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FINAL REPORT ON THE APPLICATION OF TITANATES,
NIOBATES, AND TANTALATES TO NEUTRALIZED
DEFENSE WASTE DECONTAMINATION - MATERIALS
PROPERTIES, PHYSICAL FORMS, AND REGENERATION
TECHNIQUES

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Final Report on the Application of Titanates, Niobates, and
Tantalates to Neutralized Defense Waste Decontamination -
Materials Properties, Physical Forms, and Regeneration Techniques *

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ABSTRACT

A study of the application of sodium titanate (ST) to the decontamination of neutralized defense waste has been completed. The work was directed at Sr removal from dissolved salt cake, simulated in this work with a 6.0N NaNO_3 - 0.6N NaOH solution. Three physical forms of the titanates were developed including powder, pellets, and titanate-loaded resin beads and all were found to be superior to conventional organic ion exchange in this application. When spent, the titanate materials can be calcined to an oxide form which is a stable waste form in itself or can be added directly to a glass melter to become part of a vitrified waste form.

A significant part of the Sr is believed to be present as a hydrolyzed form, $\text{Sr}(\text{OH})_x^{2-x}$, which is not effectively sorbed by conventional organic ion exchange resins. The titanates, however, exhibit both high Sr distribution coefficients ($K_d \sim 1 \times 10^5 \text{ ml/g}$) and capacities (10-12 meq Sr/g ST) in the simulant. The reference

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ST material is a powder form; however, this study concentrated on the development and characterization of forms which are more amenable to remote process operation. These included ST-loaded macroreticular anion exchange resin and pelletized ST powder.

The ST-loaded resins are prepared by incorporating a titanate anion in the resin via ion exchange followed by in situ conversion to ST. Up to 40% by weight can be loaded into the resin, which subsequently exhibits both anion and cation exchange properties. No changes in the chemistry of the ST resulting from the resin matrix were identified. Elution-regeneration methods were evaluated using either acid or EDTA for Sr elution and in doing so, the ST was found susceptible to acid attack. The hydraulic properties were determined for a 4-inch diameter bed of ST-loaded resin fabricated by a commercial supplier (Cerac, Inc. of Milwaukee, Wisconsin) and a study on the effects of radiation on the ion exchange properties of the loaded resin was completed.

Radiation stability of titanate powder and resin forms was assessed in tests in which these materials were exposed to ^{60}Co radiation. The strontium exchange capacity of the powder remained constant through a dose of 3×10^7 rads and retained 50% capacity after a dose of 2×10^9 rads. The primary mechanism involved in loss of capacity was believed to be heating associated with the irradiation. The resin forms were unchanged through a dose of 5×10^8 rads and retained 30% capacity after a dose of 2×10^9 rads. The latter dose resulted in visible degradation of the resin matrix.

Anion exchange resins loaded with sodium niobate and sodium tantalate were also prepared by similar methods and evaluated

for this application. These materials had Sr sorption properties comparable to the titanate material; however, they would have to provide a significant improvement to justify their higher cost. They did exhibit a greater stability in acid solution. Column beds of both materials could be efficiently eluted with 1N HNO₃ - no significant dissolution was detected - and regenerated for further use; however, both showed a slight susceptibility to dissolution in caustic solution.

Pelletized ST materials were supplied by Norton Co., Akron, Ohio, using sodium titanate powder prepared by Cerac, Inc., Milwaukee, Wisconsin, to Sandia specifications. The Norton materials were the products of a R & D study they performed to identify a process which would produce a high surface area pellet that retained its physical stability in caustic solution and have a minimal effect on Sr exchange properties. Pellet samples supplied to Sandia were characterized with respect to Sr capacity and K_d , and changes in physical stability resulting from contact with simulant for periods up to four months. Tests on six different batches showed that Sr sorption kinetics, capacities, and K_d values after 1 to 24 hour contact times were very similar showing little sensitivity to process conditions. However, large variations in physical stability in simulant solution were observed with pellet stability generally increasing with increasing processing temperatures.

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I. INTRODUCTION

Previous work with sodium titanate has shown that it is extremely efficient for Sr and actinide (1,2) decontamination of dissolved salt cake, a material which constitutes a significant fraction of the defense waste currently in storage at the Hanford site. The basic chemistry of sodium titanate, its application to dissolved salt cake decontamination, development of a commercial supply of powder form, and initial work in developing alternate material forms including consolidated sodium titanate powder and sodium titanate-loaded macroreticular anion exchange resin have been discussed in previous reports (1,3).

In this communication, which is intended as the final report concerning the application of titanate to Hanford defense waste decontamination, follow-up work in those areas listed above is discussed. Emphasis was placed on the development of alternate (non-powder) material forms and on development and evaluation of elution-regeneration processes which would prolong the useful lifetime of a titanate column. A study of consolidation processes applicable to sodium titanate powder has been completed by Norton Co., Akron, Ohio, and a copy of their final report is included as Appendix I. An evaluation of sodium titanate pellet samples supplied to Sandia by Norton Co. during the course of their work is included.

Sodium titanate-loaded macroreticular anion exchange resin was prepared by Cerac, Inc. of Milwaukee, Wisconsin, to Sandia specifications and the hydraulic properties of that material have been determined in tests using four inch diameter columns.

Properties of the loaded resins important to column operation including kinetics, column capacities under flow conditions, and elution-regeneration chemistry are discussed. A radiation damage study involving sodium titanate powder and sodium titanate-loaded resin has been completed (4) and the results are briefly summarized.

Sodium niobate and sodium tantalate materials were also incorporated in macroreticular anion exchange resin and evaluated as alternate materials to sodium titanate. Their primary advantage as compared to the titanates is a greater stability in acid solution, thus facilitating column elution methods. The preparation, chemical properties, and column behavior of these materials are discussed.

II. LABORATORY STUDIES INVOLVING SODIUM TITANATE AND TITANATE-, NIOBATE-, AND TANTALATE-LOADED MACRORETICULAR ANION EXCHANGE RESIN

A. Materials and Baseline Preparation Methods.

1. Materials.

The following is a partial list of chemicals and materials and sources thereof used in this work. Common chemicals and solvents used are not included, but all were of reagent grade quality. Unless otherwise noted, all water used was the product of a Millipore Super Q deionizing system.

Salt Cake Simulant - $6N$ $NaNO_3$ + $0.6N$ $NaOH$

Tetraisopropyl Titanate - DuPont, Wilmington, Delaware

((TYZOR TPT - DuPont Trade Name)

Pentaethyl Niobate - ROC/RIC Chemical Corp., Sun Valley,
California.

Tetramethylammonium Hydroxide (25 w/o solution in methanol) -
Eastman Kodak Co., Rochester, New York

AG-MP-1 Macroreticular Anion Resin - Bio-Rad Laboratories,
Richmond, California.

Dowex MSA-1, Type MP Anion Resin - Dow Chemical Co.,
Midland, Michigan

Sodium Titanate Powder (used at Norton Co.) - Cerac, Inc.,
Milwaukee, Wisconsin

Dowex 50-X8 Cation Exchange Resin - Dow Chemical Co.,
Midland, Michigan

2. Sodium Titanate Powder.

The preparation of sodium titanate has been described in detail elsewhere (5,6). However for completeness, a summary is included here. Tetraisopropyl titanate (TIPT) is reacted with a methanol solution of sodium hydroxide (10-16% NaOH by weight) by adding the titanium compound to the sodium hydroxide solution using a mole ratio of NaOH to TIPT of 1:2. The addition is made slowly with stirring to avoid vigorous boiling caused by an exothermic ester interchange reaction involving the isopropyl groups and methanol. The reaction mixture is then hydrolyzed in an acetone-water mixture, the ratio of which determines the physical characteristics of the solid product. After filtration, the sodium titanate is dried at ambient temperature either in air or vacuum.

A typical laboratory scale preparation is as follows:

568.2 grams of TIPT are added to 263.3 g of 15.19w/o solution

of NaOH in methanol. The resulting solution is added to a mixture of 2 liters of acetone and 200 milliliters of water. After filtration, the sodium titanate cake is dried at ambient temperature in vacuum for 24 hours.

Drying in air is equally effective; however, the material does sorb atmospheric CO_2 . Initial contact of air-dried material with water results in leaching of a mixture of sodium bicarbonate and sodium carbonate from the material, whereas the hydrolysis product of vacuum-dried material is sodium hydroxide. The presence of carbonates or bicarbonates has been shown to have no deleterious effect on either Sr specificity or Sr capacity associated with the material (1). The temperature used in drying the material is important in terms of total Sr capacity, but has little effect on specificity (K_d) in the range of 25°-500°C. These results are discussed in more detail in Section II-c' of this report.

Sodium titanate powder used in this work was prepared by the procedure described above using vacuum drying at ambient temperature unless otherwise noted. One exception was that used in the consolidation work done at the Norton Co., as that material was part of a 200 kg batch of sodium titanate prepared by Cerac, Inc. following a procedure which called for air drying.

3. Sodium Titanate-loaded Anion Exchange Resin.

Sodium titanate-loaded 20-50 mesh and 50-100 mesh type AG-MP-1 macroreticular anion exchange resins were prepared for laboratory use by the procedure described below, which is

applicable to one pound quantities of resin. The resin was first converted from the Cl^- form to the OH^- form in a three cycle process where each cycle consisted of soaking in one liter of 1N NaOH for 15 minutes, filtering, and washing with two liters of deionized water. Washing was continued after the final cycle until the filtrate was neutral to pH paper.

The resin (OH^- form) was added to a titanium solution prepared as follows: 568 g of tetraisopropyl titanate were reacted with 364 g of a 25% by weight solution of tetramethylammonium hydroxide in methanol. Two liters of water were added and the solution was boiled down to a volume of 2.2 liters. Another liter of water was added and boiling continued until a final volume of 2.7 liters was achieved.

The resin was contacted with the titanium solution for a period of 24 hours, filtered, and washed with water until a negative peroxide test was obtained for Ti in acidified (H_2SO_4) filtrate. The resin was then contacted with 2 liters of N NaNO_3 for 24 hours, filtered, and water washed. After the final wash (done in a 3 liter Büchner funnel with coarse glass frit), vacuum was applied until water was no longer dripping from the funnel. The resin was stored in a closed container and is subsequently referred to as "damp" ST-loaded resin.

A twenty-five pound lot of titanate-loaded resin was prepared by Cerac, Inc. to Sandia specifications which, in general, consisted of the procedure described above. The only significant difference was in the resin, where Dowex MSA-1, Type MP was substituted for the Bio-Rad material. Since the Dowex MSA-1 is

basically the same material as the Bio-Rad AG-MP-1 (it is purified with respect to metallic impurities and sieved into narrower particle size ranges), the substitution should have no effect on the chemical properties of the titanate-loaded material. The primary advantage is a significant decrease in cost ($\sim 30\times$) for the basic resin material.

The straightforward nature of the loaded-resin preparation is reflected by the material acceptance criteria, which specified only the quantity of sodium titanate contained in the resin. The specification called for the material to contain 30-40% by weight of sodium titanate based on the weight of resin plus sodium titanate after drying to constant weight at 100°C . The amount of sodium titanate is considered to be the residue resulting from heating the loaded resin in Pt for one hour at 700°C .

4. Sodium Niobate(SN)-loaded Anion Exchange Resin.

A typical laboratory-scale preparation of this material is described below: One hundred grams of AG-MP-1 resin (OH^- form) were added to a solution of tetramethylammonium niobate. The latter was prepared by reacting 140 g of pentaethyl niobate with 80.1 g of a solution of 25 w/o tetramethylammonium hydroxide in methanol, adding 700 mL of water and boiling down to a final volume of 500 mL. After 24 hours, the resin was filtered, washed with water to remove excess niobate, and contacted with 500 ml of 3N NaNO_3 for 24 hours. The resin was then washed using the same conditions previously described for the titanate resin and stored in a closed container. This material is subsequently referred to as "damp" SN-loaded resin.

