Fixation of Radioactive Waste by Hydrothermal Reactions with Clays

G. Scott Barney

January 1974

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**Atlantic Richfield Hanford Company
Richland, Washington 99352**

MASTER

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FIXATION OF RADIOACTIVE WASTES
BY HYDROTHERMAL REACTIONS WITH CLAYS

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January 1974

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ABSTRACT

A means of converting radioactive wastes to solid, relatively insoluble, aluminosilicate minerals is described. This process can be applied to caustic sodium wastes such as neutralized Purex wastes and sodium salts or oxides produced by evaporation or calcination of liquid wastes. Powdered aluminum silicate clays such as kaolin, bentonite, halloysite, or dickite are reacted with aqueous solutions or slurries of caustic waste at temperatures in the range of 30 to 100 °C. The reaction produces a salt-filled, sodium aluminosilicate with radioactive isotopes trapped in the aluminosilicate framework structure. The mineral type is feldspathoid and, for wastes which contain nitrate ion, the product has the framework structure of cancrinite. The stoichiometry of the reaction requires two moles of sodium hydroxide for each mole of cancrinite formed.

Reactions of kaolin and bentonite with actual waste show that ^{137}Cs , ^{90}Sr , and ^{106}Ru are trapped in the cancrinite along with the sodium salts present. The clay appears to go through a gel phase, then partial dissolution, and, finally, precipitation of the cancrinite from solution. Electron photomicrographs show the product to be a mass of round clusters of cancrinite crystals approximately 0.5 μm in diameter. Leaching of the powdered product with distilled water at 30 °C gives bulk leach rates in the range of 10^{-7} to 10^{-10} g sample/cm²-day.

FIXATION OF RADIOACTIVE WASTES BY HYDROTHERMAL REACTIONS WITH CLAYS

INTRODUCTION

High-level, radioactive wastes from nuclear fuel reprocessing are presently being stored in underground tanks at several U. S. Atomic Energy Commission installations. Some of these wastes are being solidified by evaporation to salt cakes in order to increase their storage safety. In the future it may be necessary to convert these wastes into a form that will decrease the possibility of movement of radionuclides to the biosphere during long-term storage. Ideally, the waste should be in a form that would resist tank leakage, groundwater leaching, leaching by floods, wind erosion, and contamination spread by handling or sabotage.

General criteria for a desirable solid waste form suggested by the above safety considerations are as follows:

- Low leachability in water.
- Good chemical and physical stability toward heat and radiation.
- High mechanical strength.
- High thermal conductivity.
- Low volume.

The cost of production and storage of the waste form is also an important consideration.

Some aluminosilicate minerals appear to meet the above criteria rather well, especially with regard to low

leachability and chemical and physical stability.^[1,2] A low-temperature process for converting the wastes to aluminosilicates with low leachability has now been found.^[3] Aqueous waste solutions containing NaOH, NaNO₃, NaNO₂, NaAlO₂, mixed fission products, and minor amounts of other salts are mixed with powdered clays (kaolin, bentonite, halloysite, or dickite) and reacted at 30 to 100 °C to form small crystals of the mineral cancrinite. The sodium aluminosilicate crystal lattice of cancrinite contains large amounts of trapped salts and radioactive fission products. The process is applicable to caustic, radioactive liquids such as neutralized Purex wastes or to salts or oxides produced by evaporation or calcination of these liquid wastes.

SUMMARY AND CONCLUSIONS

A low-temperature process for conversion of radioactive sodium salt wastes into solid, relatively insoluble, thermally stable sodium aluminosilicates is described. The reaction of the waste (in aqueous solution) with powdered clays such as kaolin, bentonite, halloysite, or dickite produces small crystals ($\approx 0.5 \mu\text{m}$) of cancrinite. Salts, including radioactive ones, are trapped in the cancrinite crystal lattice. The approximate chemical formula of the cancrinite produced is $2(\text{NaAlSiO}_4) \cdot x\text{Salt} \cdot y\text{H}_2\text{O}$, with $x = 0.52$ and $y = 0.68$ when the entrapped salt is NaNO₃. The stoichiometry requires two moles of NaOH for each mole of cancrinite formed.

