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THE USE OF TITANATES IN DECONTAMINATION
OF DEFENSE WASTE

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THE USE OF TITANATE¹ IN THE NEUTRALIZATION
OF DEFENSE WASTE*

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Abstract

Sodium titanate, an inorganic ion exchange material, has been evaluated for use in a process to remove strontium from defense waste or other alkali-soluble caustic solutions. Distribution coefficients on the order of 10^4 were observed at sub part per million concentrations of Sr, and the effects of other cation impurities and complexants in the waste were investigated.

The preparation and general chemical properties of the exchange material are discussed. This information was used in developing a commercial source which has since supplied a 100 kg batch of the material for evaluation.

In column ion exchange experiments with ^{90}Sr -tagged simulated waste, decontamination factors of 500 or greater were observed in the first 100 to 3500 bed volumes of effluent, depending on the impurities in the simulant. A -40 to +130 mesh range of sodium titanate powder was used as the baseline material, but a study to produce alternate forms of the titanate was carried in parallel. This has resulted in two materials which appear promising with respect to both simplification of handling and chemical properties. One of the materials is an agglomerated form of the titanate formed by extrusion pelletizing using water as a binder, and the second is a macroreticular organic anion resin which was loaded with 30 to 40% weight of sodium titanate. The results of initial testing of these materials are discussed.

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THE USE OF TITANATES IN DECONTAMINATION
OF DEFENSE WASTE

I. Introduction

The greater part of the current inventory of stored radioactive waste in the United States was generated in the production of nuclear materials for military applications. Millions of gallons of acidic, high level waste have been accumulated at the Hanford Site in the State of Washington as a by-product of the Purex process, a solvent extraction process used to recover fissionable material from spent reactor fuel. Neutralization of the acidic waste accommodated underground storage in mild steel tanks and reduced the potential mobility of the bulk of the radionuclides which were converted to solids by hydrolysis and subsequent precipitation. Liquid losses due to tank failure resulted in an effort to further reduce the nuclide migration potential by additional solidification.⁽¹⁾ The liquid wastes were evaporated to form slurries, which in turn were transferred back into the storage tanks and upon cooling, formed a semi-solid referred to as salt cake and a small quantity of highly caustic supernatant liquid known as residual liquor. An inventory of about 50 million gallons of salt cake and 2-3 million gallons of residual liquor is projected for the early 1980's when the evaporation process has been completed.^(2,3)

The salt cake, which is primarily sodium nitrate (60-80%) and NaOH (2-20%), contains significant quantities of ^{137}Cs and ^{90}Sr along with other fission products and some actinides,⁽²⁾ and must be stored as a radioactive waste. Since it is highly soluble in water, further processing is desirable

to insure containment over the long period of time in which the nuclides remain biologically hazardous. Among the means being considered is the removal of radionuclides from redissolved salt cake by aqueous separation techniques to the extent that the large volumes of salts could be stored as nonradioactive chemical waste.

Ion exchange is attractive in this application; it is a continuous process and can be scaled to give the large throughput volumes which would be required. However, few ion exchange materials exhibit stability in caustic and radiation environments and the high selectivity which allows removal of trace concentrations of radionuclides from nearly saturated sodium salt solutions. One material is sodium titanate, an inorganic ion exchange material developed in these laboratories. This report describes the preparation of the titanate material and its properties in a dissolved salt cake matrix and summarizes the work which has been done in applying the material to a process for Sr decontamination. The results of a parallel investigation of methods for converting sodium titanate powder into a more easily manageable form by agglomeration or incorporation in another substrate are included.

II. Ion Exchange Material

A. Background

The sodium titanate (ST) material was one of a group of materials which included sodium niobate, sodium zirconate, and sodium tantalate which were developed for use in the solidification of high level liquid waste⁽⁴⁾ such as that expected from a commercial fuel reprocessing plant. The high level waste solution was passed through a column of ST which resulted in the quantitative sorption of cation fission products and actinides. Subsequent pressure sintering of the loaded column material produced a dense ceramic waste form which was resistant to leaching and suitable for long term storage.

High decontamination factors ($\sim 10^9$) observed in the high level waste studies prompted an investigation of the applicability of these materials to the decontamination of other liquid wastes such as tank-stored Defense Waste. The salt cake mentioned previously represents one such waste. The composition given in Table 1 is that of the simulant used in this work and is typical of salt cake dissolved in a minimum quantity of water. The high sodium concentration precludes the use of the materials for cesium removal as distribution coefficients (K_d 's) of 12.5, 0.48, 0.1, and 0.01 were observed for sodium niobate, sodium tantalate, sodium titanate and sodium zirconate, respectively. Strontium, however, was very efficiently sorbed by the titanate material, and K_d 's were typically greater than 10^4 .

