low permeability, and good resistance to corrosion. This is another example of a type of coating that presumably also could be used to coat calcine particles.

2. INVESTMENT IN MATRICES

The calcine particles individually have a high intra-particle porosity, and being granular, also have a considerable inter-particle void space when stored in a bin. If this total void space, which may amount to as much as 70% of the total volume, were filled with a highly insoluble, high heat-conducting matrix, the leachability of the fission products

Figure 1 Calcined Alumina Particles Coated with Aluminum

Figure 2 Calcined Alumina Particles Coated with Steel

contained in the calcine would be greatly reduced, and the heat transfer properties would be significantly increased. Several scoping experiments^(7,8) have been run at the ICPP to incorporate the calcine into a matrix using various materials.

2.1 Metals

Calcined alumina solids were imbedded in both aluminum metal and a tin-lead mixture by packing the calcine in a stainless steel tube, then filling the void spaces with molten metal using a vacuum technique⁽⁷⁾. The tube was then cooled, allowing the metal to solidify in place. Cross sections of the two specimens with the metal container removed are shown in Figures 3 and 4. Examination of these specimens indicated that the inter-particle void space was virtually completely filled by the metal, but that the intra-particle void space was only partially filled.

By allowing the metal to extend beyond the metal oxide at both ends of the tube, a totally sealed unit is formed which is completely non-leachable until the cladding is penetrated by corrosion. Even then, only a small, highly insoluble surface is exposed, and the leachability should still be orders of magnitude less than for the granular metal oxide itself.

The heat conducting properties of the metal-metal oxide system is relatively high by virtue of the metal matrix. Calculated thermal conductivities for an aluminum oxide-aluminum system indicate that the thermal conductivities may be as much as 100 times greater than for the aluminum oxide alone. Thus, the metal matrix should be particularly useful in treating waste of high fission product content, which requires the dissipation of large amounts of heat.

Figure 3 Calcined Alumina Particles (+100 - 60 mesh) Imbedded in an Aluminum Matrix

Figure 4 Calcined Alumina Particles (~12 mesh) Imbedded in a Tin-Lead Matrix

2.2 Salts

Scoping studies were made⁽⁸⁾ on a laboratory scale to determine if a molten inorganic matrix could be used to fill the intra-particle as well as the inter-particle voids of the calcine. The ability of molten inorganic salts to wet the alumina calcine was considered to be a measure of their ability to fill the intra-particle voids.

These materials were tested for wettability by heating in a muffle furnace with calcined alumina at temperatures slightly above the melting point of the matrix material. Samples were then mounted in plastic and examined under a stereoscopic microscope for completeness of coating and penetration. Table III is a summary of the results.

TABLE III
WETTABILITY OF CALCINED ALUMINA WITH VARIOUS MATERIALS

<u>Materials Which Wet</u> <u>Calcined Alumina</u>	<u>Melting Point</u> <u>(°C)</u>	<u>Materials Which Do Not</u> <u>Wet Calcined Alumina</u>	<u>Melting Point</u> <u>(°C)</u>
Bismuth trioxide	820	Aluminum	660
Cupric bromide	504	Antimony trioxide	656
Cupric chloride	422	Lead	327
Lead chloride	501	Lithium fluoride	855
Lead fluoride	855	Potassium fluoride	870
Lead oxide (litharge)	888	Sodium fluoride	990
Lithium carbonate	618	Sodium pyrophosphate	880
Molybdenum trioxide	795	Tellurium	450
Potassium chromate	968	Tin	232
Potassium fluoborate	530	Zinc	420
Sodium tetraborate	741	Zinc orthophosphate	900
Sodium carbonate	851		
Sulfur	119		
Vanadium pentoxide	690		

In general, the oxides and chlorides wet the alumina in an air atmosphere while the metals do not. Mixtures of salts and oxides, which were blended to produce lower melting points or less costly matrices, also coated the alumina calcine particles. Mixtures which were tested include lead oxide and vanadium oxide at PbO-to-V₂O₅ weight ratios of 55/45 (M.P. 475°C) and 94.6 (M.P. 760°C), mixtures of lead oxide and lead chloride at PbO-to-PbCl₂ weight ratios of 70/30 (M.P. 700°C) and 20/80 (M.P. 430°C), and mixtures of lead sulfide and lead chloride with PbS-to-PbCl₂ weight ratios of 20/80 (M.P. 430°C), 35/65 (M.P. 560°C) and 60/40 (M.P. 835°C).