The reaction occurs at temperatures as low as 30 °C. However there is a large temperature effect on the rate. The half-times for the reaction of kaolin with standard waste at 100, 75, and 50 °C are, respectively, 1, 10, and 150 hours. The corresponding half-times for the bentonite

reaction are 1, 19, and 60 hours.

The cancrinite product has a low leach rate. Values obtained by leaching with distilled water are in the range of 10^{-7} to 10^{-9} g of sample/cm²-day. Diffusion rate of cesium ion from the product into the leachant is slower than for the sodium ion.

The melting range of cancrinite products is about 900 to 1200 °C. Zeolytic water is removed over the range of 100 to 300 °C. At about 700 °C the trapped NaNO₂ and NaNO₃ begin to decompose to Na₂O and nitrogen oxides. A change in crystal structure to nepheline occurs at 530 to 595 °C.

The thermal conductivity of cancrinite products ranges from 0.11 to 0.67 Btu/(hr)(ft²)(°F/ft). These values appear to be high enough to prevent large temperature gradients in products made from Hanford Stored Waste.

The mechanical strength of the product can be improved by adding hardeners or binders. Various inorganic cements, including Portland cement, can be used to bind the cancrinite crystals together to make a stronger product. Organic polymers can also be used. Binders appear to be most effective when the cancrinite is made from fired clays in which the clay structure has been destroyed. Various alternatives for the process are presented which depend on whether or not a binder is necessary and at what point in the process a binder is added.

The volumes of the clay and waste solution are nearly additive. Therefore the amount of clay necessary to form an acceptable product will determine the volume increase for the process. Fired clays appear to give the smallest volume increase (as low as 20% for the standard waste solution).

EXPERIMENTAL

MATERIALS

Several sources of clays were used in these experiments. The compositions of these clays are given in Table I.

TABLE I
ANALYSES OF CLAY REAGENTS*

Component	Weight Percent of Component in			
	Kaolin #1	Kaolin #2	Bentonite #1	Bentonite #2
SiO ₂	46.20	43.97	54.74	
Al ₂ O ₃	38.06	41.93	19.25	15.83
Na ₂ O	0.067	0.220	3.51	3.27
Fe ₂ O ₃	0.36		3.60	
MgO	0.041		2.84	
CaO	0.0007		0.14	
H ₂ O	11.7	13.4	11.1	10.6
Total	96.4287		95.18	

*Sources of clays: Kaolin #1--J. T. Baker Chemical Company.
Kaolin #2--Georgia Kaolin Company,
KCS-SD.
Bentonite #1--Robinson Laboratory.
Bentonite #2--Georgia Kaolin Company,
MC-101.

Fired clays were prepared by heating the bentonite and kaolin at 600 to 700 °C for 24 to 48 hours.

Two synthetic waste solutions were used. The compositions of these solutions, along with that of an actual waste solution (from Hanford Tank 103-BY), are given in Table II.

TABLE II
COMPOSITION OF SYNTHETIC AND ACTUAL WASTE SOLUTIONS

<u>Component</u>	<u>Molar Concentration of Components in</u>		
	<u>Synthetic</u> <u>Waste #1</u>	<u>Standard</u> <u>Synthetic Waste</u>	<u>Actual Waste*</u>
NaOH	5.0	3.6	5.2
NaNO ₃	2.0	3.4	1.9
NaNO ₂	1.0	2.1	2.0
NaAlO ₂	1.8	1.8	2.7
Na ₂ CO ₃	0.1	0	-
Na ₂ SO ₄	0.05	0	-
H ₂ O	-	40	

*From Tank 103-BY, also containing 4.60×10^5 $\mu\text{Ci/liter}$ ^{137}Cs .

PROCEDURE

For most reactions, measured amounts of clay and waste solution were mixed thoroughly in polypropylene bottles. The bottles were then sealed and placed in a constant temperature oven (Blue M Electric Company), shaker bath (Precision Scientific Company), or boiling water bath for a specified amount of time. For kinetic runs the clay and waste solution were allowed to reach the desired temperature overnight. Waste solution was measured and added to the clay using a preheated plastic syringe. Samples were periodically removed from the oven and filtered hot with a 5 μm Teflon Millipore filter in a Nalgene plastic filter holder. The filtrate was collected and the solids washed five times with 10-ml portions of distilled water. The solids were then air-dried and weighed.