5. Sodium Tantalate(STAN)-loaded Anion Exchange Resin.

A typical laboratory-scale preparation of this material is described below: The procedure used in preparing the tetramethylammonium tantalate solution varies from those described for analogous titanate and niobate solutions. Pentaethyl tantalate, 89.3 g, was added to 40.1 g of a 25% by weight solution of tetramethylammonium hydroxide in methanol. The mixture was stirred until a clear, single phase solution was obtained and this solution was added to one quart of acetone containing 18 mL of water, resulting in precipitation of a tetramethylammonium tantalate compound. After filtering, this compound was dissolved in 500 mL of water, boiled down to a volume of 300 mL, diluted to 500 mL with water, and boiled down to a final volume of 400 mL. The boiling steps were used to volatilize any organic solvent which may have been entrapped; however, this step can be eliminated by drying the material in vacuum at 25°C prior to dissolution in water.

Fifty grams of AG-MP-1 resin (OH^- form) were added to the tantalate solution and equilibrated for a period of four days after which it was filtered, washed with water to remove excess tantalate, and added to 500 mL of $3N$ NaNO_3 . After two days, the resin was washed with water as previously described for the ST-loaded resin, and stored in a closed container. This material is subsequently referred to as "damp" STAN-loaded resin.

6. General Discussion of Loaded-Resin Preparation.

The methods described for making the ST-, SN-, and STAN-loaded resins were those employed in preparing the materials used in this work. Parametric studies to determine optimum

conditions with respect to equilibration time, solution volumes, and solution concentrations have not been done.

The technique used in preparing the tetramethylammonium tantalate solution is also applicable to the titanium and niobium analogues. The tetramethylammonium niobate and tantalate compounds prepared by hydrolysis in acetone-water can be dried in vacuum at ambient temperature and stored for long periods of time (several years) in air in open containers with no apparent change in chemical properties. The titanate can also be dried in vacuum to remove excess solvent. However, if it is stored in air in an open container, it becomes water insoluble within a few days. When stored in a sealed container, the titanate compound also remains water soluble indefinitely.

The use of this technique would simplify the preparation of loaded resin. Large quantities of the quaternary ammonium compounds could be prepared and stored for use as needed. Their use would eliminate the time-consuming boiling steps used to convert from alcoholic to aqueous solution.

B. Properties of Sodium Titanate Powder Dried at Ambient Temperature - Comparison with Dowex 50 Cation Exchange Resin.

The application of sodium titanate (ST) to Sr decontamination of dissolved salt cake results from its high Sr specificity and capacity in caustic, near-saturated sodium nitrate solution. The Sr sorption properties of ST under these conditions were contrasted with those of a common strongly acidic cation exchange resin, Dowex 50, a divinyl benzene-styrene copolymer containing a sulfonic acid functional group. Distribution coefficients for

Sr on both ST and Dowex 50 in mixtures of water, sodium nitrate and/or sodium hydroxide are plotted as a function of sodium concentration in neutral or 0.1 N NaOH solution and as a function of hydroxide concentration in 1 to 5 M sodium solutions in Figures 1 and 2, respectively. Distribution coefficients (K_d) are defined as the ratio of the Sr concentration on the solid phase to that in the liquid phase after a specified contact time and have units of mL/g. The K_d 's values in Figures 1 and 2 were measured using solutions containing 200 ppm of stable Sr doped with 0.02 μ Ci/mL of Sr-85. Samples of Dowex 50 resin and ST weighing 1.0 g and 0.15-0.2 g, respectively, were contacted with 25 mL volumes of solution for a period of 24 hours. The weights, concentrations, and volumes used were such that a minimum of a five fold excess of Dowex 50 or ST (based on the measured capacities of these materials) were present in all measurements. Liquid phase analytical samples were taken through a 0.8 μ filter (Acropore, Gelman Instr. Co., Ann Arbor, Michigan) and counted using a 3-inch diameter NaI well detector incorporated in an 1185 Series automatic gamma counting system (Tracor Analytic, Des Plaines, Illinois). Solid phase Sr concentrations were determined by mass balance calculations.

The Dowex 50 resin behaved as expected showing a definite decrease in Sr sorption with increasing sodium concentration (Fig. 1). For an ion exchange reaction involving divalent Sr, the following stoichiometry should apply,

FIG.1 STRONTIUM DISTRIBUTION COEFFICIENTS
AS A FUNCTION OF SODIUM CONCENTRATION*

*MATERIALS USED WERE Na TITANATE POWDER AND DOWEX-50 CATION EXCHANGE RESIN. FEED SOLUTION WAS A DISSOLVED SALT CAKE SIMULANT CONTAINING 200 PPM STABLE Sr DOPED WITH Sr-85. LIQUID-TO-SOLID RATIOS WERE 170 AND 25 ML/G, FOR TITANATE AND DOWEX-50, RESPECTIVELY. CONTACT TIMES WERE 24 HOURS FOR ALL SAMPLES.

FIG.2 STRONTIUM DISTRIBUTION COEFFICIENTS
AS A FUNCTION OF HYDROXIDE CONCENTRATION*

*MATERIALS USED WERE Na TITANATE POWDER AND DOWEX-50 CATION EXCHANGE RESIN. FEED SOLUTION WAS A DISSOLVED SALT CAKE SIMULANT CONTAINING 200 PPM STABLE Sr DOPED WITH Sr-85. LIQUID-TO-SOLID RATIOS WERE 170 AND 25 ML/G, FOR TITANATE AND DOWEX-50, RESPECTIVELY. CONTACT TIMES WERE 24 HOURS.

where R represents the resin functional-group and the equilibrium relationship,

$$K = \frac{[Na^+]^2 [Sr \cdot R_2]}{[Sr^{++}] [Na \cdot R]} \cdot T \quad (2)$$

should pertain, where T represents an activity coefficient quotient.

Since the resin was present in large excess, $[Na \cdot R] \approx \text{constant}$ and T was assumed to be constant

$$\frac{K [Na \cdot R]}{T} = K' = \frac{[Na^+]^2 [Sr \cdot R_2]}{[Sr^{++}]} \quad (3)$$

Eq. (3) can be written as

$$\log \frac{[Sr \cdot R_2]}{[Sr^{++}]} = -2 \log [Na^+] + \log K' \quad (4)$$

and a plot of $\log \frac{[Sr \cdot R_2]}{[Sr^{++}]}$ vs. $\log [Na^+]$ should exhibit a slope of -2. Over a range of 0.1 N to 5.0 N sodium ion concentration, a slope of -1.95 was determined experimentally for Sr sorption on Dowex 50 resin. The value of K (Eq. 2) over the same range was found to have a mean value of 11.3 ± 1.8 where the average deviation from the mean is based on seven measurements using different sodium ion concentration within the range given above. The value is certainly empirical as the variation in T with ionic strength is unknown. The relatively small variance in K suggests the treating T as a constant was a reasonable approximation for these conditions.

The sorption of Sr on ST is not as straightforward since the K_d is relatively independent of sodium ion concentration in 0.1N NaOH solution (Fig. 1), suggesting a mechanism other than simple ion exchange. In the pH range of 4 to 9, the Sr capacity of ST is equivalent to the sodium content of the material, i.e., 4-5 meq/g depending on how the material was dried. In more basic solutions, pH>10, the Sr capacity more than doubles (11-12 meq/g), the reason for which is not known. The increase could result from a second exchange site such as a bridging hydroxyl group which is "activated" in caustic solution due to breaking the O-H bond or possibly from a change in Sr species where the effective charge on the Sr species is decreased. The decrease in strontium K_d with increasing OH^- concentration at constant Na^+ concentration (Fig. 2) could also be explained by a change in Sr species at high pH.

The Dowex 50 resin also exhibits a decrease in Sr sorption with increasing OH^- concentration (Figs. 1 & 2). Since the OH^- should not interact with the sodium-substituted sulfonic acid group on the resin, the most likely explanation for this behavior is the formation of a second Sr species, $\text{Sr}(\text{OH})_x^{2-x}$, in solution. As ST exhibits high K_d 's (>1000) for Sr in strongly basic solution, the Sr species is probably cationic rather than neutral or anionic. This suggests $\text{Sr}(\text{OH})^+$ and if the assumptions are made that the Sr remaining in solution after contact with Dowex 50 is a mixture of Sr^{++} and $\text{Sr}(\text{OH})^+$ and further, that $\text{Sr}(\text{OH})^+$ is not sorbed by the resin and does not influence the Sr^{++} -resin equilibrium, an empirical formation constant for $\text{Sr}(\text{OH})^+$,

$$K_f = \frac{[\text{SrOH}^+]}{[\text{Sr}^{++}][\text{OH}^-]} \quad (5)$$

can be estimated. A value for K_f of 1.2 ± 0.2 was calculated and represents the mean and average deviation from the mean of seven measurements made in the range of 0.1N to 1.0N NaOH at constant 1N Na^+ concentration. Based on this result, in a typical salt cake simulant used in this work approximately 40% of the Sr present would be in the form of the hydrolyzed species not readily sorbed on the resin ion exchanger.

C. Effects of the Thermal History of Sodium Titanate on Interaction with Sr in Salt Cake Simulant

The thermal history is of little concern when using the powder form of sodium titanate as ambient temperatures are adequate to dry the material. However, it is important in consolidating the powder into forms which are better suited to continuous, remote column operation as most consolidation methods require elevated temperature processing. A general observation seems to be that the physical stability of the consolidated product increases as processing temperatures are increased. Previous work has shown that Sr capacity on sodium titanate decreases with increasing processing temperature where material calcined at 500°C shows an approximate 10-fold decrease in capacity as compared to material dried at ambient temperature.

The decrease in Sr capacity may result from the loss of hydroxyl sites as the material is converted from a hydrated form to a crystalline form, $\text{Na}_2\text{Ti}_4\text{O}_9$, by heating. Calcining also results in a decrease in surface area as indicated in Figure 3,

which is a plot of ST powder surface area versus calcine temperatures. In this experiment, a single batch of ST was prepared and divided into two parts prior to drying. One was dried at 25°C in vacuum and the other in a CO₂ atmosphere at 25°C. The materials were put into Pt containers and heated for one hour at 100°C, cooled to ambient temperature, and sampled. The remaining materials were put back into the furnace, the temperature increased to 300°C, and after one hour, samples were taken. This procedure was repeated at 500°C and 700°C. Surface area measurements using standard BET techniques were made on the samples after each temperature soak (Fig. 3).

The presence of carbonate-bicarbonate in the CO₂ dried sample appears to result in slightly higher surface areas in the 100°-500°C range and promote densification in the 500°-700°C range. These results are in line with previous observations that the presence of sorbed CO₂ in sodium titanate does not cause large changes in the properties of the material. Strontium capacity is not directly proportional to surface area as the 3.5- and 2.8-fold decreases in surface area in the 100° to 500°C range for the vacuum dried and CO₂ dried ST, respectively, are significantly less than the 10-fold decrease in Sr capacity observed for these materials over the same temperature range.

Conversely, the Sr specificity does not show any definitive trend over the 100°-500°C temperature range. Distribution coefficients for vacuum dried ST powder as a function of calcine temperature in the range of 100° to 700°C (one hour at temperature) are given in Figure 4. The measurements were made in dissolved

FIG.3 SURFACE AREA OF SODIUM TITANATE POWDER
AS A FUNCTION OF CALCINE TEMPERATURE*

*MATERIALS USED WERE SODIUM TITANATE POWDER DRIED AT AMBIENT TEMPERATURE IN VACUUM OR CARBON DIOXIDE ATMOSPHERE. SURFACE AREAS WERE DETERMINED USING BET TECHNIQUES.

