FIXATION OF RADIOACTIVE WASTE
BY REACTIONS WITH CLAYS:
PROGRESS REPORT

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ABSTRACT

Reactions of clay with Hanford-type radioactive wastes (liquids, salt cake, and sludge) were studied as a means of immobilization of radionuclides contained in the waste. Products of these reactions were identified as the crystalline sodium aluminosilicates, cancrinite and nepheline. Radionuclides are entrapped in these crystalline minerals. Conceptual flow diagrams for conversion of high-salt wastes to cancrinite and nepheline were defined and tested. The mineral products were evaluated for use as forms for long-term storage of radioactive waste.

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INTRODUCTION

This work is a continuation of that reported in 1974^[1] concerning the immobilization of radioactive waste generated by reprocessing of nuclear fuel at Hanford. Conversion of present wastes to a more immobile form may be necessary to prevent migration of hazardous radionuclides into the biosphere during long-term storage. Prior work showed that the major radioactive elements in the waste, cesium and strontium, could be fixed by reactions of aqueous waste with aluminum silicate clays. These reactions yielded cancrinite, a sodium aluminosilicate mineral which entraps waste salts in its crystalline lattice structure. Some of the relevant chemical and physical properties of the cancrinite product were determined, such as leach rate, thermal stability, volume, hardness, and crystal size. These studies showed cancrinite to be a promising storage form for radioactive waste.

The objectives of the present work were to further evaluate cancrinite as a waste form, identify and quantify important reaction variables, and evaluate process alternatives. Application of clay reactions to fixation of the three major types of waste stored at Hanford [salt cake, sludge, and caustic terminal liquor (from liquid waste evaporation)] was studied.

SUMMARY AND CONCLUSIONS

Additional characteristics of reactions of clays with Hanford wastes were studied. The rate of cancrinite formation by reaction of caustic waste liquor with calcined clays (kaolin, bentonite) is 5 to 30 times greater than for uncalcined clays. Half-times for the calcined kaolin reactions at 100, 75, and 50° C are, respectively, <0.2, 0.7, and 4 hours. The corresponding half-times for calcined bentonite reactions are 0.1, 0.6, and 6 hours. Measurements of cesium uptake during cancrinite formation show that the amount of cesium entrapped increases as more cancrinite is formed. There is, however, a large initial amount of cesium on bentonite due to ion exchange.

Heats of reaction were measured for reactions of synthetic caustic waste solution with calcined and uncalcined clays (kaolin and bentonite). Values for the uncalcined clays were significantly less (kaolin = -49.5 ± 3.6 cal/g, bentonite = -46.7 ± 1.3 cal/g) than for the same clays after calcination (kaolin = -190.7 ± 3.5 cal/g, bentonite = -105.9 ± 3.2 cal/g). Results of measurements using several different commercially available calcined kaolins show that the source of the clays significantly affects the heat of reaction. Estimated values for the rise in temperature of a 1 g clay/ml waste range from 38 to 41° C for uncalcined clays to 87 to 156° C for calcined clays (assuming adiabatic conditions).

A conceptual flow diagram is presented in which caustic (terminal) liquor, salt cake, and dissolved salt cake are converted to cancrinite or nepheline. Three basic process alternatives are given:

1. The Rich Clay process in which a stoichiometric excess of clay is mixed with liquid waste and reacted to form a cancrinite-clay-salt mixture.

2. The Lean Clay process in which clay and liquid waste are converted to relatively pure cancrinite by control of the mole ratios of reactants. A binder is used to form a massive product from the small cancrinite crystals.
3. The Clay Calcination process in which solid or liquid waste is mixed with clay and fired at 600 to 1000° C to form a nepheline product.

Products from each of these processes were evaluated with respect to leach rate, thermal and radiation stability, mechanical strength, volume, and density. A comparison of product properties (Table I) shows that application of the Lean Clay process to salt cake yields an unmanageably high volume of product. Thus, the Lean Clay process can be eliminated from further consideration except, perhaps, for applications where product volume is not important. The Clay Calcination alternative yields a product with improved leachability, mechanical strength, thermal and radiolytic stability, and a significantly lower volume than the other processes. The principal disadvantages are, of course, the higher processing temperature and the necessity for off-gas treatment.

EXPERIMENTAL

MATERIALS

Forty-nine commercially available bentonites and calcined and uncalcined kaolins were screened for product quality. In addition, some calcined bentonites and kaolins were prepared by heating the clays at 600 to 700° C for 6 to 48 hours. Compositions of fired and unfired bentonites and kaolins used in most experiments are given in Table II.