Leach rates were measured by shaking 1.0 gram of powdered sample with 200 ml of distilled water in a constant temperature bath set at 30 °C. The mixtures were periodically filtered and the solids contacted with fresh 200-ml

portions of distilled water. The leachates were then analyzed for various cations.

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 diluted to 100.0 ml and analyzed by atomic absorption (Varian Techtron Model 385). Cations in leachates were also measured with this instrument.

Crystalline products were identified by X-ray diffraction using a General Electric XRD-5 powder diffractometer. Thermal analyses were performed with a Mettler Recording Vacuum Thermoanalyzer. Surface areas of powdered samples were measured using the B.E.T. method. Thermal conductivity of clay-waste mixtures and reaction products were measured according to the method of Underwood and McTaggart.^[4] Hardness of several products was measured with a Soiltest, Inc., Penetrometer, Model CL-700. Scanning electron microscope photographs of the crystalline products were obtained from Battelle Pacific Northwest Laboratories. The volume of "free liquid" left after a reaction was measured by filtering the cooled reaction mixture through an 0.5 μ m "Solvinert" Millipore filter under a pressure of 100 psi until no more filtrate could be obtained.

RESULTS AND DISCUSSION

FORMATION AND IDENTIFICATION OF PRODUCT

The reaction of kaolin with basic solutions of various salts has previously been studied by Barrer and co-workers.^[5-8] They obtained salt-filled cancrinites from

the reaction of kaolin with NaOH solutions containing NaNO_3 , Na_2SO_4 , Na_2CrO_4 , and several other salts. The salts are incorporated into the 11-hedral cancrinite cages and into the wide channels enclosed by these.^[9] The entrained salts could not be released except by decomposition of the aluminosilicate with mineral acid. The present work will show that radioactive salts of cesium and strontium can also be entrapped in the cancrinite product.

Identification of Products

The crystalline product obtained from reaction of the clays with either the synthetic or actual wastes was identified as cancrinite. A comparison of the X-ray diffraction patterns of the clay reaction product with three other types of cancrinites is given in Table III. The match with natural cancrinite and synthetic cancrinite is very good.

TABLE III
COMPARISON OF X-RAY DIFFRACTION PATTERNS
OF CANCRINITES AND CLAY REACTION PRODUCT

<u>Natural Cancrinite^a</u>		<u>Synthetic Cancrinite^b</u>		<u>Natrodavyn^c</u>		<u>Clay Reaction Product</u>	
<u>dÅ</u>	<u>I/I₁</u>	<u>dÅ</u>	<u>I/I₁</u>	<u>dÅ</u>	<u>I/I₁</u>	<u>dÅ</u>	<u>I/I₁</u>
11.0	30						
6.32	60			6.38	70	6.27	50
5.47	10						
4.64	80	4.70	80	4.64	10	4.68	60
4.13	30						
3.75	10						
3.65	50	3.67	80	3.68	100	3.63	80
3.22	100	3.25	100	3.21	10	3.23	100
3.03	30						
2.97	30						
		2.82	16	2.85	25		
2.73	60	2.76	35			2.73	35
2.61	50	2.63	30	2.60	35	2.61	30
2.56	60	2.57	16			2.58	35

^aASTM Powder Diffraction File, Card No. 20-257.

^bASTM Powder Diffraction File, Card No. 15-734.

^cASTM Powder Diffraction File, Card No. 15-469.

The presence of small amounts of fission products in the waste does not affect the formation of cancrinite. Reactions of bentonite and synthetic waste spiked with large amounts of Cs^+ and Sr^{++} gave only cancrinite, even when the concentrations were many times greater than those expected in reprocessing wastes. At yet higher concentrations of Cs^+ and Sr^{++} other products were formed, as shown in Table IV.