Hydrous ferric oxide along with strontium and calcium phosphates have been evaluated as strontium scavengers⁽⁵⁾ and the results are compared with those of similar experiments using ST in Table 2. The process used was a co-precipitation or batch process, and with the exception of the ST, these materials do not lend themselves to a column flow process.

Materials which were evaluated for use in a column ion exchange process included Duolite ARC-359, a phenol-based resin made by the Diamond Shamrock Co., and Chelex-100, a divinylbenzene copolymer containing iminodiacetate functional groups supplied by Bio-Rad Laboratories. The reported results of survey experiments using these resins^(5,6) are compared with those of similar experiments using ST in Figures 1 and 2. The use of ^{85}Sr rather than ^{90}Sr tracer allowed the use of gamma spectroscopy in associated analyses. These favorable results prompted further investigation into the application of ST to Sr decontamination and this study is summarized in the following discussion.

B. Material Preparation

The preparation of the sodium titanate used in this work has been described in detail elsewhere.⁽⁴⁾ In brief, tetraisopropyl titanate (duPont de Nemours & Co., Wilmington, Del.) is reacted with sodium hydroxide in methanol followed by hydrolysis in an acetone-water mixture. The reactants were chosen to yield a mole ratio of sodium to titanium of 0.5 and 100% recovery is achieved in the preparation. After vacuum or air drying at ambient temperature, the product is a friable powder consisting of agglomerates of 50-100 μ particles. Heating the material to 400°C results in a weight loss of approximately 20%, the volatiles consisting primarily of water along with some methanol, isopropanol, and acetone.

The method used in drying the material is important in determining its ion exchange properties. Damp or vacuum dried material absorbs CO_2 from the atmosphere, which produces a measurable effect on strontium distribution coefficients. Drying at elevated temperatures results in significant decreases in ion exchange capacity. Both of these effects are discussed in detail in subsequent sections of this report.

C. Interaction with Strontium

In prior work with waste solutions containing cations in neutral or slightly acidic solution, ST showed an ion exchange capacity approximating that expected from complete exchange of sodium in a material with an empirical formula of $\text{NaTi}_2\text{O}_5\text{H}$. Capacities of 4 meq. per gram of vacuum dried material or 5 meq. per gram of titanate after calcining were typically observed for both di- and trivalent species. In alkaline media, the exchange capacity for Sr^{++} was approximately doubled as indicated in the data in Figure 3, which are results obtained by measuring the Sr uptake of 0.5 g of ST in 100 ml of a solution containing 0.08N $\text{Sr}(\text{NO}_3)_2$, 6.0N NaNO_3 , and 0.6N NaOH . The -40

to +140 mesh range material sorbed 2.9 meq. of Sr per gram in the first 30 seconds of contact time and this increased to 9.1 meq. after 24 hours. Samples of the -400 mesh ST from the same batch had a faster absorption rate during the first hour of contact, but had the same total capacity after 24 hours. No further absorption was observed during longer contact times.

The rate determining step in the reaction of excess Sr^{++} with ST appears to be intergranular or particle diffusion as suggested by the inverse relationship between particle size and reaction rate. Mathematical treatment of data gives the best fit using a particle diffusion model.⁽⁷⁾ In both size ranges, significant sorption, 6 meq. Sr/gram is observed after contact times of ten minutes which are readily achievable in ion exchange column processes.

The rate of sorption of trace quantities of ^{85}Sr from a salt cake simulant solution is shown in Figure 4. One-tenth gram samples of ST were contacted with 10 ml of simulant containing 1 $\mu\text{Ci/ml}$ of ^{85}Sr which represents a total strontium concentration including stable isotopes in the range of 0.3 to 0.03 ppm. The ratio of ^{85}Sr activity in solution after one hour to the initial activity (C/C_0) was 2.9×10^{-3} . This decreased to 1.3×10^{-3} after two hours and remained approximately the same for the following seven days when the final measurement was made.

The method used in drying the ST has a measurable effect on the ^{85}Sr distribution coefficients observed in batch contacting experiments. Dried in vacuum at ambient temperature and subsequently stored in a closed vessel contains about 0.25% $\text{CO}_3^{=}$. Material which is dried in air, or vacuum dried ST which is allowed to stand in air, absorbs CO_2 until an equilibrium value of about 5 w/o $\text{CO}_3^{=}$ is reached. The change in K_d 's resulting from increasing the $\text{CO}_3^{=}$ in the ST is shown in Table 3 and is positive. The reason for the

effect is not known since the carbonate in the ST dissolves immediately upon contact with the simulant solution and the relatively large concentration of carbonate in the simulant tends to negate the possibility of strontium carbonate precipitation causing the difference in the observed K_d 's.