TABLE I
COMPARISON OF ALTERNATIVE CLAY FIXATION PROCESSES

<u>Product Characteristics</u>	<u>Rich Clay Process</u>	<u>Lean Clay Process</u>	<u>Clay Calcination Process</u>
Mineral form	Cancrinite	Cancrinite	Nepheline
Volume	1.3 x caustic terminal liquor 3 x salt cake	2 x caustic terminal liquor 6 x salt cake	0.8 x caustic terminal liquor 1.5 x salt cake
Leachability, g/cm ² -day	10 ⁻⁴ to 10 ⁻²	10 ⁻⁵ to 10 ⁻³	10 ⁻⁵ to 10 ⁻³
Thermal and radiolytic stability	Good	Good	Excellent
Mechanical strength	Poor-to-good	Excellent	Excellent
Bulk density, g/ml	1.5 to 1.7	1.6 to 2.0	1.6 to 2.0

TABLE II
COMPOSITIONS OF CLAY REAGENTS*

Component	Weight Percent of Component in								
	Bentonite #1	Bentonite #2	Calcined Bentonite #1	Calcined Bentonite #2	Kaolin #1	Kaolin #2	Calcined Kaolin #1	Calcined Kaolin #2	Mixed Kaolin Bentonite
SiO ₂	66.8	59.9	72.5	64.3	45.30	46.9	52.8	54.4	49.6
Al ₂ O ₃	16.4	19.8	17.8	21.3	38.38	38.2	44.7	44.3	33.3
Na ₂ O	2.48	2.2	2.7	2.4	0.27	0.04	0.31	0.05	0.4
Fe ₂ O ₃	3.4	3.9	3.7	4.2	0.30	0.35	0.35	0.41	1.2
MgO	1.84	1.3	2.0	1.4	0.25	0.58	0.29	0.67	0.1
CaO	2.77	0.6	3.0	0.6	0.05	0.43	0.06	0.50	0.2
H ₂ O	8.0	6.5	0	0	13.97	13.9	0	0	12.8
TOTAL	101.7	94.2	101.7	94.2	98.52	100.4	98.5	100.3	97.6

*Sources of clay reagents:

Bentonite #1:	MC-101, Georgia Kaolin Company
Bentonite #2:	Wyo-Bond, Federal Bentonite Company
Calcined Bentonite #1:	Calcined MC-101, 700°C for 24 hours
Calcined Bentonite #2:	Calcined Wyo-Bond, 700° C for 24 hours
Kaolin #1:	Astra-Glaze, Georgia Kaolin Company
Kaolin #2:	6-Tile, Georgia Kaolin Company
Calcined Kaolin #1:	Calcined Astra-Glaze, 700° C for 24 hours
Calcined Kaolin #2:	Calcined 6-Tile, 700° C for 24 hours
Mixed Kaolin-Bentonite:	Indian Hill, Interpace Corporation.

A number of synthetic and genuine waste solutions were used. The compositions of these solutions are given in Table III along with the synthetic salt cake composition used. Table IV shows the composition of the genuine Purex sludge employed in one experiment. Materials used to formulate the synthetic wastes were reagent grade.

TABLE III
COMPOSITIONS OF SYNTHETIC AND GENUINE WASTES

Component	Molar Concentrations of Components in Caustic Terminal Liquor				Weight Percent Component in Salt Cake
	Synthetic Waste #1	Synthetic Waste #2	Synthetic Waste #3	Genuine Waste*	
NaOH	3.6	3.0	10.0	3.42	10
NaNO ₃	3.4	2.5	2.0	2.84	60
NaNO ₂	2.1	0	0	1.67	20
NaAlO ₂	1.8	1.0	0	1.99	0
Al(OH) ₃	0	0	0	0	10
H ₂ O	40	-	-	-	0

*From Hanford Waste Tank 241-BX-110, also containing 3.47×10^5 $\mu\text{Ci/liter}$ ^{137}Cs .

TABLE IV
COMPOSITION OF HANFORD WASTE TANK 241-A-104 SLUDGE

<u>Component</u>	<u>Concentration</u>
H ₂ O	42%
Al	2.82M
Si	0.83M
Fe	4.99M
Mg	0.11M
Cd	0.41M
Ba	0.009M
Mn	0.71M
Sr	<0.055M
$^{89+90}\text{Sr}$	4.39×10^7 $\mu\text{Ci/liter}$
^{137}Cs	1.15×10^6 $\mu\text{Ci/liter}$
^{134}Cs	3.33×10^4 $\mu\text{Ci/liter}$
^{239}Pu	0.11 g/liter
Density	1.64 g/ml

Several organic and inorganic binders were evaluated. Forty-one Baume sodium silicate solutions mixed with zinc oxide or calcium oxide gave one type of inorganic binder. Portland type III cement (Kaiser Cement and Gypsum Corporation) was the other inorganic binder tested. Polystyrene and polymethylmethacrylate were the organic binders. All binders except the portland cement were reagent grade.

ANALYSES

Elemental analyses of the solid products were obtained by fusing the sample with lithium metaborate at 1000° C and then dissolving the melt in 10% HCl. The resulting solutions were analyzed by atomic absorption. Nonradioactive cations in the leachates were also analyzed by atomic absorption. Elemental analyses of most of the clays were supplied by their vendors.

Analyses for cesium and ruthenium were performed by gamma energy analysis. Radiostrontium was determined by an extraction, mounting, and counting technique and plutonium by thenoyltrifluoroacetone extraction followed by both total alpha and alpha energy analyses.