FIG.4 Sr-85 DISTRIBUTION COEFFICIENTS ON
CALCINED SODIUM TITANATE POWDER*

*MATERIALS WERE SODIUM TITANATE POWDERS CALCINED FOR ONE HOUR AT GIVEN TEMPERATURES. SOLUTION WAS A DISSOLVED SALT CAKE SIMULANT DOPED WITH 0.1 MICROCURIE PER MILLILITER OF Sr-85. LIQUID-TO-SOLID RATIOS WERE 50 ML/G AND CONTACT TIMES WERE 24 HOURS.

salt cake simulant doped with 0.1 $\mu\text{Ci/mL}$ of Sr-85 using solid-to-liquid ratios of 50 mL/g and contact times of 24 hours. A definite decrease in K_d is observed for calcine temperatures greater than 500°C; however, the values remain relatively high, >1000.

The relative importance of capacity vs. specificity in applying ST to salt cake decontamination has not been clearly determined. Previous work with ST powder (dried at ambient temperature) columns and salt cake simulant doped with trace quantities of Sr-85 (0.1 $\mu\text{Ci/mL}$) showed a Sr breakthrough ($C/C_0 \geq 10^{-4}$) at approximately 3000 bed volumes of throughput; however, calculations showed that the total Sr input to the column at breakthrough represented only 1% of the column capacity.

Strontium breakthrough curves for ST calcined at 500°C were determined using salt cake simulant containing 824 ppm of stable Sr. The column was 1.1 cm in diameter and contained 2.6 g of calcined ST. Flow rates of approximately one bed volume per hour were used. The percent total capacity added to the column was based on a capacity of 1 meq Sr per gram of the calcined ST. After breakthrough was observed ($C/C_0 \sim 0.1$), the column was eluted with a 0.1 M EDTA solution at pH 9. This procedure was repeated until three load-elute cycles were completed and the breakthrough curves are shown in Figure 5.

Of interest is the increase in column capacity with each succeeding load cycle. The mechanism here is not understood as similar increases in capacity could not be achieved by simply soaking the material in salt cake simulant for various times prior to contact with a Sr solution. The calcined ST is definitely

FIG.5 STRONTIUM BREAKTHRU CURVES FOR
CALCINED SODIUM TITANATE COLUMN*

LOAD-CYCLE 1 LOAD-CYCLE 2 LOAD-CYCLE 3

*COLUMN MATERIAL WAS SODIUM TITANATE POWDER CALCINED FOR ONE HOUR AT 500 DEGREES CENTIGRADE. FEED SOLUTION WAS A DISSOLVED SALT CAKE SIMULANT CONTAINING 824 PPM OF STABLE Sr. STRONTIUM BREAKTHRU CURVES ARE SHOWN FOR THREE CONSECUTIVE LOAD-ELUTE CYCLES ON THE SAME COLUMN. A 0.1M EDTA SOLUTION WAS USED TO ELUTE Sr. FLOW RATES WERE ONE BED VOLUME PER HOUR. TOTAL CAPACITY IS BASED ON 1 MEQ Sr PER GRAM OF CALCINED SODIUM TITANATE.

FIG.6 STRONTIUM SORPTION ON ST POWDER AND
ST-LOADED RESIN AS A FUNCTION OF TIME*

50-100 MESH LOADED RESIN 20-50 MESH LOADED RESIN 40-140 MESH ST POWDER

*ALL MEASUREMENTS WERE MADE IN SALT CAKE SIMULANT CONTAINING STABLE Sr. SOLUTIONS CONTAINED 50% TO 150% EXCESS Sr BASED ON A CAPACITY OF 12 MEQ Sr/G ST. LOADING IS BASED ON WEIGHT OF ST IN MATERIAL AFTER CALCINING AT 700 DEGREES CENTIGRADE. LOADING AFTER 24 HOURS WAS 11.95, 8.53, AND 11.72 MEQ Sr/G ST FOR 50-100 RESIN, 20-50 RESIN, AND 40-140 POWDER, RESPECTIVELY.

less efficient than ambient dried ST as the loadings observed for the three cycles represent a range of 10 to 25% of the loading observed for a comparable amount of ambient dried material. However, the use of elution steps to remove the economic penalty of greater material consumption and the advantages of higher processing temperatures applicable to consolidation processes may offset the decrease in column performance. This approach has not been applied at Sandia or at Norton Co. as minimum processing temperatures were sought in all consolidation efforts with the intent of maximizing column capacity. It should be considered in any future plans to improve the physical form of the material for this or other applications.

D. Properties of Loaded AG-MP-1 Macroreticular Resin Forms

The AG-MP-1 type anion exchange resins have been evaluated as vehicles for sodium titanate, sodium niobate, and sodium tantalate because they provide a reproducible matrix with respect to particle size and shape; the loaded resins show no particular attrition as a result of storage or liquid contact, and they have hydraulic properties which are well characterized and familiar to those who apply ion exchange in the process industries. The greater part of the resin work was directed toward sodium titanate-loaded AG-MP-1 type macroreticular anion exchange resin (the initial development work leading to these materials has been reported (1)). In general, the incorporation of sodium titanate on an atomic scale within the resin beads has not been found to alter the chemistry of the material relative to this application.

The commercially proven, favorable hydraulic properties of the resin form as compared to ST powder and the potential for periodic elution, regeneration, and re-use both tend to offset the higher initial material cost and disposal problems associated with organic resins. The work to be described concerning resin forms was directed toward elution-regeneration processes and consisted of the determination of some materials properties deemed to be important in that context and short term column tests using salt cake simulants containing stable Sr (0.01 to 0.1 N).

The most desirable, as well as the most efficient, column eluent would be an acid solution. However, with a material such as ST, acid elutes not only the Sr but also the Na and neither preferentially. In addition, the ST has a significant solubility in acid solutions with concentrations greater than one-tenth normal. These two problems, one requiring large amounts of acid for elution and the other dictating against the use of concentrated acid solutions, severely restrict the development of acid elution methods for ST.

Using carefully controlled conditions, acid elution can be accomplished in a reasonably efficient manner which is subsequently described. EDTA elution has also been evaluated and appears more amenable to titanates as no matrix attack has been observed, only the Sr is eluted, and the entire load-elute cycle is done in basic solution.

Tantalate- and niobate-loaded resins were also evaluated primarily because these materials were known to be stable in strong acid solution thus facilitating column elution, but also to

determine if they had any unique (with respect to titanates) properties in this application. Both materials are very efficient in sorbing Sr from salt cake simulant; however, both appear to be very slightly soluble in caustic solution. This property, which has not been determined quantitatively, along with the higher material cost discourages the use of niobates or tantalates in this application. However, these materials are new and may have application in other areas of waste management.

1. Sodium Titanate-loaded Resin.

Although the sodium titanate incorporated in AG-MP-1 resin is homogeneously distributed (elemental distribution mapping with a scanning electron microscope did not detect any Sr segregation on a 1 micron scale) within the resin structure, Sr sorption properties remain nearly identical to those of ST powder. The data in Fig. 6 provide a comparison of the Sr sorption capacities of the resin and powder forms as a function of time. The measurements were made by contacting 0.25-0.30 g of ST powder with 50-100 mL of 0.098N Sr^{++} in salt cake simulant or 1.25-1.35 g samples of 50-100 mesh AG-MP-1 resin (19.4% ST) and 20-50 mesh AG-MP-1 resin (21.7% ST) with 65-75 mL volumes of 0.07N Sr in salt cake simulant for various periods of time, taking samples of the liquid through 0.8 μ filters (Acropore), and determining the Sr remaining in the liquid phase by EDTA analysis. The sorption kinetics of the powder and the ST in the 50-100 mesh resin were very similar as were the total amounts sorbed after a twenty four hour period. Note that the Sr loading is based only on the quantity of ST present, thus the capacity based on total weight of exchanger or

bed volume would be significantly lower for the resin material. The sorption rate of the 20-50 mesh resin is significantly slower during the first hour of contact making it less desirable for column use.

The sorption of trace quantities of Sr-85 on the 50-100 mesh resin versus equilibration time is shown in Fig. 7 where sorption is expressed in terms of distribution coefficients. The resin sorbed approximately 10% of the Sr-85 in the first minute of contact and 99.8% after the first 30 min. The K_d values for the resin over the time period shown in Fig. 7 and up to 24 hours of contact time were a factor of 2-4 lower than those observed for ST powder.

The difference in sorption kinetics observed for the 20-50 mesh and 50-100 mesh loaded resins in static tests is also evident in column flow experiments, Fig. 8. Five to six gram beds of the resins were formed in 1.1 cm diameter columns by standard techniques and salt cake simulant containing 0.07N Sr was pumped through the columns using a tubing pump. Flow rates of one and five column bed volumes per hour were used and individual bed volumes were collected for analysis by atomic absorption spectroscopy. The units of "% column capacity added to column" are based on the weight ST remaining after calcining the resin at 700°C assuming a capacity of 12 meq of Sr per gram of ST. At the same flow rate, 1 column volume per hour (cv/hr), Sr breakthrough, $C/C_0 > 10^{-3}$ is observed at 15% and 86% capacity for the 20-50 mesh and 50-100 mesh resins, respectively. Increasing the flow rate (5 cv/hr) through a 50-100 mesh resin bed resulted in an earlier breakthrough,

60% capacity, but the material was still more efficient than the larger size resin bed.

Both acid and EDTA solutions have been used to elute Sr from sodium titanate-loaded AG-MP-1 resin columns. Acidic solutions are preferred as they efficiently remove all sorbed cations from a titanate bed. However, the titanate matrix is soluble in acid solution, the extent of which at ambient temperature is dependent on acid strength and the thermal history of the titanate material. The data in Table 1 illustrate the solubility of ambient temperature dried sodium titanate powder in acid. One gram samples of ST were soaked in 80 ml volumes of nitric acid for 80 minutes. Sufficient acid was added to stoichiometrically elute the sodium from the ST and provide excess amounts calculated to give acid concentrations in the liquid phase ranging from 0.001N to 0.5N. The liquids were analyzed by atomic absorption spectroscopy to determine Ti concentrations and the amount of ST dissolved was calculated from these results. Dissolution is quite extensive even in 0.1N acid solution where 6.1% of the ST is dissolved. A 0.01N acid solution could be used as an eluent, but a volume of 400 to 450 mL is needed to elute the sodium alone from one gram of ambient dried ST and the volume would be more than twice as great if the material were fully loaded with S. Another problem which has been observed in using dilute acid for elution of ST beds is hydrolysis and subsequent precipitation of the small quantities of dissolved titanium. This precipitation occurs within the column at the acid-water interface and results in column plugging. Salt cake simulant is washed from the column with water after Sr loading or it as well would consume acid.

FIG.7 Sr-85 Kd ON SODIUM TITANATE-LOADED RESIN AS A FUNCTION OF EQUILIBRATION TIME*

*RESIN WAS DAMP 50-100 MESH AGMP1 TYPE CONTAINING 19.4% ST. FOUR GRAMS OF LOADED RESIN WERE CONTACTED WITH 85 ML OF SALT CAKE SIMULANT DOPED WITH 0.54 MICROCURIES OF Sr-85 PER MILLILITER. Kd IS BASED ON THE WEIGHT OF ST IN THE RESIN.

FIG.8 COLUMN BREAKTHRU CURVES FOR ST-LOADED RESIN-DEPENDENCE ON RESIN MESH AND FLOW RATE*

*RESIN WAS DAMP SODIUM TITANATE-LOADED AGMP1 CONTAINING 19.4% ST. COLUMNS WERE 1.1 CM IN DIAMETER AND CONTAINED 5 TO 6 GRAMS OF RESIN. FEED SOLUTION WAS SALT CAKE SIMULANT WITH 0.07N STABLE Sr. FLOW RATES ARE GIVEN IN COLUMN BED VOLUMES PER HOUR (CV/HR). COLUMN CAPACITY WAS BASED ON 12 MEQ OF Sr PER GRAM OF ST IN THE RESIN.

The acid solubility of ST decreases with increasing processing temperature of the ST powder as might also be the case for some of the consolidated ST forms. However, materials calcined at temperatures as high as 500°C still undergo significant attack in strong acid solution if contacted for extended periods of time (Fig. 9), a possibility which cannot be eliminated in a plant operation.