D. Effect of Complexants and Other Cations on Sr Decontamination

The caustic nature of salt cake serves not only to immobilize the great majority of multivalent fission products and actinides, but also limits the concentration of stable multivalent elements which could interfere with the ion exchange process for Sr removal. A salt cake solution was analyzed for common contaminants and suspected impurities including Ni, Fe, Mn, Mg, Ca and Ba.⁽⁸⁾ None of these species were detected at the estimated detection limits shown in Table 4. These concentrations were taken as nominal upper limits and a simulated salt cake solution was doped at these levels. Precipitation of some or all of the species was observed and after filtration, the concentrations remaining were determined by atomic absorption spectroscopy and are listed in Table 4.

Both the cation-doped simulant and a control or undoped simulant were spiked with 1 $\mu\text{Ci/ml}$ of ^{85}Sr and 25 ml aliquots of each were used in batch equilibrations with 0.0005 g, 0.001 g, 0.002 g, 0.1 g and 0.5 g of sodium titanate. Analytical samples were taken after 24, 48 and 144 hour equilibration periods. Decontamination factors and K_d 's are listed in Table 5.

The presence of the added cations in the simulant has a small effect on K_d 's--less than a factor of two in the samples containing 2 mg or less of ST. This illustrates the Sr specificity of the material since combined equivalents of Fe, Ni and Ca are 6.6×10^{-6} , based on the analysis of the simulant, as compared to 2×10^{-7} to 2×10^{-8} equivalents of Sr in the 25 ml

sample; the capacity of the ST is on the order of 9×10^{-6} equivalents per milligram. In the samples containing 0.1 and 0.5 g of ST, which represent a large excess of exchange capacity, no trends in the K_d 's are observed. Also of interest is the order of magnitude increase in K_d 's in both simulant solutions over the three orders of magnitude range of ST concentrations.

The smallest quantity of titanate used was based on an approximation of relative material consumption for a column versus a batch process. Using two 6' diameter by 6' high sodium titanate beds charged with fresh ST after each 2000 bed volumes of throughput to represent a column process, a flow rate of 1 column volume per hour would have to be maintained continuously for two years to achieve decontamination of 4.5×10^6 gallons. This is equivalent to a concentration of about 0.0005 g titanate per 25 mls of waste solution. On the other hand, the results in Table 5 show that the use of a batch equilibration process to achieve Sr decontamination factors of more than 100 would require quantities of titanate several hundred times that estimated for a column process.

The presence of chelating agents in the salt cake waste is likely. The most probable are ethylenediaminetetraacetic acid (EDTA) or derivatives thereof at a wide range of concentrations. A series of experiments was done to determine what effect EDTA would have on the Sr-ST reaction.

In addition to ST, other cation forms of the titanate material were evaluated in an attempt to identify any exchangeable cation which forms a more stable EDTA complex than strontium to minimize the effect of high EDTA concentrations according to the reaction

where Y = anion of EDTA and $x = 1$ when $n = 1$ and $x = 2$ in all other cases.

Stability constants for EDTA-metal complexes in strongly basic, high ionic strength solutions were not found in the literature. Cu(II), Ca(II), Ni(II), and Fe(III) titanates were chosen based on stability constants⁽⁹⁾ in $\text{NH}_4\text{OH} - \text{NH}_4\text{Cl}$ buffer solutions at ionic strengths of 0.1. The titanates were prepared by soaking ST in solutions containing a threefold or greater excess of the metal salt of interest. The sodium-metal ion exchange was stoichiometric as the product typically contained less than 0.1% of residual sodium. Kd measurements were made for both the metal titanates and ST in 6N HNO_3 - 0.6N NaOH solution containing 0.002N Sr^{++} - 0.002N EDTA and in salt cake simulant containing 1 $\mu\text{Ci/ml}$ of ^{85}Sr with EDTA to Sr^{++} molar ratios ranging from 8×10^{-5} to 2560. The range reflects the uncertainty of the total Sr concentration in the ^{85}Sr isotope solution. In all cases, one gram of the exchange material was equilibrated with 50 ml of solution for one hour. The results are shown in Table 6.

The addition of EDTA at concentrations which approximate or are lower than the Sr^{++} concentrations in the simulant has a small effect on the Kd values for any given material. There is no definitive trend, as the EDTA causes decreases in the Kd on some materials and slight increases on others. At 90 ppm Sr concentrations, which are high compared to those expected in the waste, strontium removal is enhanced by the use of the Cu(II) and Ca(II) titanate materials. At process or tracer level strontium concentrations, no advantage in using the other titanate materials is apparent.

In the solutions containing excess EDTA, decreases in Kd's of approximately an order of magnitude are observed for all the titanate materials. In all tracer experiments summarized in Table 6, sodium titanate is superior to the other titanates in removing Sr from solution. The information obtained in these experiments has been applied to regeneration or stripping of ST

columns and this subject is addressed in subsequent sections.