Crystalline products were identified by powder X-ray diffraction. Unconfined compressive strength was measured with a soil penetrometer. Thermal stabilities of products and extents of product formation were determined by differential thermal and thermogravimetric analyses. Scanning electron microscope (SEM) photographs were made to determine product particle sizes and shapes.

PROCEDURES

For most waste solution reactions, measured amounts of clay and waste solution were mixed thoroughly in

polyethylene or polypropylene bottles. The bottles were then sealed and placed in a constant temperature oven set at 30 to 100° C. For reactions of clay with sludge, measured portions of clay, sludge, and 50% caustic solution were mixed. The mixtures were then cast as cylinders and reacted at 70° C in a sand heat bath. Reaction mixtures of clay with salt cake were mechanically blended, then fired at 900 to 1000° C.

Binders were blended with washed and powdered products to form massive products of reduced surface area. Polystyrene and polymethylmethacrylate binders were prepared by mixing the monomers (plus catalyst) with powdered products and curing at 50 to 70° C. Mixtures of aluminosilicate products, portland cement, and water were cured in sealed containers for a minimum of 21 days. Mixtures of aluminosilicate products and sodium silicate solution (using zinc or calcium oxide as hardeners) generally were cured by heating to 100° C for several hours.

For kinetic experiments, the clays and waste solutions were allowed to reach reaction temperature overnight. To begin the reaction, waste solution was measured and rapidly added to the clay using a plastic syringe. Samples were removed periodically from the reaction oven and immediately filtered to terminate the reaction. The filtrate was collected and the solids washed with distilled water. The solids were air-dried, weighed, and analyzed.

Massive pieces of final products (powdered products which were bound) were leached according to the standard method proposed by the International Atomic Energy Agency.^[2] Following this method, the sample was placed in a plastic container and covered with distilled water as leachant. The distilled water was renewed periodically. Leachates from

this method were analyzed for cesium and occasionally for strontium, plutonium, or ruthenium-rhodium. Geometric surface areas (rather than B.E.T. or true surface areas) were used to calculate leach rates for the massive samples.

Heats of reaction were determined by reacting synthetic waste #3 with a substoichiometric amount of clay. These reactions were run in an isoperabol reaction calorimeter.

The radiolytic stability of certain reaction products was investigated using a 3×10^5 curie cobalt-60 source. At the irradiation site, samples received a dose rate of 2×10^5 rads per minute. After irradiation, the samples were analyzed gravimetrically by X-ray diffraction, by thermal analysis, and by scanning electron microscopy.

RESULTS AND DISCUSSION

REACTION CHARACTERISTICS

Three specific reaction characteristics for reactions of clay with radioactive waste were studied. These characteristics were stoichiometry, kinetics, and heats of reactions.

Stoichiometry

The principal products obtained from reactions of clays with Hanford wastes are sodium nitrate cancrinite, $2(\text{NaAlSiO}_4) \cdot 0.52\text{NaNO}_3 \cdot 0.68\text{H}_2\text{O}$, and nepheline, NaAlSiO_4 . The stoichiometry of the formation of cancrinite from kaolin or bentonite and waste liquor has been reported.^[1] Sodium nitrate cancrinite is converted to nepheline by heating above 530°C .^[3] Nepheline may also be synthesized directly from sodium nitrate salt cake and kaolin according to the idealized reaction

by heating mixtures of the reactants above 600° C. Other sodium salts (*i.e.*, NaNO_2 , Na_2CO_3) can be substituted for NaNO_3 in this reaction if they decompose to form Na_2O at the reaction temperatures.

Kinetics

The kinetics of reactions of uncalcined kaolin and bentonite to form cancrinite from standard synthetic waste solution have been reported.^[1] The kinetics of the reactions of calcined kaolin #1 and calcined bentonite #1 with synthetic waste #1 were studied at three temperatures: 50, 75, and 100° C. The course of these reactions was followed by analysis of sodium in the solids at various times.

Reaction rate curves for the calcined kaolin-waste reaction and the calcined bentonite-waste reaction at the three reaction temperatures are shown in Figures 1 and 2, respectively. It should be pointed out that there was an excess of clay in these experiments, thus leaving unreacted clay in the solids.

As expected, the calcined clays show an increasing reaction rate with temperature. Additionally, the half-times of reaction for these calcined clays are 5 to 30 times less than those for the corresponding uncalcined clays. Table V compares the rate data for the calcined and uncalcined clays.

The kinetics of cesium uptake by the calcined and uncalcined #2 clays (bentonite and kaolin) was studied. Synthetic waste #2, spiked with radioactive cesium, was reacted with those clays at 100° C. The extents of cesium

FIGURE 1
EFFECT OF TEMPERATURE ON REACTION RATE (CALCINED KAOLIN-WASTE)

FIGURE 2
EFFECT OF TEMPERATURE ON REACTION RATE (CALCINED BENTONITE-WASTE)

uptake were determined by analysis of the radiocesium present in the washed product solids.