The results indicated that some of the salts and oxides could be used as matrices for filling the inter- and intra-particle voids in calcined waste. By mixing salts and oxides, there are a large number of prospective matrices that will wet the calcined alumina; consequently, matrices can be selected for various process conditions and to achieve the characteristics desired. By blending, low cost mineral dressed ores or refined chemicals possibly could be used to produce mixtures for a process.

2.3 Asphalt

A method for incorporating radioactive liquid wastes into asphalt has been developed at ORNL⁽⁹⁾. This method requires that the wastes have low heat generation rates or be stored in small geometries because of the fluid nature of the asphalt mixture at moderate temperature and because of susceptibility of the asphalt to radiation damage⁽⁹⁾.

Calcine probably could be incorporated readily into emulsified asphalt. The volume of the calcine would not change since the asphalt would be used merely to fill the inter- and intra-particle void spaces, thus immobilizing the individual particles and reducing the leachability of the radionuclides.

The maximum activity level of the ORNL asphalt-waste product used in the development work contained about 52 curies of mixed fission products per gallon of waste product. This would have a calculated heat generation rate of about 8.5×10^{-5} watts/g assuming that the waste solid was calcine containing a fission product spectrum similar to that in MTR-type calcined waste aged for two years. This level of activity produced an internal radiation dose of 1×10^8 rads over 838 days, and the product appeared to be physically stable; however additional studies⁽⁹⁾ indicated that the radiation damage to the asphalt probably would occur between 10^8 and 10^9 rads.

In general, susceptibility to radiation damage appears to be more likely to be the limiting factor in long term storage for an asphalt-calcine product than does self-heating. A heat generation rate of 8.5×10^{-5} watts/g would not produce a significant increase in the center line temperature of a moderate size container (a 55-gallon drum) filled with calcine.

Leaching studies⁽⁹⁾ indicated that the irradiated asphalt-waste products have a steady state value of about 4×10^{-4} (fraction leached) (sq-cm per gram)⁻¹ day⁻¹. Calcine incorporated into an asphalt matrix would be expected to have a similar leaching rate.

2.4 Plastics

The use of plastics to form a matrix for waste sludges has been investigated⁽¹⁰⁾. The technique involved stirring the sludge with molten polyvinyl chloride (PVC) or polyethylene at 160°C followed by pressing at 1500 psi and 160°C to form a solid block. Using various mixtures of polyethylene, PVC, and sludge, mixtures containing at least 60% plastics gave products that were mechanically strong,

non-porous, and of good chemical resistance. This approach probably could be adapted to the treatment of calcine; however, this technique apparently is limited to a radiation dose limit of about 2×10^8 rads⁽¹⁰⁾, so that susceptibility to radiation damage would limit this process as it does the asphalt process, to moderate-level activity waste in which radiation damage rather than self-heating becomes the limiting factor.

Bench-scale laboratory tests at the ICPP demonstrated that alumina calcine was effectively retained in a plastic matrix by mixing dry calcine and polystyrene beads (2 volumes calcine/3 volumes polystyrene) then heating to about 180° to 200°C. No stirring or pressure was used. A cross section of a sample prepared in this manner is shown in Figure 5.

A similar approach, that appears promising but has not yet been tried, consists essentially of filling the void spaces in a bed of calcine with a liquid monomer, such as styrene, then polymerizing this in situ by heating. Reportedly⁽¹¹⁾ styrene can be polymerized to form a hard glassy solid by using 2% benzoyl peroxide as a catalyst and heating at 70°C for two hours. The polymerization can also be accomplished by irradiation.