TABLE IV
EFFECT OF Cs^+ AND Sr^{++} CONCENTRATION
IN SYNTHETIC WASTE ON REACTION PRODUCTS*

Sample #	Molarity of Cs^+ or Sr^{++} in Synthetic Waste #1	Products
122	0.37M Cs^+	Cancrinite
123	0.75M Cs^+	Cancrinite + unknown
124	1.50M Cs^+	Cancrinite + unknown
125	2.25M Cs^+	Cancrinite + pollucite
126	0.10M Sr^{++}	Cancrinite
127	0.38M Sr^{++}	Cancrinite + $\text{Sr}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$
128	1.00M Sr^{++}	Cancrinite + $\text{Sr}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ + SrCO_3
129	1.30M Sr^{++}	Cancrinite + $\text{Sr}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ + SrCO_3

*20 ml of solution were reacted with 5.0 g of bentonite at 100 °C for 10 days.

The clay/waste solution ratio appears to have no effect on the identity of the crystalline aluminosilicate product. Reactions over wide ranges of clay/synthetic waste ratio gave only cancrinite for those clays studied (bentonite, kaolin, halloysite, and dickite). Also, the reaction of actual waste solution (Tank 103-BY) with bentonite over the range 0.05 to 2.0 grams of clay/ml solution gave only cancrinite (plus unreacted bentonite at the higher ratios).

Cancrinite was also formed by reacting ignited kaolin and bentonite with synthetic waste. All the interlayer and hydroxyl water was removed from these clays before using them by heating at 600 to 700 °C for 24 to 48 hours. The

product from these reactions will presumably have a smaller volume because of the removal of the water.

Stoichiometry

The stoichiometry of the formation of cancrinite from kaolin was studied. The amount of NaOH which reacts with a given amount of clay was determined by reacting the clay with a solution containing various concentrations of NaOH and a constant concentration of NaNO₃ (necessary to form the cancrinite). Essentially all of the NaOH in the solutions was reacted during cancrinite formation. The mole ratios of NaOH, NaNO₃, and kaolin reacted are given in Table V, based on the formula Al₂Si₂O₇·2H₂O for kaolin (M.W. = 259).

TABLE V
MOLE RATIOS OF REACTANTS USED*

<u>[NaOH], M</u>	<u>moles NaOH</u>	<u>moles NaNO₃</u>
	<u>moles Kaolin Reacted</u>	<u>moles Kaolin Reacted</u>
1.0	1.7	0.62
2.0	1.7	0.47
3.0	2.1	0.57
4.0	2.0	0.47
5.0	2.1	0.45
	average = 1.9	average = 0.52

*5 ml of 2.0M NaNO₃ at the given NaOH concentration were reacted with 5.0 g of kaolin #1 for 11 days at 100 °C.

The amount of zeolytic water in the cancrinite was found to be ≈0.68 moles per mole of cancrinite formed. These observations can be summarized by the reaction

The cancrinite composition is very near that reported by Barrer,^[8] $2(\text{NaAlSiO}_4) \cdot 0.65\text{NaNO}_3 \cdot 0.60\text{H}_2\text{O}$.

Similar equations can be written for the reaction of bentonite (which consists mainly of the mineral montmorillonite) with the caustic NaNO_3 solutions. Assuming the formula of the cancrinite is the same as above,

or, in the presence of NaAlO_2 ,

Other salts, in addition to NaNO_3 , can be trapped in the cancrinite lattice.

Kinetics

The kinetics of the reactions of bentonite #2 and kaolin #2 clays with standard synthetic waste solution were studied at three different temperatures: 50, 75, and 100 °C. The extent of the kaolin reaction was measured by determining (using thermal analysis) the amount of hydroxyl water associated with the unreacted kaolin in the solid product. The amount of unreacted bentonite was estimated by measuring the area of the endotherm due to loss of hydroxyl water from the bentonite. Reaction rate curves for the kaolin clay-waste reaction and bentonite clay-waste reaction at the above temperatures are shown in Figures 1 and 2, respectively. The large effect of temperature on the rate of

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

TIME, HOURS

FIGURE 2

EFFECT OF TEMPERATURE ON REACTION RATE (BENTONITE-WASTE REACTION)

reaction is apparent from these curves. It should be pointed out that there was an excess of clay in these experiments so that the maximum amount of clay reacted could only be $\approx 80\%$. Since the standard waste solution contains only 3.6M NaOH, it is expected that higher concentrations of hydroxide will increase the reaction rate.