TABLE V
COMPARISON OF REACTION HALF-TIMES*
FOR UNCALCINED AND CALCINED CLAYS

<u>Temperature, °C</u>	<u>Kaolin</u>		<u>Bentonite</u>	
	<u>Uncalcined</u>	<u>Calcined</u>	<u>Uncalcined</u>	<u>Calcined</u>
100	1	0.2	1	0.1
75	10	0.7	9	0.6
50	150	4	60	6

*All half-times given in hours.

Figure 3 shows the cesium uptake (fraction of cesium in the liquid waste reporting to solid phase) curves for calcined and uncalcined bentonite. Both curves show rapid initial cesium uptake which was probably due to the ion exchange with bentonite. Upon crystallization of cancrinite, however, the cesium content of the solids decreased and plateaued. The rate of cesium uptake with calcined bentonite was about double that with uncalcined bentonite.

Figure 4 gives the cesium uptake curves for calcined and uncalcined kaolin. These clays incorporated cesium smoothly and rapidly at the outset of reaction, then gradually reached equilibrium. Calcination of the kaolin reactant increased the rate of cesium uptake roughly 50-fold.

Heats of Reaction

The heats of reaction of clays with synthetic waste solution #3 were measured. This information is necessary for estimation of the temperature rise during large-scale reactions of clay-waste mixtures. Both calcined and uncalcined kaolin #1 and bentonite #1 were used in these

FIGURE 3
CESIUM UPTAKE FOR BENTONITE REACTION SOLIDS

FIGURE 4
CESIUM UPTAKE FOR KAOLIN REACTION SOLIDS

experiments in addition to calcined PAB Kaolin® (J. R. Simplot) and the calcined Kaolin Satintone 1® (Engelhard Minerals and Chemicals). The high NaOH concentration of synthetic waste solution #3 accelerated the reactions, thus diminishing heat leak and drift problems in the calorimeter. All mixtures were allowed to react at 70° C. The results of these experiments are given in Table VI. Also, an estimated temperature rise for a 1 g clay/ml waste solution is given (assuming adiabatic conditions and heat capacities of 1.0 cal/ml-°C and 0.22 cal/g-°C for the waste solution and clay, respectively).

TABLE VI
HEAT OF REACTION AND TEMPERATURE RISE FOR
CLAY-WASTE MIXTURES AT 70° C

Clay	Heat of Reaction cal/g	Estimated Temperature Rise, °C
Kaolin #1	- 49.5 ± 3.6	41
Calcined Kaolin #1	-190.7 ± 3.5	156
Calcined Kaolin (Satintone)	-128.7 ± 2.5	105
Calcined Kaolin (PAB)	-159 ± 15	130
Bentonite #1	- 46.7 ± 1.3	38
Calcined Bentonite #1	-105.9 ± 3.2	87

As expected, heats of reaction for uncalcined clays are significantly less than for calcined clays. The relatively wide range of values for different calcined kaolins is probably due to different calcination temperatures and times. The data show that heat must be removed from reacting calcined clay-waste mixtures in order to prevent overheating and possible hazardous vaporization of liquid.

Reaction curves showing the heat evolved (Q, cal/g) versus time yielded information concerning the mechanisms of the reactions. Curves for calcined and uncalcined kaolin #1 and bentonite #1 are shown in Figure 5. Each of these shows

FIGURE 5
HEAT EVOLVED (Q) VERSUS TIME
FOR CLAY-WASTE REACTIONS AT 70° C

a rapid initial exothermic reaction due to adsorption of waste solution on the clay. Values for adsorption heats range from -2.5 cal/g of clay for uncalcined kaolin to -17 cal/g of clay for uncalcined bentonite. The complex curve shown for uncalcined kaolin indicates that at least two steps (in addition to adsorption) are involved. The portion of the curve after adsorption probably reflects the destruction of the kaolin crystal structure and formation of a gel phase (as observed previously by X-ray diffraction of the solid phase during reaction). The portion of the curve after the inflection is then due to crystallization of the gel to form cancrinite.

CONCEPTUAL FLOW DIAGRAM FOR ALTERNATIVE PROCESSES

It has been shown that radioactive waste solutions containing high sodium salt concentrations can be hydrothermally reacted with clays to form cancrinite--a solid, relatively insoluble and thermally stable aluminosilicate mineral.^[1] Firing the cancrinite above 600° C yields nepheline, another durable aluminosilicate mineral. Nepheline may also be formed from kaolin and sodium salt cake waste by reaction at 600 to 1000° C. Through these two minerals and different clay and waste feeds, many varied products and product properties are available. A conceptual flow diagram for these processing alternatives is shown in Figure 6.