As expected, the acid dissolution also applied to the ST-loaded resin as the chemistry of ST in the resin has been shown to be approximately the same as that of the ambient temperature dried powder. A five cycle load-elute experiment was done by batch contacting. A 1.4 gram sample of 50-100 mesh AG-MP-1 resin (19.4% ST) was contacted with approximately 70 mL of 0.07 N Sr in salt cake simulant for 10 minutes, washed, and contacted with 50 mL of 0.5 N HNO₃ for 5 minutes, and washed with water. This sequence was repeated five times. The amount of Sr sorbed in units of meq Sr/g ST in resin were 6.1, 6.2, 6.5, 6.1, and 5.9 for loading steps 1 through 5, respectively. The quantity of Ti dissolved in each elution step expressed as percent Ti initially present in resin were 0.51%, 0.70%, 0.81%, 0.70% and 0.59% for loading steps 1 through 5 representing a total dissolution of 3.4% of the titanate in the resin during the five elution cycles.

The batch load-elute experiment with ST-resin provided results leading to the following conclusions. First of all, it demonstrated that after acid elution, ST can be regenerated in salt cake simulant with little or no effect on the Sr sorption

properties. Secondly, it showed that ST incorporated in resin was susceptible to acid dissolution. In subsequent experiments, ST-resin columns eluted with acid by gravity flow were susceptible to column plugging by the same mechanism mentioned previously for ST beds.

On the other hand, resin ST columns can be efficiently eluted with acid solution with minimal Ti dissolution if acid concentrations, volumes, and process steps are carefully controlled. The initial acid contact with the bed is done by backflowing into the column one bed volume of acid of sufficient strength to elute all of the Sr and Na sorbed on the bed and provide a final solution pH of 2 to 3. The backflow method elevates and disperses the bed and eliminates column plugging problems. The initial bed volume is added at as high a flow as possible to minimize contact time of any part of the bed with the strong acid. The Sr along with Na is subsequently washed from the bed with a dilute, 0.01M acid solution using the normal flow direction.

The Sr elution curve shown in Fig. 10 is the result of applying the method to a column which had been loaded to 8.5% capacity with a salt cake simulant solution containing stable Sr. The bed was 1.1 cm in diameter and contained 5 g of damp AG-MP-1 resin (19.4% ST) with a bed volume of 7.24 mL. After loading, it was washed with 1.2 bed volumes of water, and 1 bed volume of 1.01N HNO_3 acid was backflowed into the column. After standing 5 minutes, the column was drained at a rate of 24 bed volumes per hour and washed with 1.7 bed volumes of 0.01N HNO_3 , 4.9 bed volumes of water, and 3.5 bed volumes of salt cake simulant

FIG.9 SOLUBILITY OF ST IN 1N NITRIC ACID
AS A FUNCTION OF CALCINE TEMPERATURE *

*SODIUM TITANATE POWDER WAS CALCINED FOR ONE HOUR AT TEMPERATURE. ONE GRAM SAMPLES OF CALCINED POWDER WERE SOAKED IN 50 ML VOLUMES OF 1N NITRIC ACID FOR A PERIOD OF 24 HOURS. A VALUE OF 200 MG TI DISSOLVED REPRESENTS DISSOLUTION OF APPROXIMATELY 40% OF THE SAMPLE.

FIG.10 NITRIC ACID ELUTION OF Sr FROM
ST-RESIN COLUMN LOADED TO 8.5% CAPACITY*

*RESIN WAS SODIUM TITANATE-LOADED AGMP1 TYPE. COLUMN WAS LOADED WITH Sr TO 8.5% CAPACITY BASED ON 12 MEQ OF Sr PER GRAM OF ST IN THE RESIN. ONE BED VOLUME OF 1N NITRIC ACID WAS ADDED BY REVERSE FLOW AND DRAINED. THE BED WAS THEN WASHED WITH 0.01N NITRIC ACID. FLOW RATES OF 13 TO 20 BED VOLUMES PER HOUR WERE USED.

to regenerate the column. The washing steps were done at flow rates in the ranges of 13 to 20 bed volumes per hour. The initial bed volume of effluent (added as 1.01N HNO_3) contained 54% of the total Sr, was 0.09N in HNO_3 , and contained 65 ppm Ti which represents 0.10% of that in the column. The entire effluent contained 0.28% of the total Ti in the column bed.

An EDTA elution curve for a 50-100 mesh ST-resin column is shown in Fig. 11. The column was 1.1 cm in diameter and contained a 10 g bed of damp resin (19.4% ST) which was loaded to 25% capacity with Sr from a salt cake simulant. The column was washed with water to remove excess salt cake solution prior to elution as the stability of the Sr-EDTA complex decreases with increasing basicity above pH 10. This would be unnecessary in practice as the only problem foreseen in following the feed solution directly with EDTA eluent would be reduced efficiency for the initial bed volume of eluent. The eluent solution was a 0.1M EDTA solution with a pH of 9 and was used at a flow rate of 1 bed volume per hour.

The results in Fig. 11 showing that only approximately 97% of the Sr was eluted are probably misleading. The calculation was based on the total Sr added to the column and the combined analysis of individual 3 mL volumes of effluent by atomic absorption spectroscopy. The combined error associated with these analyses could easily account for the 3% of Sr apparently remaining on the column. Of the total amount of Sr found in seven bed volumes of effluent used, 99.96% was contained in the first four bed volumes of effluent.

A three cycle load-elute experiment was done using a 5 g bed of damp AG-MP-1 resin (19.4% ST) in a 1.1 cm diameter column. The Sr breakthrough curves for the three column loading operations are shown in Fig. 12. Loading was done at a flow rate of 1.2 bed volumes per hour using a salt cake simulant with 0.06N Sr in the first two cycles and 0.092N in the final cycle. A 0.1M EDTA solution (pH 9) was used as the eluent at a flow rate of one bed volume per hour. The column was not washed with water between load-elute or elute-load operations. The efficiency of the ST-resin bed remained relatively constant through the three cycles, showing that EDTA elution did not adversely effect further use of the bed. After the final elution step the resin was removed from the column and soaked in 25 mL of 0.1M EDTA (pH 9) solution for 40 hours. The Sr found in the solution represented 0.04% of the total amount of Sr sorbed on the column during all three loading steps.

2. Sodium Niobate- and Sodium Tantalate-loaded Resin.

The Sr sorption properties (from salt cake simulant) of sodium niobate(SN)-loaded resin and sodium tantalate(STAN)-loaded resin were compared with ST-loaded resin. All three resin samples were 18% SN, 23.7% STAN and 19.4% ST, respectively. The results are shown in Fig. 13. The capacities are based on the weight of the oxide residue resulting from calcining the resin at 700°C. Samples of damp resin, 1.25-1.30 g, were contacted for various times with salt cake simulant containing 0.065-0.07N Sr. Values for SN- STAN-resin after 24 hours were 7.68 and 6.67 meq Sr/g, respectively. Sorption rates for SN- and STAN-resin based on

FIG.11 EDTA ELUTION OF Sr FROM ST-RESIN
COLUMN LOADED TO 25% OF CAPACITY*

*COLUMN WAS 1.1 CM IN DIAMETER AND CONTAINED 10 GRAMS OF DAMP 50-100 MESH AGMP1 RESIN LOADED WITH 19.4% ST. COLUMN WAS LOADED WITH A SALT CAKE SIMULANT-STABLE Sr SOLUTION TO 25% OF CAPACITY AND WASHED WITH WATER. Sr WAS ELUTED WITH 0.1M EDTA (pH9) AT A FLOW RATE OF 1 BED VOLUME PER HOUR.

FIG.12 Sr BREAKTHRU CURVES FROM THREE LOAD-
ELUTE CYCLES ON A ST-RESIN COLUMN*

*COLUMN WAS 1.1 CM IN DIAMETER AND CONTAINED 5 GRAMS OF DAMP ST-LOADED AGMP1 RESIN(19.4% ST). COLUMN WAS LOADED WITH SALT CAKE SIMULANT CONTAINING 0.06,0.06, AND 0.09N Sr FOR LOAD CYCLES 1,2, AND 3, RESPECTIVELY. ELUTION WAS DONE WITH 0.1M EDTA (pH9) AFTER EACH LOADING STEP. FLOW RATES FOR LOADING WERE 1.2 BED VOLUMES PER HOUR.

fraction of 24 hour capacity sorbed as a function of time during the first hour of contact were comparable to or higher than that of the ST-resin.

The total Sr capacity in units of meq/g for SN- and STAN-resin is expected to be lower than that of ST-resin due to the higher molecular weights of the former. Using the measured ST-resin capacity of 11.95 meq Sr/g ST and ratios of the molecular weights of the empirical formulas used to represent the stoichiometry of the 700°C calcined products - $\text{Na}_2\text{Ti}_4\text{O}_9$, $\text{Na}_2\text{Nb}_4\text{O}_{11}$, and $\text{Na}_2\text{Ta}_4\text{O}_{11}$ - Sr capacities of 7.68 and 4.82 meq Sr/g are estimated for SN and STAN, respectively. Note that the value calculated for SN corresponds exactly to the measured value while the measured capacity for STAN is about 40% higher than would be expected.

Strontium breakthrough curves from a two cycle load-elute experiment with STAN-resin are presented in Fig. 14. A 5.3 g bed of 50-100 mesh STAN-resin (23.7% STAN) was formed in a 1.1 cm diameter column. Feed solution was a salt cake simulant containing 0.064N Sr which was run through the column at a rate of 1 bed volume per hour until the Sr concentration in the effluent was equal to that of the feed. Sr was first detected in the effluent $C/C_0 = 10^{-3}$, after approximately 70% of the total column Sr capacity (based on 1.58 meq Sr per gram of damp resin) had been added to the column. The column bed was washed with water and 1N HNO_3 was used to elute the bed at a flow rate of 1 bed volume per hour. The column was loaded again using the same conditions described for the first cycle and breakthrough, $C/C_0 = 10^{-3}$, was observed after 76% of the total Sr capacity was added to the

column. The results indicate that a STAN-resin column can be eluted with strong acid, regenerated, and re-used with no apparent decrease in efficiency

The Sr elution profile is shown in Fig. 15. Greater than 99.9% of the total Sr eluted was contained in the first five bed volumes of eluent. No evidence of column plugging was seen and dissolved Ta was not detected by atomic absorption techniques in any of the acid effluent.

The presence of Ta was detected in salt cake simulant effluent collected prior to Sr breakthrough during the loading process. The effluent samples, which were clear solutions, were acidified and diluted prior to Sr analysis. The addition of acid resulted in precipitation of small quantities of tantalic acid. Unfortunately, the extent of dissolution was never quantified due to the loss of a large portion of the bed during a calcining operation which was intended to determine the amount of sodium tantalate remaining in the resin. A qualitative check of SN-loaded resin showed that SN was also slightly soluble in salt cake simulant.

Tantalum was not observed in any of the salt cake simulant effluent collected subsequent to the breakthrough of Sr. Experience with the water soluble quaternary ammonium compounds used in preparing the loaded resins has shown that the Ti, Nb, and Ta anions react with most polyvalent cations to form compounds which are very insoluble in water. Precipitation of dissolved tantalum by excess Sr within the resin beads provides the most likely explanation for the absence of dissolved Ta in the salt cake simulant after Sr breakthrough had occurred.

FIG.13 COMPARISON OF Sr SORPTION ON ST-, SN-,
AND STAN-LOADED 50-100 MESH AGMP1 RESIN*

*RESINS WERE DAMP 50-100 MESH AGMP1 TYPE CONTAINING 19.4% ST, 18% SN, AND 23.7% STAN, RESPECTIVELY. 1.25-1.30 GRAM SAMPLES WERE ADDED TO 70-72 ML VOLUMES OF SALT CAKE SIMULANT CONTAINING 0.065-0.07N Sr. SORPTION VALUES WERE BASED ON THE WEIGHT OF ST,SN, OR STAN IN THE RESIN. VALUES AFTER 24 HOURS WERE 11.95, 7.64, AND 6.67 MEQ Sr/G FOR ST,SN, AND STAN RESINS, RESPECTIVELY.