The performance of the Ca(II), Cu(II) and Fe(III) titanates is interesting from the standpoint of the effect of cation impurities in the salt cake waste. In the solutions which did not contain EDTA, each of these materials had a strontium K_d greater than 2.5×10^3 which is only a factor of three less than the ST material. If these results are extrapolated to column operations, a ST bed which has been partially or completely exchanged with other cations from the waste should still function as a strontium sorbent.

III. Actinide Removal From Salt Cake

Previous work with high level waste solutions has shown that ST has an extremely high affinity for the actinide elements.⁽⁴⁾ Decontamination factors $> 10^8$ for gross alpha activity in high level waste were observed on ST columns with effluents containing about 6 dpm/ml total alpha activity. A single experiment has been done with an actinide, Pu, in salt cake simulant, and the results indicate that ST performs in the same manner in this matrix.

Sixty milliliters of salt cake simulant solution were spiked with 20 milligrams of ^{238}Pu contained in a nitric acid solution. The bulk of the Pu hydrolyzed and precipitated and a final solution activity of 2.4×10^6 dpm/ml, which corresponds to about 0.06 ppm of Pu was measured. The solution was passed through a column of ST in which the 60 ml volume represented slightly more than three bed volumes. No activity above background was detected in the column effluent by liquid scintillation counting.

IV. Strontium Sorption in Residual Liquor

Residual liquor is the supernatant liquid in equilibrium with crystallized salt cake in storage tanks. The total volume of residual liquor is small ($\sim 5\%$) in comparison with the salt cake; however, the Sr content may be one to two orders of magnitude higher in the residual liquor, which has a nominal

composition as shown in Table 7. Distribution coefficients for ^{85}Sr on ST in simulated residual liquor and various dilutions thereof are also listed in Table 7. Comparison of the values for undiluted liquor with those determined in salt cake simulant (Table 5) shows a decrease of two to three orders of magnitude. Dilution of the residual liquor with water results in increasing Kd values; however, after fivefold dilution, the Kd is still less than that observed in the salt cake simulant.

The aluminate ion has been shown to have no interaction with ST and this is also true for the nitrite ion. In the fivefold dilution of the residual liquor simulant, the Na^+ , NO_3^- and $\text{CO}_3^{=}$ concentrations are the same or lower than in the salt cake simulant. This indicates that the higher hydroxide concentrations contribute to the decreased affinity for Sr in residual liquor solutions.

V. Sodium Titanate Column Experiments

Column experiments were necessary to determine whether the titanate in the powder form was amenable for use in this application which requires both large volume throughput and high decontamination factors. The column was 1 cm in diameter and contained a 3 cm^3 bed of +40 to -140 mesh, air-dried sodium titanate. The feed solution was a dissolved salt cake simulant (Table 1) doped with 1 $\mu\text{Ci/ml}$ of ^{85}Sr . The column flow rate was controlled by the use of a variable speed peristaltic pump and was varied during the experiment to determine the dependence of decontamination factor on flow rate. In Figure 5, the flow rate profile and the ratio of ^{85}Sr in the effluent to the feed concentration C/C_0 are plotted versus throughput in bed volumes.

Column breakthrough is considered to have occurred when a decontamination factor of less than 500 ($C/C_0 > 20 \times 10^{-4}$) is observed in the effluent. In this experiment, breakthrough occurred at about 3500 column volumes which

which corresponds to 0.1 to 1% loading of the total column capacity based on the amount of Sr put through the column. A dependence of C/C_0 on flow rate was not observed, but flow rate does not appear to be a significant factor in determining the breakthrough volume. The data for column volumes greater than 4100 may be biased in that the column inadvertently went dry after 4300 column volumes. Feed was added to the column and the bed was stirred with a glass rod to remove entrapped air prior to resuming flow through the column.

A second column of the same configuration was run with a dissolved salt cake simulant containing the cation impurities as listed in Table 4 along with 1 μ Ci/ml of ^{89}Sr . The entire elution curve and flow rate profile for the experiment is shown in Figure 6. The initial portion of the data is shown in more detail in Figure 7. No dependence of C/C_0 on flow rate was discernible prior to breakthrough at approximately 2000 column volumes. A significant decrease in C/C_0 was observed when the flow rate was dropped to 1 column volume near the end of the run.

The elution curves for both columns are shown in Figure 8.

The cations added to the simulant were obviously a factor in determining the breakthrough volume of the column as predicted by batch data (Table 5). A visual comparison of the columns showed that the ST bed used with the salt cake simulant remained white while the top two thirds of the bed used with the cation dope feed were light brown and the bottom third appeared to be light green, which are the colors of ferric titanate and nickel titanate, respectively.