One possible interesting advantage of this approach is the potential use of waste plastics as the source of matrix material. Chemical Week⁽¹²⁾ estimates that by 1976, the plastic wastes generated in the U. S. will amount to at least six billion and may be as high as 11 billion pounds per year. Blanco⁽¹³⁾ estimates the annual solid waste production from high level waste in the U. S. will be 3,300 ft³/yr by the year 1980. Assuming that the total solid waste volume produced was three times higher due to wastes other than high-level (10,000 ft³/yr) and that all of it could be treated with plastic, approximately 15,000 ft³ of plastic would be needed. Since six billion pounds of plastic would amount to about 1×10^8 ft³, the amount of waste plastic available would be several orders of magnitude greater than that needed to treat all of the radioactive waste solids produced by the nuclear industry in the U. S. The cost of collecting and delivering the plastics to a treatment plant would, of course, be a critical factor in determining the feasibility of using waste plastics.

Figure 5 Calcined Alumina Particles Imbedded in a Plastic Matrix

2.5 Concrete

The use of Portland cement to form a concrete incorporating radioactive solid or liquid wastes into the mix has received widespread

attention since the advent of the atomic energy industry. A Portland cement-type concrete could be used to fill the inter-particle void spaces simply by mechanically mixing the calcine with a wet concrete mix. Some filling of the intra-particle voids would also occur. Recent studies⁽¹¹⁾ have shown that preformed Portland cement can be fully impregnated with a monomer and the monomer polymerized in situ either by radiation or by thermal-catalytic techniques. The resulting concrete-polymer product shows a remarkable improvement in properties over ordinary concrete. Among the property changes are a four-fold increase in compressive strength and tensile strength, and a decrease in water permeability and corrosion by distilled water to negligible values. The first two property changes would minimize the amount of reinforcing required to maintain structural integrity. The last two changes would be valuable in a radioactive waste product for long-term storage. These changes in the properties of Portland cement possibly could be accomplished during storage by using the heat and radiation that would be generated by the radioactive calcine itself.

Portland cement-type concrete has been used in prestressed concrete-pressure-vessels and the effect of temperature (up to 260°C) on the properties of the concrete studied⁽¹⁴⁾. The results of the study indicate that degradation of the concrete consisted of a decrease in the compressive and flexural strength and the modulus of elasticity. Temperatures up to 120°C were considered suitable for reactor vessels; however, temperatures up to 260°C may be suitable for waste treatment since the structural integrity requirements would be less demanding. Temperatures up to 260°C would permit the use of concrete for MTR-type calcine in moderate size storage containers such as 55 gallon drums.

Gamma radiation also causes loss of strength in concrete but only at high total doses. Loss of strength was observed in 3-inch diameter concrete specimens irradiated up to 10¹¹R in the Materials Testing Reactor Canal at the National Reactor Testing Station⁽¹⁵⁾.

2.6 Grout

A considerable amount of laboratory and field work has been done to develop hydraulic fracturing as a method for disposal of radioactive wastes⁽¹⁶⁾. In this approach, liquid waste is mixed with cement and injected into a well casing extending 1500 to 2000 feet into the ground. When pressure is applied, the liquid grout is extruded through a slot near the bottom of the casing. This fractures the shale enough to accommodate a horizontal layer of grout extending out as much as 1000 feet. The grout hardens into a hard insoluble cement. The "setting time" for the grout is determined by the composition of the mixture. A modification of this technique conceivably could be used to fill the void space in a bed of calcine. Water could be used to prepare the grout instead of waste and, if desired, the grout mixture might be added directly to a storage bin to "fix" the calcine in the form of a large, solid mass.

3. CHANGE OF PHYSICAL FORM

3.1 Formation of a Homogeneous Glass

One of the most widely studied methods for treating highly radioactive wastes is to convert the wastes to glass-like solids. The alumina calcine produced in the WCF is particularly suitable for conversion to a glass, because all of the liquid phase has already been removed, and laboratory experiments⁽¹⁷⁾ have shown that it is only necessary to add the appropriate fluxing agents and apply heat to convert the granular alumina to a good quality glass.