The simplest, least expensive route, called the Rich Clay process, yields a product with relatively higher leach rates and lower cohesion of the cancrinite particles than the other processes. Waste solution and a stoichiometric excess of clay are simply blended and allowed to react at temperatures of <100° C. The excess clay serves to bind the

FIGURE 6
A CONCEPTUAL FLOW DIAGRAM FOR THE CONVERSION OF
RADIOACTIVE WASTES TO ALUMINOSILICATE MINERALS.

cancrinite crystals together. Rich Clay products made from uncalcined clays, however, will swell and crack if soaked in water. This is due to swelling of the unreacted clay. This alternative is applicable to caustic waste solution and caustic fortified salt cake solutions.

Leach rates are improved significantly in the Lean Clay process for the following reasons: the actual surface area is reduced by more efficient binding of the cancrinite crystals and unreacted salts are washed from the product. Stoichiometric or substoichiometric amounts of clay are reacted with waste in this process so that no unreacted clay appears in the product. The cancrinite product is washed and the salt-containing wash is then recycled for reaction with fresh clay and waste. The final product is made by binding the washed crystals into massive shapes (*i.e.*, bricks) of reduced surface area. Waste solution or caustic-fortified salt cake solution may be immobilized through this alternative.

As in the Rich Clay process, the Clay Calcination process may be applied to caustic waste solutions or caustic-fortified salt cake solutions. However, in this scheme the reaction mixture is heated past the cancrinite reaction temperature to 600 to 1000° C. The product is the mineral nepheline. Leach rates are improved over Rich Clay products again because of reduced product surface area and more complete reaction of salts. In addition, water is vaporized and nitrate, nitrite, and carbonate salts are decomposed, forming gaseous products (NO_x , CO_2 , O_2) at these temperatures. The loss of these compounds improves the thermal and radiolytic stabilities of nepheline and in this respect makes nepheline a better waste form than cancrinite.

The Clay Calcination alternative may also be applied to

undissolved salt cake or sludge. Reactions at 600 to 100° C of sodium nitrate salt cake and clay yield nepheline without passing through a cancrinite intermediate. The reaction with sludge would obviously be much more complex and would probably result in more than the single nepheline phase. The clay and waste mixture may be reacted either as pressed bricks or as loose powders. In the loose powder option, the powdered reaction product would then be mixed with a binder to form a bricked product. One advantage of the bound product over the fired bricks is lower product volume. In addition, firing the loose mixture allows facile release of evolved gases (NO_x , H_2O , CO_2), thus preventing the cracks found in pre-molded nepheline products.

PRODUCT PROPERTIES

Properties of products obtained from the three alternative processes were measured and compared.

Rich Clay Process

Simply mixing and reacting a stoichiometric excess of clay with caustic waste solution results in a solid radioactive waste form which is definitely more stable than waste liquor or salt cake. Because of its simplicity, much of the initial work on Hanford waste immobilization (using clays) was concerned with this process. The Rich Clay process has fewer and simpler processing steps than the other alternatives. However, Rich Clay products are generally softer, more leachable, less cohesive, and may yield a larger volume of product per volume of waste than products from competing processes. Product properties are also the most sensitive to the nature of the clay reactant for this process.

For this reason, 49 commercially available clays were reacted by the Rich Clay process to compare product quality.

This survey aided in eliminating clays which yielded soft products, high-product volumes, or products with low liquid sorptive capacity. Clays with high cost or small material reserves were also eliminated. Calcined and uncalcined kaolin and bentonite were considered as potential reagents for the process. To the extent of the market survey, no source currently supplies calcined bentonite although kaolin is routinely calcined at many plants. Therefore limited studies were done using laboratory calcined bentonite.

The product quality survey showed that generally each of the four types of clays behaves as a group. With few exceptions, then, all calcined kaolin products have roughly the same properties. Uncalcined kaolin products are also similar among themselves as are the products of calcined and uncalcined bentonite (Table VII).

The clay/waste solution ratio is stoichiometrically high in clay in the Rich Clay process. As the clay/waste ratio increases, of course, product volume and hardness increase. The minimum amounts of clay necessary to form solid products from standard waste solutions have been defined.^[1] At a 1.0 g/ml clay/waste ratio, product volumes are roughly 45% higher than initial waste volumes for the calcined and uncalcined kaolin products and the calcined bentonite products. For uncalcined bentonite, the product volume increase is approximately 55%. For a given clay/waste ratio, product hardness decreases according to the series: calcined kaolin > calcined bentonite, kaolin >> bentonite. In all cases, product hardness may be vastly improved by driving off excess water by curing at ~100° C.

Leaching experiments performed on cylindrical samples (10-40 grams each) show that uncalcined kaolin and bentonite products swell and crack on soaking in water. In contrast,

TABLE VII
PHYSICAL PROPERTIES OF RICH CLAY PRODUCTS*

<u>Name of Clay, Source</u>	<u>Type of Clay</u>	<u>Hardness kg/cm²†</u>	<u>Volume Product/ Volume Feed</u>
BL-42, Baroid Division, National Lead Company	Bentonite	3.2	1.57
MC-101, Georgia Kaolin Company	Bentonite	3.3	1.53
Wyo-Bond, Federal Bentonite Company	Bentonite	3.5	1.50
Calcined BL-42	Calcined bentonite	18	1.43
Calcined MC-101	Calcined bentonite	9.5	1.50
Calcined Wyo-Bond	Calcined bentonite	19	1.50
KCS, Georgia Kaolin Company	Kaolin	28	1.47
Catalpo, Freeport Kaolin Company	Kaolin	28	1.40
PAB, J. R. Simplot Company	Kaolin	22	1.48
Calcined PAB,	Calcined kaolin	>45	1.47
Satintone 1, Engelhard Industries	Calcined kaolin	>45	1.40
Glomax PVR, Georgia Kaolin Company	Calcined kaolin	>45	1.40

*Products made by reaction of synthetic waste #1 at 1.0 g/ml clay/waste ratio at 60° C for 5 days.