FIG.14 TWO CONSECUTIVE Sr LOADING STEPS
ON A SODIUM TANTALATE-AGMP1 RESIN COLUMN*

*COLUMN WAS 1.1 CM IN DIAMETER AND CONTAINED 5.3 G OF DAMP 50-100 MESH STAN-AGMP1(23.7%)RESIN. COLUMN Sr LOADING WAS DONE WITH SALT CAKE SIMULANT-0.064N Sr SOLUTION AT A FLOW RATE OF 1 BED VOLUME PER HOUR. COLUMN WAS ELUTED WITH 1N NITRIC ACID BETWEEN LOADING STEPS. COLUMN CAPACITY WAS BASED ON 1.58 MEQ Sr PER GRAM OF DAMP RESIN.

FIG.15 ELUTION OF Sr FROM A STAN-AGMP1 RESIN
COLUMN LOADED TO 100% CAPACITY*

*COLUMN WAS 1.1 CM IN DIAMETER AND CONTAINED 5.3 GRAMS OF DAMP 50-100 MESH SODIUM TANTALATE-LOADED AGMP1 RESIN CONTAINING 23.7% STAN. COLUMN WAS LOADED WITH A SALT CAKE SIMULANT-Sr SOLUTION AND Sr WAS ELUTED WITH 1N NITRIC ACID AT A FLOW RATE OF 1 BED VOLUME PER HOUR.

Neither the SN- nor STAN-loaded resins offer any advantages as compared to the ST-resin in the area of Sr sorption from salt cake simulant. They are more expensive than the titanates, primarily because the alkoxide raw materials are available only in research quantities and not in bulk as are the comparable Ti compounds. Pending quantitation of the solubility or dissolution rates, this phenomena has to be considered a major drawback to using these materials in situations where they would be in contact with caustic solutions for extended periods of time. These factors are judged to outweigh the advantage of acid stability shown by the SN and STAN materials and these materials should not be given further consideration for this application. However, they could be useful for other waste streams comprised of neutral or weakly acid liquids or in instances where the nuclides cannot be eluted by EDTA complexation.

E. Hydraulic Properties of Sodium Titanate-loaded Resin Beds.

The hydraulic properties studied included pressure drop through the column, compaction and compression of the bed, channeling, attrition of fines, and elution of titanium. To study these properties, a column of ST-resin (supplied by Cerac, Inc.) 10 cm diameter by 45 cm height, was prepared and operated continuously for 527 hours. The column feed was salt cake simulant, a solution containing $6N$ $NaNO_3$ and $0.6N$ $NaOH$. Nitrogen at 1.5 psig was used to maintain flow at or near a rate of 412 mL/min (superficial velocity of 10 ft/hr). The feed was recirculated to minimize the volume needed for the experiment.

The bed was formed by flowing 1N NaNO_3 up through the column while the resin was fed into the top of the column. A 1N NaNO_3 solution was used as it is applicable to both ST-loaded AG-MP-1 and to unloaded AG-MP-1 resin (the latter material floats in salt cake simulant), but salt cake simulant could be used as well. The flow rate, bed height, and titanium content of the effluent were monitored over the life of the experiment.

The 412 mL/minute flow rate was maintained as long as the nitrogen pressure was kept at 1.5 psig. When the nitrogen pressure was reduced, the flow rate dropped accordingly, but could be restored to the nominal value by adjusting the pressure back to 1.5 psig. Table 2 gives values of the bed resistance (pressure drop/flow rate) at various times during the experiment. The data show that bed resistance stayed fairly constant indicating that attrition of "fines" leading to column plugging was not a problem.

Compaction and compression of the bed were not identified as a problem since the bed height remained constant through the duration of the experiment. There was no visible evidence of column channeling.

Samples of column effluent were taken periodically for Ti analysis using a colorimetric technique based on the formation of a titanium peroxide complex by addition of hydrogen peroxide to an acidified (H_2SO_4) solution (7). Titanium content in the effluent ranged between 1.5 and 9.5 ppm. The maximum titanium concentration (equivalent to less than 0.1% of the titanium in the column) occurred during the initial 30 to 54 hours, and had decreased to 5.3 ppm at the end of the experiment. Since it was a closed system,

the decrease indicates that Ti was being sorbed by the column support, tubing or resin bed. Post-test analysis showed that the column support, a stainless steel frit, retained only 1.5 milligrams of titanium. Filtration of the column effluent through 0.8 μ and 0.2 μ filters (Gelman Acropore) prior to Ti analysis had no effect on the analytical result indicating that the Ti present in the simulant was either dissolved or in colloidal suspension, conditions which would have no effect on column operation.

In summary, the column experiment indicated that the flow characteristics of a bed of sodium titanate-loaded macroreticular resin, MSA-1, are not adversely altered by:

- a. Increasing bed resistance - bed resistance remained constant
- b. Attrition - no "fines" were detected
- c. Compaction or compression of bed - bed height remained constant
- d. Channeling - none was observed
- e. Titanate dissolution - the ST which dissolved was not significant in terms of changing bed capacity and in a form which did not alter column flow properties.

F. Radiation Stability of Sodium Titanate and Sodium Titanate Loaded AG-MP-1 Resin

A study to determine the radiation stability of sodium titanate and sodium titanate-loaded AG-MP-1 Resin has been completed by Kenna (3) and the following summary of the work is included for completeness of this report. Samples of these materials were irradiated using a ^{60}Co gamma source which provided 1.2×10^5 rads/min at the irradiation point used for the samples. Samples were exposed

for times ranging from three hours to eleven days corresponding to absorbed radiation doses ranging from 10^7 to 2×10^9 rads, a range based on estimated total doses for the materials when in actual use. The ^{66}Co source and samples were in close proximity in an air environment with temperatures ranging up to 100°C .

The Sr exchange capacity of ST powder remained constant through a dose of 3×10^7 rad, and decreased to approximately 50% of its initial value after 7×10^8 rads and remained constant through 2×10^9 rads. The decrease in exchange capacity is believed to result from heating associated with the irradiation rather than from some other form of radiation damage.

The Sr ion exchange capacity of the ST-resin remains constant through 5×10^8 rads and then decreases rapidly to about 30% of its initial capacity after a dose of 2×10^9 rads. The loss of capacity was attributed to sufficient radiation damage to the organic resin matrix to physically and/or chemically inhibit ion-exchange reaction with the titanate. This was supported by visible color changes of the organic and a severe decrease in anion exchange capacity of both the loaded resin and a control sample of the unloaded resin material in the nitrate form.

The conclusion drawn from the study is that problems may arise if a sodium titanate-loaded AG-MP-1 resin is exposed to a radiation dose level $>5 \times 10^8$ rads. If a column is simply loaded until breakthrough occurs and discarded, no problems are foreseen for this application. However, consideration must be given to the potential effects of radiation degradation if sustained column use via elution-regeneration processes are proposed.

III. PELLETIZED SODIUM TITANATE MATERIALS.

Arrangements were made for Norton Co., Akron, Ohio, to perform a R & D study on the application of state-of-the-art methods to the consolidation of sodium titanate powder on a best-effort basis. The goal was to produce a form which retained its physical stability in caustic, sodium nitrate solution using a process which resulted in as little adverse effect on the exchange properties - capacity and specificity - as practicable. The latter poses difficulty as consolidation of inorganic oxide materials typically involves elevated temperature and, as was mentioned previously, the ion exchange capacity may be adversely effected by increasing temperature.

During the course of the Norton study, samples of materials which appeared to be promising were sent to Sandia for further evaluation. In general, the samples sent to Sandia were prepared by adding 10-30% by weight of a binder material (calcium aluminate compound or alumina) to sodium titanate powder, extruding the mixture in the form of 1/16" diameter cylindrical pellets, followed by a curing step in a temperature range of ambient to 340°C.

Pellet samples evaluated at Sandia are listed in Table 3 which contains information supplied by Norton Co. along with the results of simple weight loss measurements which provide a qualitative indication of the thermal history of the pellets. Strontium capacities and distribution coefficients were determined and the results are given in Fig. 1-17 and Fig. 18-19, respectively. These measurements were made both on the pellet forms and on powder obtained by grinding the pellets to pass a 100 mesh screen. This

separates the effects of changes in material properties which may have resulted from either the binder addition and thermal processing or from those due to a decrease in effective surface area as a result of the pelletizing operation. Finally, a crush test was used to provide a qualitative basis for comparing the physical stability of the as-received pellets and to indicate changes that resulted from contact with salt cake simulant. These results are given in Table 4.

The Sr capacities of the Norton pellets were determined by contacting the pellets or powdered pellets with a salt cake simulant containing 0.07N to 0.09N Sr. Contact times of one hour and 16-24 hours were used with liquid-to-solid ratios of approximately 200 mL/g. Results of the capacity measurements are given in Figures 16 and 17. Processing temperature or binder composition does not appear to influence Sr sorption during the initial hour of contact with simulant. The pellets all sorb approximately the same relative amount of Sr during this period; however, the relative increase at longer contact times was greater for pellets with higher processing temperatures. Assuming the binder material is not influencing the sorption process, the most significant factor relative to the amount of Sr sorbed appears to be pellet porosity which relates to effective surface area or that fraction of the material comprising the pellet which actually contacts the liquid phase. This observation is supported by sorption data for the powdered pellets, Fig. 17, where higher surface areas were produced by a grinding operation which resulted in larger increases in total Sr sorption in the materials processed

at low temperatures (63316 and 63317). The relatively small change between the pellet and powder forms for materials processed at higher temperatures suggests an increase in pellet porosity. An expected increase in Sr sorption rates for all powdered materials due to increased surface areas or more favorable liquid volume to geometrical surface area ratios are apparent.

Sr-85 distribution coefficients (K_d) were also determined for both pellet samples and powders obtained by grinding the pellets to pass a 100 mesh screen. The measurement was made by contacting 0.5 gram samples of pellet or powder with salt cake simulant containing approximately 1 $\mu\text{Ci/mL}$ of Sr-85 using liquid-to-solid ratios of 50 mL/g. The K_d calculation was based on analysis of Sr-85 activity in liquid phase samples taken through 0.8 μ filters (Acropore) after contact times of 1 and 24 hours. The results for the pellet and powder forms are shown in Fig. 18 and Fig. 19, respectively.

The K_d values for all pellets tested were comparable after one hour contact time and with the exception of the 63317 sample, the same was true after 24 hour contacts (Fig. 18). The powder samples had K_d values which were 5 to 10 times higher than the corresponding pellets and, as observed in the capacity measurements, higher sorption rates at the shorter contact times (Fig. 19). The high distribution coefficients, $\sim 10^5$ mL/g, and the Sr capacities of the powdered pellets processed at lower temperatures (63316 and 63317) are comparable to those observed on pure sodium titanate powder dried at ambient temperature in vacuum. This suggests that the presence of the binder added by Norton does not significantly affect the Sr sorption properties of the material.

The results of the Sr capacity and K_d experiments do not point to a given pellet sample (processing method) which is clearly superior or inferior with respect to the others. They do lead to the conclusion that a desirable process would employ low temperature processing to form a pellet with open porosity.

The degree of porosity becomes a compromise between effective surface area and the strength or durability of the pellets. A simple crush test was used to provide a qualitative estimate of the relative pellet stabilities in the as-received condition and after soaking in salt cake simulant for various periods of time (the lengths of which are related to the date the material was received from Norton relative to the time this study was ended). A one day soak in salt cake simulant was applied to all samples such that any "instantaneous" effects would be identified and to provide a more consistent baseline for assessing the effects of longer contact times. This test did show that the 63316 pellets were significantly degraded after one hour of contact, and for that reason, K_d and further crush tests on this material were not performed.