VI. Commercial Supply of Sodium Titanate Powder

During the course of this study, a parallel effort was made to identify and develop a commercial source of sodium titanate powder. Although all reactants are commercially available in large quantities and the material

preparation is straightforward, the development of a commercial source is an unequivocal means of eliminating any stigma of "laboratory curiosity" from a material.

Included below are the material preparation methods, material acceptance criteria, and the analytical methods suggested to verify these criteria which were sent to potential suppliers.

A. Preparation of Sodium Titanate

Materials -

Titanium Isopropoxide - $\text{Ti}(\text{OC}_3\text{H}_7)_4$ 16.87 $\pm$.2 wt% Ti

NaOH, C.P.

Acetone, Tech. Grade

Methanol, Tech. Grade

Preparation of Materials

NaOH - To be used as methanol solution containing from 10% to 15% by weight of NaOH. Following dissolution of NaOH in methanol, the solution is to be clarified via filtration to remove insolubles and the NaOH content determined to $\pm$ 0.1% of the amount present, i.e., 15 $\pm$ 0.1%.

Preparation of Sodium Titanate

Step 1 - Reaction of titanium isopropoxide with NaOH-methanol solution. (Note 1)

Step 2 - Hydrolysis of reaction mixture from Step 1 in water-acetone mixture. (Note 2)

Step 3 - Filtration of Step 2 reaction product. (Note 3)

Step 4 - Drying of Step 2 reaction product. (Note 4)

Step 5 - Sizing of dried sodium titanate. (Note 5)

- Note 1. Titanium isopropoxide and NaOH are reacted in a molar ratio of 2:1, respectively. The titanium isopropoxide is added to the NaOH-methanol solution with stirring. The overall reaction is exothermic and if the rate of addition is too rapid, boiling and resultant foaming occur. Hydrolysis can be done immediately after the reaction.
- Note 2. Hydrolysis is done by pouring the titanium isopropoxide-NaOH mixture into an acetone-water mixture containing 8.5% water by volume. One liter of the acetone-water mixture is required for each mole of titanium hydrolyzed.
- Note 3. Filtration can be done immediately after hydrolysis. The hydrolyzed material is coarse and can be easily and rapidly filtered through a coarse (50 μ) frit with the aid of vacuum. Sodium, hydroxide, or titanium ions are not detected in the filtrate.
- Note 4. Material is dried at ambient temperature under vacuum. Material is considered to be "dry" when firing at 700°C results in less than 30% weight loss from the material.
- Note 5. The desired size range for the material is 10 μ to 420 μ or that material which passes a No. 40 U.S. Standard sieve and is retained on a No. 140 U.S. Standard sieve. All coarse material should be forced through the 40 mesh sieve. The sizing operation typically results in 20 to 50% "fines," i.e., material which passes to No. 140 sieve. This material can be recycled by addition to the titanium isopropoxide-NaOH reaction mixture prior to hydrolysis in amounts up to 30% by weight of the sodium titanate in the reaction mixture.

Typical Lab Scale Sodium Titanate Prep

1. Two moles of tetraisopropyl titanate (570.2 g) are added to 296.3 g of 13.5 wt% NaOH in methanol.
2. The reaction mixture from 1. is added to two liters of 8.5 wt% H_2O -91.5 wt% acetone mixture.
3. Solid sodium titanate is filtered on a coarse (50 μ) glass frit and dried under vacuum at room temperature until weight loss from material at 700°C is less than 30% by weight.
4. Material is screened and -40 mesh to +140 mesh is retained and kept in a closed container.
5. Retain "fines" for inclusion in subsequent preps, i.e., up to 75 g of "fines" can be added to reaction mixture from step 1 above prior to hydrolysis.

a. Material Acceptance Criteria

The following criteria are important for sodium titanate material intended for use as an ion exchange material. Characteristics 1-3 are the natural result of following the foregoing method of preparation, while the fourth is easily met by limiting contact of the material with air.

1. The molar ratio of sodium to titanium in the final product should be in the range of 0.48 to 0.52%.
2. Weight loss as a result of calcining at 700°C for 2 hours should be less than 30% by weight. This is dependent on drying time and/or efficiency.
3. After vacuum drying at ambient temperature, the capacity of the material for Sr^{++} should be equal to or greater than 3.5 meq per gram of material. The capacity is determined by contacting 1 gram of material with 100 ml of water containing 17.5 meq of Sr^{++} , added as

$\text{Sr}(\text{NO}_3)_2$, for twenty-four hours. (Typical capacity for material which loses 25 wt.% at 700°C is 4.2 meq Sr^{++} /gram.)

4. The material should contain less than 5% by weight of carbonate calculated as $\text{CO}_3^{=}$. The formation of carbonate results from reaction with atmospheric carbon dioxide.