†Hardness figure indicates pressure necessary for a cylindrical probe to penetrate 0.635 cm into product sample.

products from calcined clays remain structurally intact while leaching. In spite of cracking, uncalcined bentonite products give vastly superior leach rates over products from other clays (Table VIII).

Also to be noted from Table VIII are the substantially higher leach rate values quoted there than those reported earlier.^[1] The difference in values lies in the physical

TABLE VIII
TYPICAL BULK LEACH RATES OF RICH CLAY PRODUCTS
MADE FROM GENUINE WASTE*

Clay	Bulk Leach Rate, g/cm ² -day [†]	
	1 day	21 days
Kaolin	5 x 10 ⁻¹	3 x 10 ⁻²
Calcined Kaolin	3 x 10 ⁻¹	1 x 10 ⁻²
Bentonite	1 x 10 ⁻³	3 x 10 ⁻⁴
Calcined Bentonite	2 x 10 ⁻²	1 x 10 ⁻³
Indian Hill ®	2.6 x 10 ⁻³	6.7 x 10 ⁻⁴

*Products made at 1.0 g/ml clay/waste ratio with Hanford waste tank 241-BX-110 waste solution.

[†]Bulk Leach Rate = $\frac{(\text{fraction Cs leached})(\text{sample weight})}{(\text{geometric surface area})(\text{time})}$

form of the product. In the earlier report, powders were leached whereas this report deals with massive products. For the powder, surface areas were determined by the B.E.T. gas adsorption method. For massive samples, geometric surface areas were used because they are more easily measured and they are specified by the IAEA standard test leach procedure. Since massive Rich Clay products have rough and porous surfaces, it is clear that their true, or B.E.T., surface areas are much larger than their geometric surface areas. The surface area term appears in the denominator of the leach rate expression. Thus use of geometric surface area results in higher apparent leach rates.

A study was made to determine the effectiveness of the Rich Clay process to immobilize ¹⁰⁶Ru. Calcined and uncalcined kaolin and Indian Hill® clay were used as reactants. None of these three is effective in fixing the ruthenium from a caustic-fortified waste liquor. A simple water wash of these products resulted in a loss of ~99% of the ruthenium from the solids. It appears that ruthenium (as RuO₄²⁻) is not entrapped in the crystalline framework of cancrinite.

However, because of the short half-life (~ 1 year) of ^{106}Ru this is not considered a serious problem for long-term storage.

Rich Clay products prepared from synthetic waste solution and several different clays were irradiated to a total dose of $\sim 10^9$ rads of ^{60}Co radiation to determine their radiolytic stability. This dose is 10 times the calculated upper dose limit anticipated for Rich Clay products. X-ray diffraction analyses of the irradiated products were compared with nonirradiated control samples. Significantly, the cancrinite structure remained unchanged after irradiation. Differential thermal and thermogravimetric analyses for the irradiated and control samples were virtually identical. This indicates that radiolysis of chemically bound water and nitrate salts in these products was small at 10 rads.

The Rich Clay process was applied to Purex sludge fortified with caustic. Reaction of Purex sludge with clay but without additional caustic resulted in crumbly products. Various ratios of Indian Hill clay, Purex sludge, and 50% NaOH solution (Table IX) were reacted as pellets, then leached.

TABLE IX
FORMULATION OF RICH CLAY/SLUDGE PRODUCTS

<u>Product</u>	<u>Clay</u> <u>Weight, g</u>	<u>Sludge</u> <u>Weight, g</u>	<u>50% NaOH</u> <u>Volume, ml</u>
A	4	1	4
B	4	3	3
C	4	6	2

Table X gives the bulk leach rates of the products based on the cesium, strontium and plutonium nuclides

leached. The leach rates based on ^{137}Cs are similar to leach rates obtained for Indian Hill/waste solution products. The leach rates based on strontium and plutonium increase slightly with increasing clay/sludge ratios. The reason for this unexpected trend has not yet been determined. As in other Rich Clay products, increasing the clay/waste ratio results in increased underwater mechanical stability.