The crush tests were made using an Instron Tester, Model TT6, capable of applying pressures to the pellet samples in the range of 10 grams to 4550 Kg. Pellets soaked in salt cake simulant were washed with water and dried at 100°C prior to testing, which consisted of subjecting three individual pellets, 1/4" in length, to a constantly increasing pressure until failure (crushing) was recorded. The applied loads at failure in units of grams are tabulated in Table 4 as the mean and average deviation from the mean for three tests.

The crush tests did show some significant differences between the pellet samples. In the as-received condition, the pellets processed at low temperature (63316 and 63317) had the highest crush strengths; however, pellet-to-pellet variations in the intermediate and higher temperature materials precludes differentiation. The apparent strengths of the higher temperature pellets (63275 and 63287) appear to have increased after a one day soak in salt cake simulant, while the pellets soaked for 4 months were of the same order as the as-received samples.

The low temperature Ca aluminate binder containing materials had the poorest resistance in salt cake simulant. The 63316 pellets were significantly degraded after one hour. The pellets cracked in a radial direction and a significant fraction completely degraded to powder and, as a result, were not subjected to the entire test regime. The 63317 pellets were not visually degraded after one hour. However after a 2 month period the pellets had broken up to the extent that none of the pieces were large enough to test.

The pellets processed at intermediate temperatures remained intact during the soaking periods, at least by visual inspection. The strength of the 63321 pellets appears to have been decreased after a one day soak, while the 63327 material may have increased in crush strength during this period. Although the pellets remained intact, the crush strength of the 63321 material decreased drastically during the following two months. Further testing of the 63327 material would be necessary to draw any conclusions relative to the long term stability of these pellets.

FIG.16 Sr CAPACITY OF SODIUM TITANATE
PELLET SAMPLES FROM NORTON CO.*

*STRONTIUM CAPACITIES WERE MEASURED IN SALT CAKE SIMULANT CONTAINING 0.07N TO 0.09N Sr USING LIQUID-TO-SOLID RATIOS OF 200 ML/GRAM. THE OPEN AREAS REPRESENT SORPTION DURING THE FIRST HOUR. THE CROSS-HATCHED AREAS THAT IN THE NEXT 15 TO 23 HOURS. NO FURTHER SORPTION WAS OBSERVED FOR THE 63317 PELLETS AFTER THE FIRST HOUR.

FIG.17 Sr CAPACITY OF POWDERED SODIUM
TITANATE PELLET SAMPLES FROM NORTON CO. *

*STRONTIUM CAPACITIES WERE MEASURED IN SALT CAKE SIMULANT CONTAINING 0.07N TO 0.09N Sr USING LIQUID-TO-SOLID RATIOS OF 200 ML/GRAM. THE OPEN AREAS REPRESENT SORPTION DURING THE FIRST HOUR. THE CROSS-HATCHED AREAS THAT IN THE NEXT 15 TO 23 HOURS. PELLETS WERE GROUND TO PASS A 100 MESH SCREEN.

FIG.18 Sr DISTRIBUTION COEFFICIENTS ON
NORTON CO. SODIUM TITANATE PELLET SAMPLES *

*DISTRIBUTION COEFFICIENTS (K_d) WERE DETERMINED BY CONTACTING 0.5 GRAM SAMPLES OF PELLETS WITH 25 ML SALT CAKE SIMULANT DOPED WITH 1 MICROCURIE PER MILLILITER OF Sr-85 FOR A PERIOD OF ONE HOUR OR 24 HOURS.

FIG.19 Sr DISTRIBUTION COEFFICIENTS ON
POWDERED SODIUM TITANATE PELLET SAMPLES*

*PELLET SAMPLES WERE GROUND TO PASS A 100 MESH SCREEN. THE DISTRIBUTION COEFFICIENTS (K_d) WERE DETERMINED BY CONTACTING 0.5 GRAM SAMPLES OF POWDER WITH 25 ML OF SALT CAKE SIMULANT DOPED WITH 1 MICROCURIE PER MILLILITER OF Sr-85 FOR A PERIOD OF ONE HOUR OR 24 HOURS.

Despite the qualitative nature of the crush test, which limits its usefulness to comparison of similar materials under identical conditions, and the large variation in results for tests on "identical" pellets, it does provide some information leading to the following conclusions. First, the test is not useful as a qualifying test on as-received material if it is intended to use the results to infer stability under process conditions. Finally, increased temperature during processing or use of alumina rather than Ca aluminate binder results in pellets with greater physical stability in salt cake simulant over extended contact times.

A more complete discussion of the pellet processing work is given in Appendix I in which the final report from Norton Co. describing their work is reproduced in part.

IV. SODIUM TITANATE FORMS - SUMMARY

All of the sodium titanate (ST) forms used in this work are shown in Photographs A through D in Fig. 21. The resin (Photo A) is 20-50 mesh macroreticular anion exchange resin (Bio-Rad AG-MP-1) loaded with approximately 35% by weight of ST. The material shown in Photo B is the ST residue which results from calcining the loaded resin thus volatilizing the organic fraction. The ST spheres have ion exchange properties comparable to the 500°C calcined ST powder discussed in Section IIC. Sodium titanate powder which was dried at ambient temperature and passed through a 40 mesh screen and ST pellets prepared by Norton Co. using the powder as the starting material are shown in Photos C and D, respectively, in Fig. 21.

FIG.21 PHYSICAL FORMS OF SODIUM TITANATE

A. ANION EXCHANGE RESIN LOADED
WITH 35% SODIUM TITANATE (20X)

B. SODIUM TITANATE SPHERES — RESIDUE
AFTER CALCINING ANION RESIN (20X).

C. SODIUM TITANATE POWDER (-40 MESH)
DRIED AT AMBIENT TEMPERATURE (20X)

D. EXTRUDED SODIUM TITANATE PELLETS
PREPARED BY NORTON CO. (10X)

IV. SUMMARY AND CONCLUSIONS

The Sr sorption properties of sodium titanate (ST) and a commonly used organic cation exchange resin, a polyvinylbenzene-styrene copolymer containing a sulfonic acid functional group, were compared under conditions applicable to Defense Waste, i.e., caustic solutions containing high sodium concentrations. Strontium distribution coefficients (K_d) on ST were found to be nearly independent of sodium ion concentration in the range of $0.1N$ to $5.0N$ whereas a 5 order of magnitude decrease in K_d was observed for the cation resin over the same range (Fig. 1). In the absence of organic complexing ligands, Sr found in salt cake solution probably exists as an equilibrium mixture of the divalent ion and one or more hydrated forms, $Sr(OH)_x^{2-x}$. Postulating a species represented empirically as $Sr(OH)^+$ and assuming that sorption of the species on the organic resin would be negligible in concentrated sodium solutions, a formation constant for $Sr(OH)^+$ of 1.2 ± 0.2 was estimated for a hydroxide concentration range of $0.1N$ to $1N$ at a constant $1N$ sodium ion concentration. Using this value, approximately 50% of the Sr dissolved in a $1N$ NaOH solution would be present as a divalent cation. High Sr distribution coefficients ($K_d \sim 1 \times 10^5$) observed on ST in $2N$ sodium solutions with hydroxide concentrations ranging from $0.1N$ to $2N$ suggest that all Sr species are efficiently sorbed. These characteristics of ST, Sr sorption properties which are nearly independent of sodium concentration, the minimal effects of caustic, and a high Sr capacity are the basis for its application to neutralized Defense Waste.

The reference process for preparing ST results in a powder form, and while it can be effectively employed in laboratory ion exchange columns, there are several drawbacks with respect to its use in a remote process. These include problems associated with handling powders and the tendency of a ST column bed to "weld" together after extended contact with salt cake simulant. The latter does not seem to alter the flow properties of the bed, but it complicates the use of backflow techniques to restore a bed which has become plugged due to solids in the feed stream or other process excursions. Two non-powder forms of ST have been developed, characterized, and obtained in small quantities from commercial suppliers. These include ST incorporated within a macroreticular anion exchange resin and cylindrical pellets of ST produced by an extrusion process which involves the use of a binder to enhance the physical stability of the product.

Incorporation of ST in macroreticular resin eliminates problems associated with the powder form as the product has a constant and reproducible geometry, shows no evidence of particulate attrition of any kind, and has hydraulic properties which are well known in industry. Preparation of the loaded resin is a straightforward process involving contacting the resin with an aqueous solution of tetramethylammonium titanate to load titanium into the resin via anion exchange followed by a soak in sodium nitrate solution to form ST within the resin matrix. The chemistry of the ST relative to Sr sorption is not changed by the resin matrix; however, differences in sorption rates are observed depending on the resin size. The sorption rates of 50-100 mesh are

comparable to the ST powder and significantly greater than the same resin material in the 20-50 mesh range (Fig. 6). Both the Sr capacity and K_d values for the resin material are based on the weight of ST in the resin rather than the weight of ST plus resin due to the uncertainty in the water content of the resin which varies widely with drying method. For quantitative purposes, the percent of ST is based on the weight obtained by drying the loaded resin to constant weight at 100°C. On this basis, typical loaded resin used in this work contained 35-40% of ST.

The final disposition of a spent loaded-resin column would be similar to that of a ST powder column, i.e., calcining either material at 600°-700°C results in residues of identical composition. However, the higher cost and more favorable hydraulic properties of the resin make elution, regeneration, and subsequent re-use of a column bed more attractive. Both acid and EDTA solutions were evaluated as eluents and either can be used. Acid solutions would be most desirable as they elute all cations, including the sodium, from the ST bed; however, their use is complicated by the fact that acid solutions of sufficient strength to be practicable as eluents (>0.5 M) attack the titanate matrix (Fig. 9). Using carefully controlled conditions relative to acid concentration, volume, and process steps it was possible to elute Sr from a ST-resin bed (Fig. 10) with minimal dissolution of the titanate ($<0.3\%$). The column is readily regenerated with salt cake simulant with no adverse effects on the capacity of the bed in subsequent loading steps.

Because tight controls must be applied to acid elution techniques, EDTA eluent is suggested for use with titanate

columns. A 0.1M EDTA solution at pH 9 will efficiently remove the Sr from a ST bed (Fig. 11). The EDTA eluent is selective in that only those cations which form a more stable complex with EDTA than ST under a given set of conditions (pH, ionic strength, etc.) are eluted. Since the entire load-elute cycle is done in basic solutions, EDTA solutions can be added to the column directly following the feed solution and vice versa, thus eliminating any column washing or regenerating operation. Three cycle load-elute experiments showed that the EDTA eluent does not adversely effect the Sr sorption characteristics of the ST-resin bed.

The hydraulic properties of a ST-resin column 10 cm in diameter and 45 cm in height were evaluated. The ST-resin was prepared by and obtained from Cerac, Inc. of Milwaukee, Wisconsin. The column was operated continuously for 527 hours using a salt cake simulant feed at a superficial velocity of 10 ft/hr. Bed resistance and height remained constant and no evidence of particulate attrition or channeling were observed. Titanate dissolution was insignificant (<0.1%) and that which was present in the feed was either dissolved or in colloidal suspension and did not affect column flow.

As is the case for most organic materials, the resin was found to be susceptible to radiation damage. Since the resin serves only as a vehicle for the ST, radiation effects would be expected to be negligible until sufficient degradation occurs to impede contact between the feed solution and the ST. This was shown to occur at doses of 5×10^8 rads or greater in experi-

ments using a ^{60}Co radiation source. The Sr capacity of Sr-resin material remained constant up to a total dose of 5×10^8 rads and decreased to 30% of its initial capacity after a dose of 2×10^9 rads.

Sodium niobate- and sodium tantalate-loaded macroreticular anion exchange resins were prepared by the same techniques used for the titanates. On a molar basis, both materials have comparable or higher Sr exchange capacities in salt cake simulant than do the titanates; however, the latter is more efficient in terms of capacity per unit weight or bed volume. Elution and re-use of these materials would be essential as the cost of raw materials make them considerably more expensive than the titanates.