Results of experiments done in our laboratory to determine CO_2 pick-up are as follows:

<u>Sample</u>	<u>Drying Conditions</u>	<u>Wt% $\text{CO}_3^{=}$</u>
A-1	Minimum air exposure - Sample A was transferred from filter to vacuum drying chamber immediately after filtration	0.25%
A-2	Sample A after vacuum drying plus 72 hours in static air.	4.58%
A-3	Sample A after vacuum drying plus 408 hours in static air.	4.71%
B-1	Sample B remained in filter in flowing air for 75 minutes prior to vacuum drying.	3.50%
B-2	Sample B after vacuum drying plus 72 hours in static air.	4.65%
C-1	Sample C remained in filter in flowing air for 19 hours.	5.45%
C-2	Sample C after 528 hours in filter in flowing air.	4.93%

Samples A, B, and C were equal amounts of a single batch of sodium titanate subjected to the drying conditions as listed.

b. Shipping Requirements

1. Material to be packaged in plastic bags to minimize moisture and carbon dioxide absorption from air and shipped in metal or cardboard containers.

2. Containers will have to be palletized to prevent "fines" formation which could result from accidental container damage. Formation of "fines" in vibration tests has been negligible, however, drop tests have resulted in considerable particle degradation. (10)

B. Analytical Methods

Na

Sodium is determined via atomic absorption spectroscopy. The sample is dissolved in 6 to 12 M HCl and diluted to give a Na concentration of 1-10 µg per milliliter prior to analysis.

Ti

Titanium is determined as TiO_2 after precipitation as the cupferronate and subsequent drying. Sufficient sample to give 0.3 to 0.5 g of Ti is dissolved in 6 to 12 M HCl and diluted to give 200 ml containing ~12% concentrated HCl. The solution is cooled to ~5°C and the Ti is precipitated by addition of ~50 ml of a cold, 6 w/o solution of cupferron in water while stirring. The precipitate is kept at 5°C for one hour and then filtered through a Whatman #42 filter paper or equivalent. Transfer and washing are done with a cold (5°-10°C) 1% HCl solution containing 5 ml of the 6 w/o cupferron solution per 250 ml. The filter paper and precipitate are put into a Pt crucible and then into a muffle furnace at ambient temperature. Conversion to TiO_2 is done by raising the temperature to 700°C and holding at temperature for one hour.

$CO_3^{=}$

Two grams of sodium titanate are weighed into a plastic beaker. Two hundred ml of H_2O are added, and the beaker is covered with a tight fitting cap and put on a wrist shaker for 20-24 hours. Part of the supernatant is centrifuged (12-14,000 rpm) and/or filtered to give a clear or just slightly cloudy solution. Twenty-five to fifty ml aliquots of the clarified supernate

are titrated with 0.01 N HCl using a pH meter. One-tenth ml additions are used in the vicinity of the endpoints, pH $\approx$ 8.0 to 8.3 and pH $\approx$ 4.2 - 4.4, which are then determined by standard graphical techniques.

The first endpoint represents the titer for CO_3^{2-} and OH^- , which occurs due to hydrolysis. The titer between the 1st and 2nd endpoints represents the HCO_3^- initially in solution and that formed from the acid-carbonate reaction and is used to calculate the weight percent CO_3^{2-} in the sample.

$$\text{wt } \% \text{ CO}_3^{2-} = \frac{(\text{2nd E.P. vol} - \text{1st E.P. vol}) \times 0.01 \times .060 \times 100 \times \frac{200}{\text{aliquot vol}}}{2,000 \text{ g}}$$

Sr Capacity

Approximately 1.5 g samples of sodium titanate are accurately weighed into plastic beakers, 25 ml of 0.90 N $\text{Sr}(\text{NO}_3)_2$ are added followed by 125 ml of deionized H_2O . The beaker is tightly capped and put on a wrist shaker for 16-20 hours. The supernatant is then centrifuged and/or filtered to give a clear or slightly cloudy solution.

Twenty-five milliliter aliquots of the clarified supernatant are added to 60 ml of 0.1 N NaOH and titrated with 0.0904 N EDTA using methylthymol blue indicator. The color change at the endpoint is blue to gray or blue to colorless depending on the amount of indicator used.

The difference between the initial and final Sr^{++} concentrations is used to calculate the amount of Sr per gram of the solid.

Two vendors, G. F. Smith and Co., Columbus, Ohio, and Cerac, Inc., Milwaukee, Wisconsin, prepared 200 g samples of sodium titanate for evaluation. Both materials were found to be satisfactory in tests in our laboratory. Cerac, Inc., subsequently supplied a 200 kg batch of the material which was also found to meet the above specifications.