A phosphate glass was prepared from calcine at the ICPP by remote handling techniques using full-level radioactive calcine from the WCF. Alumina calcine, sodium monobasic phosphate, and lead oxide were mixed dry and heated to 400°C to remove the water from the phosphate. They were then fused at 900°C for 16 hours in porcelain crucibles. After fusing, the glass was molded in graphite crucibles at 600°C and cooled slowly from four to five hours to anneal the specimens. Molds of known dimension were used so that the surface area could be determined accurately.

Glass specimens prepared from 25 weight percent non-radioactive calcine are shown in Figure 6. These specimens were homogeneous and had no visible defects. The reduction in waste volume produced by calcining to alumina in the WCF is approximately 10, whereas there is a volume increase of about 1.3 produced by converting alumina to a homogeneous glass. This gives an overall volume reduction of about 7.7 which is within the range for results reported for direct vitrification of a similar type waste starting with a waste solution⁽¹⁸⁾.

Laboratory tests indicated initial leaching rates for the glass prepared at the ICPP of about 10^{-4} decreasing to $<10^{-6}$ grams of glass/cm²-day after about 5 weeks. These rates were determined by measuring the amount of aluminum, Cs-137, and Sr-90 in the leaching solution. The leaching rate of the glass was about three orders of magnitude less for the glass than for the untreated calcine.

Figure 6 Alumina-Phosphate Glass
Prepared from Non-Radioactive WCF
Calcine

3.2 Formation of a Glass with Excess Calcine

In a modification of the preceding method, phosphate glass was prepared by fusion of the calcine with sodium phosphate and lead oxide,

then fresh calcine was added to this melt until the molten glass became in effect a matrix. When this mixture cooled, the inter- and intra-particle pore spaces of the undissolved calcine were essentially completely filled with molten glass.

A slight variation of this approach, which was considered but not tried, was to use a commercial type glass, preferably scrap materials such as old bottles, etc. to form the glass matrix. Some laboratory studies were done at ORNL⁽¹⁹⁾ using this approach with a synthetic Purex waste powder and lead-silicate glasses.

3.3 Glass Making Chemicals Added to Calciner Feed

As another alternative to adding fluxing materials to the calcine and heating to form a glass, chemicals may be added to the feed solution so that the resulting calcine would only need to be heated to convert it to a glass. At Brookhaven National Laboratory a process has been developed⁽²⁰⁾ in which phosphoric acid is added to aqueous waste, the waste mixture evaporated, and the residual solids heated to form a glass. This process is being developed on a pilot-plant scale at Battelle Northwest Laboratory⁽²¹⁾. A similar treatment of the aluminum nitrate-nitric acid raffinate used as feed to the WCF presumably would require only that phosphoric acid or sodium phosphate and a lead salt be added to the feed and the calcine heated to an elevated temperature to convert the granular material to a glass.

Recent experiments at the ICPP indicate that the calcine prepared by calcining synthetic zirconium fluoride-type waste solutions already contains the necessary materials to form a hard sintered mass if heated to at least 1000°C. Calcium fluoride resulting from the addition of calcium nitrate to the feed solution, apparently has sufficient fluxing power to cause the individual particles to fuse together. X-ray diffraction patterns indicated that ZrO_2 and CaF_2 were still present as crystalline identities up to at least 1200°C. Additional investigations are currently underway to better define the physical and chemical changes occurring at elevated temperatures, and the effect these changes may have on the leachability of the product.

4. CANNING

An obvious approach which might be considered is to put the calcine in small containers and transfer these to a central storage place. This would require removing the calcine from the stainless steel bins, placing it in containers that can be sealed, and transferring it to a new location such as a salt mine, deep cavern, a deep trench in the ocean, or possibly even shooting it into the sun using rocket power. This approach would, of course, require high integrity shipping containers and specially developed handling procedures. A complete evaluation of the economics, safety, and other consequences of such a transfer would be required to judge the applicability of this method.