The property of the niobates and tantalates which led to their consideration for this application is their stability in acid solution. A two cycle load-elute experiment with sodium tantalate-loaded resin using $1\text{N } \text{HNO}_3$ for Sr elution showed that the use of acid resulted in no detectable dissolution of tantalate and had no adverse effect on the subsequent sorption properties of the material. Dissolved tantalum was detected in simulant effluent prior to Sr breakthrough and pending quantitation of the solubility or dissolution rate, this must be considered as a major drawback in using these materials in strongly basic solution.

The potential solubility problem along with the higher cost of the material are considered to outweigh the advantage of stability in acid and no further consideration should be given these materials for this application. However, they may have

a potential use for neutral or weakly acidic waste streams or in instances where elution cannot be accomplished by EDTA complexation.

The optimum form of the titanate for this application would probably be the pure inorganic material as the highest capacity per unit bed volume would be realized and radiolysis effects would be minimized. A study was completed by Norton Co. (under contract to Sandia) which involved development of non-powder titanate forms by extrusion pelletizing techniques using binder materials to increase pellet strength. The processes used in preparing the pellets are discussed in Appendix I and compositions along with temperatures used in processing are given in Appendix I, Table II. Samples of some of the materials were sent to Sandia (Table 3) for evaluation which included Sr capacity determination (also done by Norton), Sr-85 distribution coefficients, and measurements of change in pellet strength resulting from contact with salt cake simulant.

Strontium capacities and Sr-85 distribution coefficients (K_d) were determined for the six pellet samples in as-received condition and also on pellet material which was ground to pass a 100 mesh screen. Both Sr capacity and K_d values were approximately the same for all pellet samples after a one hour contact with salt cake simulant - Sr solutions (Figs. 16 and 18); however, some significant differences were observed after longer contact times. The powdered samples exhibited more rapid sorption rates during the first hour of contact (Figs. 17 and 19) as would be expected due to more favorable liquid volume to geometrical

surface area ratios. After longer contact times, the pellets and powder containing alumina binder showed equivalent Sr capacities indicating liquid contact with all the pellet material. However, for the materials containing Ca aluminate binder, 63316 and 63317, there was a significantly greater uptake on the powdered material indicating that solution was not contacting the internal pellet material. Although the surface area and Hg pore volumes reported for 63316 and 63317 are slightly lower than those of the other samples (Appendix I, Table III), the differences do not appear to be large enough to explain the difference in the Sr sorption of these materials. A possible explanation may be that the salt cake simulant is reacting with the Ca aluminate binder resulting in a reduction in effective pellet porosity; however, further evidence is not available to support this hypothesis.

Crush strengths were measured on the as-received pellets and after soaking in salt cake simulant for one day and longer periods of time (Table 4). Although absolute values do not correspond, there is good agreement with Norton results (Appendix I, Table III) when comparing relative crush strengths of the "as-prepared" pellet samples. The pellets containing Ca aluminate binder underwent severe degradation after contact with caustic solution. Pellets prepared using alumina binder only, 63275 and 63287, retain and perhaps increase in strength over a four month period in salt cake simulant. Pellets prepared with alumina binder and NH_4OH , 63321 and 63427, are superior to those with Ca aluminate binder. However, more information is needed to adequately assess the effect of the NH_4OH .

Reviewing the test results produced at Sandia and Norton, it is apparent that none of the pellet samples can be clearly identified as the "best" material for this application. Clearly, the crush strength test cannot be used as a qualification test for "as-prepared" pellets. However, the complete degradation of the Ca aluminate containing pellets in salt cake simulant eliminates them from consideration. All pellets showed nearly identical specificity for Sr. Pellets prepared using the alumina binder with NH_4OH addition tend to have higher Sr exchange capacities, while those prepared with alumina binder only appear to have superior physical stability in caustic solution. Further testing under conditions approximating as closely as possible the envisioned use of these materials is needed if optimization is deemed necessary. Since any or all of the pellets containing alumina binder may be satisfactory, the most practical way to proceed may be to choose one material for long term testing, and if it performs adequately, consider it as the baseline process material.

VI. ACKNOWLEDGEMENTS

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TABLE 1

Acid Dissolution of Sodium Titanate Powder
Dried at Ambient Temperature*

Acid Added, meq	Final Acid Concentration		Ti Dissolved, %
	Nominal, mole/L	Actual, mole/L	
44.5	0.5	0.41	47.9
20.7	0.2	0.17	15.1
12.9	0.1	0.088	6.1
5.7	0.01	0.013	0.2
4.97	0.001	0.006	≤0.1

* One gram samples of ST powder were contacted with 80 mL volumes of solution containing sufficient HNO_3 to elute all the Na^+ and provide the nominal final acid concentration. The amount of Ti dissolved was determined by atomic absorption analysis.

TABLE 2

Hydraulic Properties of a ST-loaded Resin
Ion Exchange Column

Time of Operation, hr	Pressure Drop, PSIG	Flow rate mL/min	Bed Resistance = $\frac{\text{Pressure Drop}}{\text{flow rate}}$	
			PSIG/mL/min	PSIG/ft ³ /min
27.6	1.5	413	3.6×10^{-3}	100
122	1.25	385	3.2×10^{-3}	90
455	1.5	448	3.4×10^{-3}	94

Table 3
Sodium Titanate Pellet (Norton Co.) Samples
Evaluated at Sandia

<u>Norton Pellet #</u>	<u>% Binder</u>	<u>Tmax, °C</u>	<u>Weight Loss at 700°C, %</u>
63275	30 ⁽¹⁾	320	-11.0
63287	10 ⁽¹⁾	300	-8.6
63316	20 ⁽²⁾	ambient	-28.8
63317	20 ⁽²⁾	ambient	-29.4
63321	30 ⁽¹⁾	320	-8.8
63427	30 ⁽¹⁾	250	-9.9

(1) Alumina Binder Used.

(2) Ca aluminate Binder Used.

Table 4
Results of Crush Tests Applied to
Norton Pellet Samples

<u>Norton Pellet #</u>	<u>Ultimate Load, g⁽¹⁾</u>		
	<u>As-received Pellets</u>	<u>One Day⁽²⁾ Soak</u>	<u>Extended Soak⁽²⁾</u>
63275	1400 $\pm$ 390	4450 $\pm$ 760	2000 $\pm$ 510 - 4 months
63287	1940 $\pm$ 110	4160 $\pm$ 1160	3490 $\pm$ 1060 - 4 months
63316	3640 $\pm$ 770	(3)	(3)
63317	4100 $\pm$ 280	2570 $\pm$ 700	(3) - 2 months
63321	1940 $\pm$ 340	1180 $\pm$ 180	50 $\pm$ 25 - 2 months
63427	2150 $\pm$ 330	3150 $\pm$ 930	1650 $\pm$ 290 - 5 days

(1) Three pellets from each batch or sample were tested using an Instron Tester Model TT6. Data represent the mean and average deviation from the mean of the weight in grams needed to crush the pellet (ultimate load).

(2) Samples were soaked in salt cake simulant for the given time.

(3) The condition of the pellets precluded testing.

APPENDIX I

DEVELOPMENT OF SODIUM TITANATE
PELLETS FOR SANDIA

Report # C-12

S.A. Rolando

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I. OBJECTIVE

The purpose of this study was to develop a method for the production of pellets using sodium titanate powder. Both the forming method and a suitable bonding agent were to be determined. The pellets were to be made as strong as possible while maintaining as much of the strontium exchange capacity of the original sodium titanate powder as possible.

II. CONCLUSIONS

1. Pellets with satisfactory strength and strontium exchange capacity can be produced from a composition of 70/30/2: sodium titanate/alumina hydrate/ammonium hydroxide formulation using an acid solution to effect a bond with the alumina. The pellets are calcined at 320°C for one hour.
2. Pellets of the above formulation can be readily produced using normal ceramic production equipment.
3. The use of a calcium aluminate bonding agent produced unsatisfactory pellets which did not hold up well in the caustic solution required for this application.
4. Proposed specifications for further production of 1/16" pellets using the sodium titanate powder are given in Table I.

III. INTRODUCTION

The sodium titanate powder (S.T.) was supplied by Rockwell through Dr. R. Dosch of Sandia Labs. We were requested to produce pellets from this material for evaluation in applications involving radioactive waste materials.

The two major applications for the pellets were for high level waste solidification and for Defense Waste stabilization. The high level waste requires that the material be stable (maintain the strength and integrity of the pellet) when exposed to acid solution. The low level waste application requires stability in an alkaline solution and was of the highest priority for this study. Data supplied by Dr. Dosch indicated that the ST powder lost exchange capacity upon heating, retaining only approximately 10% of its original capacity after heating at 500°C. This required that the calcination of the pellets had to be carried out at as low a temperature as possible. In addition, we were requested to keep the pellets as porous as

possible. An initial sample of pellets, 10788, produced from the ST powder using 0.5% of an organic binder for a bond had shown an adequate strength initially but was found to lose strength on aging. Thus, a bonding agent was to be added to prevent this strength loss.

IV. RESULTS

The formulation and firing data for the samples produced are given in Table II. Table III includes this data along with the measured physical properties of the pellets. Table IV is provided for reference and lists the strontium exchange capacity of the pellets as measured by Norton Company and Sandia. Figures 1-3 give the pore size distribution of the pellets.

V. DISCUSSION

Exchange Capacity

The strontium exchange capacity of the pellets was determined by Dr. Dosch of Sandia and by D.J. Remus of Norton Company using a procedure supplied by Dr. Dosch. The procedure used at Norton is described in Appendix I.

As shown in Table IV and discussed in the Appendix, there is little agreement in the results obtained by the two laboratories. Due to this lack of correlation in the results, no attempt is made here to relate the exchange capacity data to the properties of the pellets. It is recommended that a test procedure be established which would allow for correlation of the test results between the two laboratories prior to further production of the pellets by the Norton Company.

Porosity

The effect of alumina addition on the porosity of the pellets is shown in Figure 1. Note that although sample number 63314 (30% alumina) and sample number 63287 (10% alumina) have the same total pore volume and essentially the same median pore diameter, the pore size distribution is changed considerably. The alumina bonded pellets have more large pores (>0.10 microns) and more pores less than 0.01 microns in diameter. These small pores are apparently due to the dehydration of the alumina as they are not evident in the 90% S.T. sample or the calcium aluminate bonded samples.

The effect of ammonium hydroxide addition to the alumina bonded pellets is shown in Figures 1 and 2 and Table III. A comparison of sample numbers 63314 and 63321 shows that the addition of 2 wt % of the NH_4OH caused an increase in the pore volume. A further increase to 4 wt % NH_4OH , sample number 63369, also led to an increase in the pore volume but to a lesser degree than the 2 wt % addition. Thus, ammonium hydroxide would appear to cause an increase in the pore volume of the material. This conclusion is not substantiated by the result shown in Figure 2.

Figure 2 compares sample number 63321 with sample number 63449 which was to be a remake of 63321. Sample number 63449 has a lower pore volume than any of the alumina bonded pellets. Thus, it cannot be concluded from this study that ammonium hydroxide will lead to an increase in the pore volume of the material. However, based on previous experience with the alumina used in this study and the results obtained with sample numbers 63321 and 63369, it is recommended that ammonium hydroxide be included in the formulation.

The effect of calcination temperature and soak time on the pore volume and pore size distribution is also uncertain. The results are shown in Table III and Figure 2. If a comparison is made between sample number 63321 (calcined at 320°C for 1.75 hours) and sample number 63427 (calcined at 250°C for one hour), it would appear that the lower measurable pore volume of sample number 63427 is due to the lower calcination temperature. This is particularly illustrated by the lack of pores having a diameter of less than 0.007 microns in sample number 63427. The small pores in this region are thought to be due to the dehydration of the alumina. This is substantiated by the lack of porosity in this region of sample number 63287 (90% S.T.) shown in Figure 1 and sample numbers 63316 and 63317 (calcium aluminate bond) shown in Figure 3. Previous work with alumina catalyst supports has shown that the degree of pore formation in this size range is dependent on the calcination temperature. However, the results obtained with sample numbers 63449, 63463 and 63464 did not indicate any significant change in the pore volume with a change in calcination temperature as shown in Table II and Figure 2. Sample Number 63449 was calcined at 320°C for one hour. This material was then refired for an additional hour at 320°C as sample number 63463. Sample Number 63464 was refired to 340°C for one hour. As shown in Figure 2, the pore volume and size distribution changes little with the change in temperature or soak time (sample number 63463, not shown, is nearly identical to 63449). It can be concluded that the firing temperature may effect the pore volume and thus should be

examined in more detail if further work is done on this material.