VII. Column Regeneration

The ability to regenerate an ion exchange column is of interest for economic reasons, particularly in a process which requires remote handling and minimal generation of additional waste streams. The feasibility of using EDTA for regeneration was suggested by our assessment of its effect as a constituent of the salt cake waste (Table 4). At the time this work was in progress, sodium niobate (SN) was also being considered for this application and some data on SN are included as a matter of interest.

Batch equilibration and column experiments were done to determine whether the stability of the Sr-EDTA complex was sufficient in salt cake simulant to provide a practical means of regeneration. The batch tests were done in 50 ml volumes of 7M NaNO_3 containing 73.7 ppm of stable strontium and 10^{-4} M NaOH. After equilibration with ST and SN, five milliliters samples of solution were removed for analyses and sufficient quantities of a 0.06 M EDTA-7M NaNO_3 - 10^{-4} M NaOH solution were added to give the EDTA:Sr ratios shown in Table 8. These mixtures were equilibrated for an hour and analytical samples were taken again. The results are given in Table 8 and show that EDTA does elute Sr from both ST and SN and that elution is dependent on the EDTA concentration. They also demonstrate why the ST material is preferred over the SN for this application.

In the column experiment, twelve column bed volumes (240 ml) of dissolved salt cake simulant containing 0.01 $\mu\text{Ci/ml}$ of ^{85}Sr were passed through a 1 cm diameter column of ST. ^{85}Sr was not detected in the effluent indicating a decontamination factor of $\sim 2 \times 10^3$. This was followed by 6 column bed volumes of 7 M NaNO_3 - 10^{-4} M NaOH containing 0.1N EDTA. The elution curve is shown in Figure 9 and shows that approximately 60% of the ^{85}Sr was stripped from the column. To determine the feasibility of column reuse, the EDTA was

washed from the column using two column volumes of 7M NaNO_3 containing $10^{-4}M$ NaOH. Again, 6.5 bed volumes of the ^{85}Sr doped simulant were added and ^{85}Sr was not detected in the column effluent.

Subsequent batch equilibration experiments were done to optimize the pH and total sodium ion concentration of the EDTA eluent solution. Sodium concentrations of one molar or greater are desirable as it has been observed that large variations in ionic strength result in a change in column flow properties and often in the attrition of extremely fine particulate matter. Strontium titanate was used in this work and was prepared by equilibrating ST in a 6N NaNO_3 - 0.6 N NaOH solution containing a threefold excess of Sr. The exchanged material was filtered, washed with H_2O to remove unreacted strontium, air dried to a "damp" condition, and analyzed to determine the Sr content. Approximately 0.3 g samples of the Sr-loaded titanate were added to 50 ml aliquots of 1 N NaNO_3 - 0.1 N EDTA solutions with pH ranging from 7 to 13.5. After one hour, the solutions were analyzed to determine the percent of Sr eluted from the titanate. The results are given in Table 9 and show that a pH in the range of 9 to 10 results in the most efficient elution of Sr. A similar experiment was done using a 0.1N EDTA solution at pH = 9, varying the NaNO_3 concentration between 0.5 and 4 molar. The results are also in Table 9 and show that the degree of Sr elution is independent of NaNO_3 concentration over the range studied.

In the column stripping experiment only 60% of the ^{85}Sr was recovered; however, the column was loaded to less than $3 \times 10^{-5}\%$ of total capacity. The possibility exists that the small quantity ($< 0.3 \mu\text{g}$) which was not recovered may be the result of adsorption on glass walls of the column or physical entrapment and may be constant for a given column size and independent of the total column loading. Subsequent data suggest that near

quantitative recovery of Sr should be possible from a column which is loaded to 1" or more of capacity (Table 9). Column experiments necessary for verification were not completed prior to termination of this project.

VIII. Alternate Material Forms

The use of relatively fine powders in ion exchange processes which require remote handling poses some potential problems, the most serious of which is the possibility of column plugging. This could result from swelling, compaction, attrition of "fines" which clog the bed or bed support, or from the filtering action of the bed which tends to concentrate finely divided or gelatinous material in the feed, thus forming a plug at the column inlet.

Sodium titanate ion exchange beds were thoroughly characterized during previous work with a high level waste solidification process.⁽⁴⁾ No serious problems were identified with column flow; however, that application required a total liquid throughput of only three to four bed volumes prior to conversion of the bed to ceramic form.

In this application, long term bed stability is desirable for obvious reasons and particularly if column regeneration is feasible. In addition to the 1 cm diameter column described previously, flow tests have been conducted with 2.5 cm and 10 cm diameter beds. The former was 50.5 cm in height after initial compaction and ~1000 bed volumes of 6 N NaNO_3 - 0.6 N NaOH were passed through the bed. A superficial velocity of 10 ft/hr (representing a process flow rate) was maintained for 300 bed volumes using a 2.8 to 3.9 psi pressure drop across the column; it was increased by a factor of two using a 7.3 psi pressure drop for the final 600 bed volumes. There was no appreciable change in the flow resistance of the bed during this experiment.