5. REMOVAL OR FIXATION OF FISSION PRODUCTS

5.1 Leaching of Fission Products

Attempts were made to remove the fission products from both alumina and zirconia calcine by leaching with water^(3,4). In both materials, the Cs-137 and Sr-90 were leached at a significant rate by distilled water while the radionuclides Ru-106, Ce-144, and Pu-239 were highly resistant to leaching. Although less than 50% of the Sr-90 and about 60-90% of the Cs-137 were removed by leaching for approximately 2000 hours, the rate of leaching of both radioisotopes had decreased 2-3 orders of magnitude at the end of the leaching period. Thus, the leachability had been decreased significantly; however, the benefits of this decreased leaching rate would have to be balanced against the cost of leaching the calcine, redrying it after leaching, and disposing of the leaching solution containing Cs-137 and Sr-90.

5.2 Volatilization of Fission Products

Scoping experiments using WCF calcine demonstrated that Cs-137 and Ru-106 can be volatilized from calcined alumina by heating to 800°C or higher^(22,23). Probably 90% or more of both radioisotopes can be volatilized by heating to 1000°C or higher, and recent experiments indicated that the rate of removal is accelerated greatly when a gas purge is used.

Heating the calcine to volatilize Cs-137 also converts the amorphous alumina calcine to a crystalline form, usually alpha alumina. Recent experiments indicated that during the conversion of alumina from the amorphous to a crystalline form, the Sr-90 was apparently "fixed" in a crystalline lattice, because the amount leached by distilled water from the crystalline material was only about one-tenth of that leached from the amorphous calcine.

Volatilization or fixation of the fission products by heating followed by a water leach to remove the remaining Cs-137 and Sr-90 that are readily leachable is a relatively unexplored approach. A considerable amount of study would be required to determine if it is a feasible method.

IV. DISCUSSION AND CONCLUSIONS

Some of the possible approaches that have been considered for modifying the properties of WCF calcine are summarized in Table IV.

TABLE IV
POSSIBLE METHODS OF MODIFYING PROPERTIES OF WCF CALCINE

<u>Property to be Modified</u>	<u>Method used to Modify Property</u>
1. Leachability (decreased)	Coating of Particles Investment of Particles in a Matrix Convert to a Glass Can Post-Calcination Removal of F. P.
2. Thermal Conductivity (increased)	Coating of Particles (minor effect) Investment of Particles in a Matrix Convert to Glass
3. Physical Dispersability (decreased)	Coating of Particles (minor effect) Investment of Particles in a Matrix Convert to a Glass Can

As indicated in Table IV, several methods for reducing the leachability are possible. In general, most of these methods will reduce the rate of leaching by two or more orders of magnitude, but zero leachability is obtained only when the treatment includes complete encapsulation of the product.

The highly porous, granular oxide has a low thermal conductivity as stored in bulk; however, this characteristic is countered somewhat by the good chemical stability of the system which permits high center-line storage temperatures, presumably up to the melting point of the oxide mixture. Nevertheless, the thermal conductivity probably can be increased significantly by any method that fills the void spaces, particularly if both the inter- and intra-particle void spaces are filled.

The granular calcine can be relatively easily dispersed by air or mechanical means if not contained. To reduce this tendency for easy dispersal, it is only necessary to use a method that binds the particles to each other or that fuses them into a solid mass. Canning, of course, simply provides another barrier if the particles in the can are not further treated. Coating the particles produces a minor resistance to dispersal by providing the particle with a higher density and a greater physical resistance to mechanical breaking.

The calcine normally is considered to have high chemical stability; however, some of the methods listed in Table IV produce a material with even greater chemical stability after treatment. For example, in some cases the treatment itself involves heating, which releases volatile constituents such as mercury or nitrate. The residue is then, in a sense, more stable chemically due to the removal of these volatile constituents and presumably could be permitted to attain a center line temperature near the melting point of the oxide mixture.

The formation of an insoluble coating or solid matrix has little effect on the calcine itself, but the fission products are less available for reactions with water. The formation of a glass produces a solid that is highly stable with respect to leaching by water, but it is worthy of note that, in most cases, the fusion process makes the glass readily soluble in mineral acids, so that recovery of valuable by-products from a glass is still quite feasible technically. The glass is also subject to radiation damage and possible devitrification during long-term storage, and the center line temperature of the glass must be maintained below the melting point.