TABLE X
BULK LEACH RATES BASED ON ^{137}Cs , ^{90}Sr , AND ^{239}Pu
FOR RICH CLAY SOLIDIFIED SLUDGE PRODUCTS

Product/ Element	Bulk Leach Rate, g/cm ² -day	
	1 day	23 days
A/Cs	1.4×10^{-3}	1.6×10^{-5}
B/Cs	1.4×10^{-3}	2.9×10^{-5}
C/Cs	3.5×10^{-4}	1.5×10^{-5}
A/Sr	1.7×10^{-4}	7.5×10^{-6}
B/Sr	1.3×10^{-4}	5.7×10^{-6}
C/Sr	7.0×10^{-5}	4.6×10^{-6}
A/Pu	9.4×10^{-4}	7.6×10^{-5}
B/Pu	5.0×10^{-4}	3.5×10^{-5}
C/Pu	8.0×10^{-4}	1.7×10^{-5}

Lean Clay Process

When stoichiometric or substoichiometric amounts of clay are reacted with waste liquor or dissolved salt cake fortified with caustic to form cancrinite, significant amounts of sodium nitrate and nitrite are left unreacted in solution. Recycle of these unreacted salts with fresh caustic and clay ultimately results in total reaction of the waste solution salts and production of washed, finely crystalline ($\sim 1 \mu\text{m}$) cancrinite. These cancrinite powders have high B.E.T. surface areas which may be lowered significantly by binding the cancrinite powders. Binding lowers leach

rates both by consolidating the material to massive shapes of low geometric surface area and by coating the individual cancrinite crystals. Binders also make these products structurally more durable.

The amount of NaOH to be added to the recycle stream for the Lean Clay process will vary depending on the concentration of NaNO_3 , NaNO_2 , and NaOH in the original waste solution and the type of clay used. Figure 7 outlines the volumes and compositions of the process streams using calcined kaolin and the given waste solution composition. Figure 8 shows details of the process streams for calcined bentonite.

If all NaNO_3 and NaNO_2 in 100 ml of synthetic waste #1 were fixed in cancrinite, 75 g of NaOH would be required. This would result in product volumes of ~260 ml for the kaolin product and ~320 ml for the bentonite product. These volumes would be less with higher initial NaOH and lower NaNO_3 and NaNO_2 concentrations. Predicted volumes of cancrinite products for 100 ml of waste solution with varied composition are given in Table XI.

TABLE XI
VOLUMES OF LEAN CLAY PRODUCTS AS A
FUNCTION OF $\text{OH}^-/(\text{NO}_3^- + \text{NO}_2^-)$ MOLE RATIOS*

<u>Mole Ratio of</u> <u>$\text{OH}^-/(\text{NO}_3^- + \text{NO}_2^-)$</u>	<u>Volume of Calcined Kaolin</u> <u>Product, ml</u>
4.0	89
3.0	111
2.0	147
1.0	221

*Based on 100 ml original solution volume with a total of 10M Na^+ .

FIGURE 7

QUANTIFICATION OF LEAN CLAY PROCESS
(Using Calcined Kaolin)

FIGURE 8
QUANTIFICATION OF LEAN CLAY PROCESS
(Using Calcined Bentonite)

Several materials have been tested as binders for the Lean Clay process. These materials include polystyrene, polymethylmethacrylate, portland type III cement, and sodium silicate solution cured with zinc oxide or calcium oxide. As quality requisites, these binders must give hard, radiolytically stable products having low leach rates. All the above binders give strong products which are relatively stable toward radiolysis.

However, not all binders perform equally well in leaching conditions. Scanning electron photomicrographs of surfaces of bound products show that leach rates increase with surface porosity. For example, polystyrene-bound products are less porous (and less leachable) than polymethylmethacrylate products. Likewise, increasing portland cement/cancrinite weight ratios from 0.5 to 1.0 decreases leach rates by lowering porosity. Binders of zinc oxide-cured sodium silicate solution show the lowest leach rates. As expected, these zinc silicate-bound products show the smoothest product surfaces under SEM examination.

Surprisingly, SEM studies of leached product surfaces show that both of the organic binders actually leach faster than the cancrinite aggregate. With time, of course, this action would result in disintegration of the product and exposure of bare cancrinite particles to the leach solution. In contrast, neither the portland cement nor the zinc silicate binders show dissolution by leach water.

Leach rates of some Lean Clay products made with the full-level waste solution have been determined. These products were made from Indian Hill clay and a calcined kaolin and were bound with both zinc silicate and portland cement. As can be seen in Table XII, the Lean Clay products have significantly lower leach rates than their comparable

Rich Clay products presented for contrast in this table. As in the Rich Clay process, Lean Clay products from Indian Hill clay (containing bentonite) have lower leach rates than the calcined kaolin products. Finally, the zinc silicate-bound products show lower leach rates than the portland cement-bound products.