During the kinetic experiments the solid and liquid phases were analyzed for Na^+ , Al^{3+} , Si^{4+} , NO_3^- , NO_2^- , and clay hydroxyl water. The results, given as the weight percent of a given component in the solid phase as a function of time, are shown in Figures 3 and 4. Insight into the mechanism and rate of reaction can be obtained from these plots. Figure 3 shows that for the kaolin-waste reaction a substantial amount of aluminum remains in solution while almost all the silicon is in the solid phase. Figure 4 shows that the opposite is true for the bentonite-waste reaction. The driving force for the formation of a product with an Al/Si mole ratio of one (as is the case for cancrinite) is apparent from Table VI.

TABLE VI
ALUMINUM/SILICON MOLE RATIOS FOR REACTION SYSTEM

Reaction	Al/Si Mole Ratio	
	Liquid + Solid Phase	Solid Product
Kaolin - waste	1.5	1.1
Bentonite - waste	0.82	0.96

The component (Al or Si) which is in excess for cancrinite formation remains in solution. The spikes in the Na^+ and NO_3^- - NO_2^- curves in Figure 4 at about 15 minutes are probably due to initial ion exchange of the sodium salts with bentonite.

X-Ray diffraction of the products from the above

FIGURE 3

SOLID PHASE COMPOSITION VERSUS TIME
(KAOLIN-WASTE REACTION)

FIGURE 4

SOLID PHASE COMPOSITION VERSUS TIME
(BENTONITE-WASTE REACTION)

experiments show crystalline cancrinite in each sample from the bentonite reaction (the first sample was taken at 15 minutes). However, no cancrinite is observed in the kaolin reaction until 60 minutes have elapsed. The induction period for cancrinite crystal growth is, therefore, shorter with bentonite as the reactant. This may be associated with the rate of dissolution of the clays.

Fixation of Cesium and Strontium

Actual waste solution (103-BY) was reacted with bentonite #1 in order to determine the ability of the clay to fix cesium. The clay-waste mixtures were heated at 100 °C for seven days. The percent of ^{137}Cs fixed in the product was measured as a function of the clay/liquid waste ratio. The results are plotted in Figure 5. The curve shows that a minimum of 0.75 g of bentonite #1 per ml of waste solution is needed in order to fix the ^{137}Cs .

Cesium was the only measurable radioactive component in the 103-BY waste. The fixation of other fission products could not, therefore, be studied using this waste. However, reactions of clays with synthetic waste spiked with strontium indicate that essentially all of the strontium is fixed in the solid product. Additional work with strontium and other major radioactive fission products is necessary.

CHEMICAL AND PHYSICAL PROPERTIES OF PRODUCTS

Leach Rates

Leach rates for the cancrinite products have been determined by contacting the powdered crystals with distilled water. Since leach rates generally decrease with time, measurements were made over a period of several weeks. Figure 6 gives leach rate curves for products obtained using

FIGURE 5
FIXATION OF ^{137}Cs USING VARIOUS CLAY/LIQUID WASTE RATIOS
(Reaction of Bentonite #1 with Actual 103-BY Waste)

FIGURE 6

BULK LEACH RATE OF CANCRINITE PRODUCT
CALCULATED BY THE EQUATION

$$\text{Bulk Leach Rate} = \frac{(\text{fraction of ion leached})(\text{sample weight})}{(\text{surface area})(\text{time})}$$

various clays and waste solutions. Leach rates for the two products obtained from synthetic waste were calculated from the fraction of Na^+ leached. For the radioactive product the fraction of $^{137}\text{Cs}^+$ leached was used. The lower rate for the radioactive product is probably due to slower diffusion of Cs^+ compared with Na^+ . The calculation does not take into account diffusion of the measured ions since the assumption of congruent dissolution is made. The leach rate of the aluminosilicate lattice is, therefore, lower than these calculated values. In summary, values for the bulk leach rate of the cancrinite product are in the range of 10^{-7} to 10^{-9} g/cm²-day.