Although the present method of storing the calcine in a retrievable form is considered to be adequate for WCF calcine at the ICPP, methods are available that will convert radioactive calcine to an even safer form if the need to do so exists at other fluidized bed installations or if the incentive to do so arises at some future date at the ICPP.

V. REFERENCES

1. R. E. Commander, et al, Operation of the Waste Calcining Facility with Highly Radioactive Aqueous Waste, IDO-14662 (June 1966).
2. G. E. Lohse, et al, "Calcination of Zirconium Fluoride Wastes in Pilot-Scale and Plant-Scale Fluidized Beds," presented at the Symposium on Fluidization at the Tripartite Chemical Engineering Conference at Montreal, Quebec (September 1968).
3. B. E. Paige, Leachability of Alumina Calcine Produced in the Idaho Waste Calcining Facility, IN-1011 (July 1966).
4. M. W. Wilding and D. W. Rhodes, Leachability of Zirconia Calcine Produced in the Idaho Waste Calcining Facility, IN-1298 (June 1969).
5. E. S. Grimmett, Idaho Nuclear Corporation, private communication (April 1969).
6. G. Dwimann and F. N. Longo, "Plasma-Sprayed Alumina-Titania Composite", American Ceramic Society Bulletin, 48 (February 1969) pp. 221-224.
7. James M. Morgan, Jr., Donald K. Jamison, and John D. Stevenson, Editors, Fixation of Radioactivity in Stable, Solid Media, TID-7613, Book 2 (September 1960).
8. J. R. Bower, Editor, Chemical Processing Technology Quarterly Progress Report April - June, 1963, IDO-14621 (January 1964)
9. H. W. Godbee, et al, "Development of a Process for Incorporation of Radioactive Waste Solutions and Slurries in Emulsified Asphalt", Environmental Science and Technology, 2 (November 1968) pp. 1034-1040.
10. M. J. Smyth and A. K. Ripon, The Use of Thermoplastics for the Fixation of Radioactive Wastes, AERE-M-1858 (March 1967).
11. M. Steinberg, et al, Concrete-Polymer Materials, First Topical Report, BNL 50134 (T-509) (December 1968).
12. R. R. Schulz, Editor-in-Chief "Industry Arms for War on Waste", Chemical Week (January 1968).
13. R. E. Blanco, et al, "Future Magnitude and Proposed Solutions of the Waste Disposal Problem", presented at the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, CONF-660208 (February 1966).
14. D. L. Brinkimer, et al, Heat-Resistant Concrete for Prestressed-Concrete-Pressure-Vessel (PCPV) Reactors, BMI-1855 (January 1969).
15. J. F. Sommers, Gamma Radiation Damage to Structural Concrete Immersed in Water, Health Physics, Vol. 16, pp. 503-508 (April 1969).

16. W. deLaguna, et al, Engineering Development of Hydraulic Fracturing as a Method for Permanent Disposal of Radioactive Wastes, ORNL-4259 (August 1968).
17. B. E. Paige, Leachability of Glass Prepared from Highly Radioactive Calcined Alumina Waste, IDO-14672 (February 1966).
18. H. W. Godbee, et al, "Physical Properties of Solids Incorporating Simulated Radioactive Wastes", presented at the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, CONF-660208 (February 1966).
19. H. W. Godbee, et al, Dispersion of Simulated High-Level Radioactive Waste Powders in a Glass Matrix, ORNL-TM-1897 (August 1967).
20. E. J. Tuthill, et al, "Brookhaven National Laboratory Process for the Continuous Conversion of High-Level Radioactive Waste to Phosphate Glass", presented at the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, CONF-660208 (February 1966).
21. K. J. Schneider and V. P. Kelley, Waste Solidification Program, Design Features of the Waste Solidification Engineering Prototypes, BNWL-968 (February 1969).
22. M. W. Wilding and D. W. Rhodes, Stability Studies of Highly Radioactive Alumina Calcine During High Temperature Storage, IDO-14670 (January 1966).
23. J. R. Bower, Editor, Chemical Technology Branch Annual Report, Fiscal Year 1967, IN-1087 (October 1967).