TABLE XII
BULK LEACH RATES FOR LEAN AND RICH CLAY PRODUCTS

<u>Flowsheet Alternative</u>	<u>Bulk Leach Rate, g/cm²-day</u>	
	<u>1 day</u>	<u>23 days</u>
Rich Clay Process		
a. PAB ® , calcined	2×10^{-1}	1×10^{-2}
b. Indian Hill ®	3×10^{-3}	7×10^{-4}
Lean Clay Process		
Portland Cement		
a. PAB, calcined	1×10^{-2}	4×10^{-4}
b. Indian Hill	1×10^{-3}	9×10^{-5}
Zinc Silicate		
a. PAB, calcined	1×10^{-3}	5×10^{-5}
b. Indian Hill	2×10^{-4}	9×10^{-6}

Clay Calcination Process

Comparison of the alternative processes presented in the Conceptual Flowsheet in Figure 6 shows that the Clay Calcination process has several important advantages. It can immobilize dry salt cake and sludge as well as salt cake solution and waste solution. The product volume is lower (0.8 x waste solution volume; 1.5 x salt cake) and the thermal and radiolytic stabilities of the product are improved.

There are two possible Clay Calcination processing routes--one in which the clay/waste mixture is molded into bricks and fired, and the other in which a loose reaction

mixture is fired and the powdered product bound into bricks. The latter route yields products of lower volume. Also, cracking of the products is prevented by allowing facile release of off-gases (NO_x , H_2O , CO_2) before molding into bricks. The product in either case is nepheline. However, because of the iron content of sludge, the Clay Calcination process would likely form additional crystalline phases for that waste.

Table XIII shows the effects of reacting various amounts of synthetic salt cake with kaolin and bentonite on the product crystallinity. The table shows that increasing the amount of synthetic waste in the clay/waste mixture from 10 to 40% resulted in improved crystallinity of the nepheline product. The theoretical limit for formation of pure nepheline from kaolin is 40% salt cake in the reaction mixture (assuming salt cake is pure NaNO_3). At this ratio, the theoretical volume increase is 45%. Measured volume increases for the 40% salt cake products are 53% for bentonite and 65% for kaolin.

TABLE XIII
EFFECT OF CLAY/SALT CAKE RATIO ON
CLAY CALCINATION PRODUCT* CRYSTALLINITY

<u>Product</u>	<u>Clay</u>	<u>Salt Cake in Mixture</u> %	<u>Weight Loss</u> %	<u>Product Identity</u>
1	Kaolin	10	21	Poor nepheline
2	Kaolin	20	20	Poor nepheline
3	Kaolin	30	24	Good nepheline
4	Kaolin	40	26	Good nepheline
5	Bentonite	10	18	Poor nepheline
6	Bentonite	20	22	Poor nepheline
7	Bentonite	30	22	Good nepheline
8	Bentonite	40	24	Good nepheline

*Reacted at 900 to 1000° C.

Scanning electron photomicrographs of the 40% salt cake products show the nepheline products made from bentonite to be partially fused. The $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram indicates that the higher silica content of the bentonite product does lower the melting point. The nepheline from SEM photographs, consists of small ($<0.5 \mu\text{m}$) crystals.

Massive samples were prepared by binding the products described in Table XIII. Zinc silicate and portland type III cement were again the binders studied. The compressive strengths of these massive samples show that products made from kaolin and bound with zinc silicate are relatively weak. Products made from bentonite and bound with zinc silicate, on the other hand, have compressive strengths comparable to the portland cement-bound products.

The above samples were leached and the leachates were analyzed for cesium and strontium. The leach rate data appear in Table XIV. As found for the Lean Clay products, zinc silicate-bound products have significantly lower leach rates than portland cement-bound products. Samples made from bentonite also show lower leach rates than kaolin products. This behavior was seen earlier for both Rich and Lean Clay products. Finally, leach rates based on cesium rise radically as fraction of waste in the products exceeds roughly 0.3. Strontium leach rates, however, decrease with increasing waste content.

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TABLE XIV

BULK LEACH RATES* OF MASSIVE SAMPLES OF CLAY CALCINATION PRODUCTS

Clay Type	Product Formulation		10 ⁴ x Leach Rate, g/cm ² -day			
	% Salt Cake	Binder	1 day	4 days	18 days	32 days
Kaolin	10	Zinc silicate	6.9	6.9	0.74	0.36
Kaolin	20	Zinc silicate	22	16	2.8	1.2
Kaolin	30	Zinc silicate	22	17	3.1	1.2
Kaolin	40	Zinc silicate	164	58	7.4	2.6
Bentonite	10	Zinc silicate	0.70	1.3	0.93	0.71
Bentonite	20	Zinc silicate	0.29	0.20	0.089	0.078
Bentonite	30	Zinc silicate	2.4	3.1	1.7	1.6
Bentonite	40	Zinc silicate	327	110	18	30
Kaolin	10	Portland cement	132	49	17	11
Kaolin	20	Portland cement	133	31	9.9	5.8
Kaolin	30	Portland cement	82	21	5.6	2.5
Kaolin	40	Portland cement	166	52	7.6	2.8
Bentonite	10	Portland cement	53	32	4.1	0.66
Bentonite	20	Portland cement	17	14	5.4	2.5
Bentonite	30	Portland cement	77	21	2.5	1.8
Bentonite	40	Portland cement	173	44	18	10

*Based on fraction of cesium leached.

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