The reason for the differing pore volumes of sample number 63321 and the remake of sample number 63321, sample number 63349 is not known at present. The most likely reasons for the difference, based on previous experience with catalyst carriers, would be the mixing procedure and/or some change in the S.T. powder characteristics. As noted in the experimental section, the mix procedure was altered with the production of sample number 63449. It is possible that the material was subjected to a more intensive mixing cycle which would contribute to the loss of pore volume. Also, a different lot of sodium titanate powder was used for sample number 63449 which may have an effect on pellet properties. The difference in the calcination soak time (1.0 hour for sample number 63449; 1.75 hours for sample number 63321) is not believed to be significant. As noted previously, attempts to calcine sample number 63449 for an additional hour, sample number 63463, had no significant effect on the pore volume.

As shown in Figure 3 and Table III, the pore volume of the calcium aluminate bonded pellets is considerably lower than that of the alumina bonded pellets. The alumina bonded pellets have considerably more large (> 0.1 micron) pores. This difference may explain the lower exchange capacities reported for the calcium aluminate bonded pellets.

Surface Area

The surface areas of the pellets are given in Table III. Note that the surface area of sample number 63449 is considerably higher than that of sample number 63321. This would indicate that there are a significant number of small pores (< 0.005 microns) in sample number 63449 which are beyond the range of the porosimeter. The higher surface area would also indicate that sample number 63449 may be slightly underfired as compared to sample number 63321. This is based on the similar lack of porosity in this region seen for sample number 63427 which was calcined at a lower temperature.

Crush Strength

The differences in strength shown in Table III are not significant with the exception of sample numbers 63308 and 63309. Sample numbers 63308 and 63309 were formed as 1/8" pellets to determine if the strength increase obtained by aging

the calcium-aluminate bonded pellets in water was significant. Analysis of this data indicated that the strength increase was real. Sample number 63316 and 63317 were then prepared in the 1/16" size for testing by Dr. Dosch.

VI. EXPERIMENTAL

A. Alumina Bonded Pellets

The alumina used in this study is an alpha-alumina monohydrate having the crystal structure of boehmite. A typical chemical analysis of this material is as follows:

<u>Component</u>	<u>Wt. %</u>
Al ₂ O ₃	75
Carbon	0.4
SiO ₂	0.008
Fe ₂ O ₃	0.005
Na ₂ O	0.004

All of the alumina bonded pellets were peptized with an acid solution. The ammonium hydroxide was added as a 30% solution. All of the test samples with the exception of sample number 63449 (discussed separately) were prepared as follows:

The dry ingredients (S.T. powder, alumina) were placed in a small intensive mixer and dry blended 1-3 minutes to insure thorough mixing. The batch size used varied from 0.15-1.5 kg. Liquid additions were made gradually with the mixer running. The material was then mixed 2-5 minutes until judged to be the proper consistency for extrusion. Ammonium hydroxide, when used, was added to the dry mix and mixed for one minute prior to the addition of the acid solution.

The material was formed into pellets using a high pressure hydraulic extruder with a single hole 0.080" polyethylene die. The extrudate was collected on stainless steel screens and allowed to air dry at room temperature for a minimum of 24 hours. The extrudate was broken into shorter lengths after drying as the material was generally too soft to be cut as extruded.

After drying the pellets were calcined at the temperature indicated in Table II. Calcining was done in an electrically heated lab kiln. The pellets were placed in aluminum oxide saggars approximately 1-1/2" deep and heated at a rate of 100°C per hour to the desired temperature.

Sample number 63449 was prepared in a slightly different manner due to the larger quantity required. Mixing was done in a high intensity Beardsley and Piper lab Speedmuller as follows:

1. 3.5 kg of sodium titanate powder and 1.5 kg of alumina were placed in the mixer and mixed 30 seconds.
2. With the mixer running, 100 ml of the 30% NH_4OH solution were added and mixed for two minutes.
3. With the mixer running, a solution of water and the peptizing agent were added. Mixing was continued for two-four minutes until the mixture began to gel.

Forming was done on a hydraulic ram-type extruder using a multi-hole (0.071" diameter) polyethylene die. The extrudate was caught on stainless steel screens and air dried at room temperature for a minimum of 24 hours, then broken into shorter lengths.

The pellets were calcined at 320°C for one hour in an electrically heated oven in stainless steel trays approximately 1" deep. The oven is equipped with a blower to provide a continuous flow of heated air through the pellets. The heating rate was not controlled with this oven. The pellets were cooled to room temperature in the oven and sealed in plastic prior to shipment.

B. Calcium Aluminate Bonded Pellets

The chemical analysis of the calcium aluminate bond used in this study is as follows:

<u>Component</u>	<u>Wt. %</u>
Al_2O_3	72
CaO	26
SiO_2	0.2
Fe_2O_3	0.1
$\text{K}_2\text{O} + \text{Na}_2\text{O}$	<0.5

The mixing and forming procedure used for these pellets was identical to those used for the alumina bonded samples, except that water was used in the mix in place of the acid/water solution used for the alumina. The calcium aluminate pellets were split into two lots after extrusion. One lot (Sample Number 63316) was allowed to air dry at room temperature for 24 hours. The second lot (Sample Number 63317) was dried in air for four hours. then placed in a container with sufficient water added to cover the pellets. The pellets were allowed to soak in the water for four days. The water was then poured off and the pellets allowed to dry in air. The calcium aluminate bonded pellets were not heated above room temperature during processing.

S. A. Rolando
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Research Engineer
Chemical Process Products Division

TABLE I
PROPOSED SPECIFICATION FOR 1/16" PELLETS
CONTAINING 70% SODIUM TITANATE

<u>Property</u>	<u>Specification</u>
Nominal Size, in	1/16
Pellet Diameter, in	0.0625 $\pm$ 0.005
Pellet Length, in	1/16 - 5/8
Surface Area, M ² /gm	1.55 $\pm$ 20
Crush Strength, FPCS, lbs.	2.5 min
Hg Pore Volume (High pressure to 40000psia)	
Total, cc/gm	0.65 $\pm$ 0.1
Average Pore Diameter, Microns	0.046 $\pm$ 0.005
Pore Volume at 0.1 Microns, cc/gm	0.14 min
Packing Density, lbs/ft ³	To Be Determined
Sr Exchange Capacity, meq/gm Titanate	To Be Determined*

SAR/6/5/80

*Pending establishment of a standard test procedure and correlation of results between Norton and Sadia Labs.

TABLE II
FORMULATION AND FIRING DATA FOR
SODIUM TITANATE PELLETS

<u>Sample Number</u>	<u>Wt % S.T.</u>	<u>Wt % Alumina</u>	<u>Wt % Ca Aluminate</u>	<u>Wt % NH₄OH</u>	<u>°C Firing Temp</u>	<u>Soak hrs.</u>
63272	90	10	-	-	320	1.0
63275*	70	30	-	-	320	1.0
63276	50	50	-	-	-	
63286	80	-	20	-	Air Dried	
63287*	90	10	-	-	300	1.75
63306	80	-	20	-	Soaked in H ₂ O	
63308	60	-	40	-	Air Dried	
63309	60	-	40	-	Soaked in H ₂ O	
63314	70	30	-	-	320	1.0
63316*	80	-	20	-	Air Dried	
62217*	80	-	20	-	Soaked in H ₂ O	
63321*	70	30	-	2	320	1.75
63369	70	30	-	4	320	1.75
63427*	70	30	-	2	250	1.0
63449*	70	30	-	2	320	1.0
63463	70	30	-	2	320	2.0
63464	70	30	-	2	340	1.0

SAR/6/5/80

*Samples shipped to Dr. Dosch of Sandia. 17 kg of 63449 shipped to Rockwell

TABLE III
PROPERTIES OF PELLETS CONTAINING SODIUM TITANATE

Sample Number	Wt % Bond	Bond ¹ Type	NH ₄ OH* wt %	Calc. Temp °C	Soak hrs.	Surface Area M ² /gm	Hg Pore Vol. cc/gm	Pore Dia. Microns	FPSC lbs.
63287	10	A	-	300	1.75		0.552	0.042	2.0
63314	30	A	-	320	1.0		0.552	0.043	
63321	30	A	2	320	1.75	135.4	0.755	0.049	3.0
63369	30	A	4	320	1.75	147.4	0.710	0.043	3.9
63427	30	A	2	250	1.0	172.5	0.602	0.062	3.4
63449	30	A	2	320	1.0	163.1	0.575	0.042	2.6
63463	30	A	2	320	2.0	151.0	0.570	0.041	
63464	30	A	2	340	1.0	169.6	0.550	0.040	
63286	20	CA	-	Air Dry ²					3.0
63306	20	CA	-	Aged in H ₂ O ³					4.0
63308	40	CA	-	Aged in H ₂ O					14.6
63309	40	CA	-	Air Dry					10.5
63316	20	CA	-	Air Dry		126.8	0.386	0.042	4.4
63317	20	CA	-	Aged in H ₂ O			0.513	0.045	5.5

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1 A = Alumina

* 30% soln.

CA = Calcium Aluminate

2 Dried 24 hours (min.) in air at room temperature. No heat treatment

3 Dried 4 hours in air, then covered with water and soaked for four days. Allowed to air dry after soaking.

TABLE IV
STRONTIUM EXCHANGE CAPACITY OF SODIUM
TITANATE PELLETS

Sample Number	Norton		Sandia	
	Capacity meq/gm Titanate	Exposure Time hours	Capacity meq/gm Titanate	Exposure Time hours
63272	1.72	24		
63275	1.74	24	2.65	16
63286	1.29	24		
63287	1.67	16	2.45	16
63314	5.39	24		
63316	1.26	24	1.99	18
63317	2.03	18	0.95	18
63321	5.01	24	2.77	24
63359	4.84	24		
63427	2.96	24	4.91	24
63449	6.49	24		
63454	5.24	24		

SAR/6/6/80

FIG.1 PORE SIZE DISTRIBUTION OF ALUMINA-BONDED SODIUM TITANATE PELLETS

SAMPLE
63321

SAMPLE
63369

SAMPLE
63287

SAMPLE
63314

FIG.2 PORE SIZE DIST. OF ALUMINA BONDED ST
 PELLETS CALCINED AT DIFFERENT TEMP. AND TIMES

FIG.3 PORE SIZE DISTRIBUTION OF ST PELLETS
CONTAINING DIFFERENT BONDING AGENTS

SAMPLE
63321

SAMPLE
63287

SAMPLE
63317

SAMPLE
63316

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Los Alamos, New Mexico 87545

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Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Mr. Don Ferguson
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3141 C. A. Pepmuller (5)
3151 W. L. Garner (3)
3154-3 R. P. Campbell (25)
(for DOE/TIC) (unlimited release)

4500 E. H. Beckner
4530 R. W. Lynch
4535 H. D. Sivinski
4400 A. W. Snyder
4410 D. J. McCloskey
4440 G. R. Otey
5110 R. L. Schwoebel
5500 O. E. Jones
5510 D. B. Hayes
5800 R. S. Claassen
Attn: 5820 R. E. Whan
5830 M. J. Davis
5840 N. J. Magnani

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5812 C. J. Northrup
5812 R. G. Dosch (4)
5812 B. T. Kenna
5812 A. W. Lynch
5812 E. J. Nowak
8100 W. J. Spencer
8200 A. N. Blackwell
8300 B. F. Murphy
8400 L. Gutierrez
8266 E. A. Aas