Thermal Stability

The melting points of cancrinite products are in the range of 900 to 1200 °C. Several changes in the composition of the products occur before the melting point is reached, however. The weight loss curve and differential temperature (DTA) curve for a typical product made from kaolin are given in Figure 7. The initial weight loss and associated endotherm are due to loss of zeolytic water. Since there is some unreacted kaolin present in this product, the loss of hydroxyl water from the clay is observed over the temperature range of 450 to 650 °C. At about 700 °C the trapped NaNO_3 and NaNO_2 begin to decompose to Na_2O and nitrogen oxides. There is a large exotherm and weight loss due to this decomposition.

A change in crystal structure of the product occurs at high temperature. Samples heated from 800 to 1000 °C give an X-ray diffraction pattern corresponding to nepheline. According to Barrar,^[8] sodium nitrate cancrinite decomposes to nepheline somewhere in the range of 530 to 594 °C.

FIGURE 7

THERMAL ANALYSIS OF A TYPICAL CANCRINITE SAMPLE;
CONDITIONS: 500.3 mg SAMPLE IN PLATINUM CRUCIBLE;
HEATING RATE 10 °C/min IN FLOWING AIR

Thermal Conductivity

Thermal conductivity measurements were made on clay-waste slurries and on the dried cancrinite product. These measurements represent the possible extremes. The values for the actual product, depending on the process, is somewhere in-between. The commercial clays, KCS (kaolin #2) and MC-101 (bentonite #2) were used with standard synthetic waste to make the clay-waste slurries and the dried cancrinite product. The results of these measurements are given in Table VII.

TABLE VII
THERMAL CONDUCTIVITY OF CLAY-WASTE
MIXTURES AND CANCRINITE PRODUCT

<u>Sample</u>	<u>Temperature</u> <u>°C</u>	<u>Thermal Conductivity</u> <u>Btu/(hr) (ft²) (°F/ft)</u>
Kaolin slurry (1.0 g/ml mixture)	24.9	0.670
Bentonite slurry (1.0 g/ml mixture)	24.7	0.458
Kaolin cancrinite Product (dry)	25.3	0.140
Product (dry)	44.0	0.158
Product (dry)	74.7	0.161
Bentonite cancrinite Product (dry)	26.3	0.114
Product (dry)	56.4	0.185
Product (dry)	69.0	0.175

These values are near those of dried salt cake and are high enough so that large temperature gradients should not occur in the cancrinite product made from stored Hanford wastes.

Hardness

If the solid waste form is to be handled or transported, it must be strong enough to prevent chipping and dusting of

small particles from the bulk. Pure cancrinite is quite hard (5 to 6 on Mohs' scale). However the product of clay-waste reactions is a mixture of small cancrinite crystals and unreacted kaolin (2.0 to 2.5 on Mohs' scales). The hardness of this product is, therefore, limited to that of kaolin. Also, the cancrinite product containing excess kaolin clay as a binder has been observed to soften somewhat when covered with water. If the cancrinite product contains excess bentonite clay, the product will swell and crumble when covered with water. In order to make a mechanically stronger product, several hardeners and binders have been tested. These can be added either to the reaction mixture or the cancrinite product.

Experiments thus far have shown that the addition of CaO, silica gel, or mixtures of both will give a harder product. These additions were made to the reaction mixture (10.0 g kaolin #2 plus 10 ml standard synthetic waste) and the samples were kept at 75 °C for 48 hours. The cooled, damp products were then measured for hardness with a penetrometer (Soiltest Model CL-700 penetrometer - Soiltest, Inc.). The results are given in Table VIII. The greatest increase in hardness results from the addition of a mixture of CaO and $\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

A very dramatic increase in the hardness of dried cancrinite products occurs after treatment with tetraethyl silicate (TES). Soaking the cancrinite-clay mixture in TES for several hours, either at room temperature or at 100 °C, gives a product which is difficult to scratch and which is more water-resistant. Samples treated with TES do not appear to soften even when soaked in water for months.

TABLE VIII
EFFECTS OF CaO AND $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ON THE
HARDNESS OF CANCRINITE PRODUCT

<u>Mixture #</u>	<u>Weight CaO, g</u>	<u>Weight $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, g</u>	<u>Hardness* kg/cm²</u>
1	0	0	37
2	0	0.5	22
3	0	1.0	35
4	0	2.0	>45
5	0.5	0	45
6	1.0	0	>45
7	2.0	0	>45
8	3.0	0	>45
9	2.0	0.5	>45
10**	2.0	2.0	>>45
11	1.0	2.0	>>45
12	0.5	2.0	>45

*The pressure necessary to drive the penetrometer probe 0.25 inch into the product.

**Hardest product tested.

Cancrinite crystals were used as aggregate in Portland Type III cement mixtures in order to bind the crystals together. Hard products were obtained only when the cancrinite was prepared from fired clays. It appears that any unreacted clay in the cement mixture will cause the cement to crumble when air-dried. This may be due to shrinkage of the clay upon drying.

Other organic and inorganic binders have also been tested. Polymerization of styrene or methylmethacrylate in cancrinite-monomer mixtures procures hard, rugged products. Sodium silicate solution mixed with powdered silica also appears to be an effective binder for the cancrinite.

Volume Increase

The volumes of the clay and waste solution are

approximately additive. Since the density of both kaolin and bentonite are about 2.6 g/ml, each gram of clay added results in a volume increase of 0.38 ml. The amount of clay necessary to form a solid product depends on the type of clay used and the composition of the waste solution reacted.

The minimum amount of clay necessary to completely solidify the standard waste solution was measured for several clays. A solid product is defined as one that can be filtered at 100 psi using a pressure filter, with no resulting liquid. The results of these measurements for solidification of the standard waste solution are given in Table IX.

TABLE IX
MINIMUM AMOUNT OF CLAY NECESSARY
TO SOLIDIFY THE STANDARD WASTE SOLUTION

<u>Type of Clay</u>	<u>Minimum Clay/ Liquid Waste Ratio, g/ml</u>	<u>% Volume Increase for Solid Product*</u>
Kaolin #2	0.70	26
Bentonite #1	0.84	32
Bentonite #2	1.30	49

*Compared with volume of standard waste solution.

These results indicate that less volume is necessary if kaolin is used. Reactions with fired clays have resulted in volume increases as low as 20%.^[10]

The volume increase for salt cake wastes has not yet been determined. It does seem reasonable to assume that this volume increase will be greater because of the higher concentration of salts. There are many unknown variables that can influence the volume (bulk density of salt cakes, composition, water content, etc.).

Size and Shape of Cancrinite Crystals

A series of scanning electron microscope (SEM) photographs were made of the products of reactions of standard waste with kaolin #1 and bentonite #1.^[11] These photographs are shown in Figures 8 and 9. The cancrinite appears to be a mass of small, partially agglomerated spheres. Some unreacted bentonite can be seen as irregularly shaped, flat plates in Figure 8. The sharp, bladed crystals have not been identified. These bladed crystals are not observed in the kaolin product.

DESCRIPTION OF POSSIBLE PROCESSES

It has been shown that some radioactive wastes can be converted to cancrinite, a solid, relatively insoluble, thermally stable aluminosilicate mineral. Another possible product is nepheline which can be made by firing the cancrinite. A conceptual flow diagram showing several possible alternative treatments and products is given in Figure 10. Alternative (4) is the simplest and least expensive route to a cancrinite product. This product may not, however, meet the requirement of high mechanical strength. Alternative routes (1) + (4), (2), and (3) will give a more rugged product, but will be more expensive. It may not be possible to add certain types of binders (polymers, cements, asphalt, etc.) to the reaction mixture. In this case alternative (2) must be used. The washing step was included in order to remove any unreacted salts. This step may not be necessary, depending on the kind of binder used.

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The author expresses appreciation to W. I. Winters and

10,000 X

20,000 X

FIGURE 8
SEM PHOTOGRAPHS OF THE BENTONITE PRODUCT

1,000X

5,000X

20,000X

FIGURE 9
SEM PHOTOGRAPHS OF THE KAOLIN PRODUCT

FIGURE 10
A CONCEPTUAL FLOW DIAGRAM FOR THE
CONVERSION OF RADIOACTIVE WASTES TO ALUMINOSILICATE MINERALS

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