The bed in the 10 cm diameter column was 32 cm high and was run continuously for three months at a superficial velocity of 10 ft/hr. The

initial pressure drop across the bed was 6 psi and this increased to 10 psi by the end of the run. Channeling was observed between the bed and the glass column wall, involving approximately one third of the circumference. At the end of the run, this channeling extended 23 cm down the bed and, while significant in this experiment, would be a minor perturbation to a process-sized bed. Plugging due to gelatinous material in the feed would be a problem as the particles in a titanate bed in contact with dissolved salt cake simulant seem to weld together and attempts to backflush a column result in simply lifting or floating the entire bed.

Although our experience to date indicated that the use of sodium titanate in powder form in ion exchange columns is possible, consolidation of the material into higher density particles of constant geometrical shape would simplify most operations involved in using an ST column. The technology for converting an inorganic oxide powder to a dense pellet form certainly exists, and typically involves the addition of a binder material, pelletizing or spheridizing, and thermal treatment to stabilize the product. The desired application of the titanate imposed severe constraints on both the binder material and thermal treatment of the product. The binder must be stable for extended periods in highly caustic solution, and in the case of organic binders, must allow contact of the titanate with aqueous solutions. Heating the material results in changes in the Sr capacity as shown in Figure 10, where a two-fold or greater reduction occurs at temperatures above 100°C. These constraints were important considerations in the three general approaches to sodium titanate which included:

- (1) Physical inclusion of sodium titanate powder in a porous substrate.
- (2) Consolidation of the powder by pelletization.
- (3) Chemical loading of the titanate in regular or macroreticular anion exchange resin followed by in situ conversion to the sodium form.

These are described in more detail in the following section.

A. Inclusion in a Porous Substrate

This approach involved soaking a porous substrate in an alcoholic solution of tetraisopropyl titanate and sodium hydroxide, washing with methanol, and then soaking in an acetone-water mixture to hydrolyze the material within the pores. Two porous support materials evaluated were: Porous glass particles in the range of 177 to 244 microns in diameter with a nominal pore size of 1350A and pore volume of $> 1.25 \text{ cm}^3/\text{gm}$, and 8-12 mesh molecular sieves with a nominal pore size of 4A (Type 4A Davison Molecular Sieves).

The titanate-loaded molecular sieves had Kd's on the order of 150-200 for ^{85}Sr at the 2 nCi/ml level in salt cake simulant. However, the titanate content of the sieves is estimated to be less than 1% by weight and therefore the beads have a low exchange capacity per unit volume. Washing the spheres with alcohol prior to hydrolysis was necessary to prevent an external coating of titanate powder which produced "fines" during column preparation.

The glass particles were loaded to approximately 35% by weight with sodium titanate. Scanning and transmission electron microscopy showed that the pores, although not completely filled, contained the sodium titanate. The overall capacity of the "loaded" glass for strontium per gram of sodium titanate was found to be the same as that of sodium titanate powders. Contact with liquid and column preparation resulted in attrition of "fines" to approximately the same extent as observed in the sized powder material.

B. Consolidation of Sodium Titanate Powder

A variety of techniques were used in combination with binder materials to make consolidated forms of the sodium titanate powder. These included die and isostatic pressing, web agglomeration, and extrusion pelletization.

The attempts to use die and/or isostatic pressing with various combinations of sodium titanate and binders were unsuccessful. Most samples fell apart or crumbled after drying or burnout of the organic binder. Web agglomeration involved the incorporation of approximately 1% by weight of Teflon K (Harshaw Co.) in the titanate powder by milling the mixture in a heated (100°C) ball mill. The resulting material can be obtained in the form of a fibrous mat, or by further working, an agglomerated powder. The mat retained its form in water with no apparent attrition of "fines"; however, the agglomerated powder showed a loss of integrity and "fines" were produced in what appeared to be the same relative quantities as observed for a sized sodium titanate powder. The Sr capacity of the ST was not reduced in the mat process, but this physical form is not easily adaptable to this application.

Two epoxy binder materials, EPON 828 and EPON 1001, were evaluated. Sodium titanate powder was either soaked or sprayed with a dilute solution of the epoxy in toluene calculated to produce about 30% by weight of epoxy in the product. The resulting slurry was forced through a 1/8" mesh screen and dried to remove the solvent. The product had excellent physical stability, i.e., it was not possible to degrade the pellets by rubbing them between fingers. The particles also showed good stability in salt cake simulant, but were difficult to wet and showed a low rate of Sr adsorption (Table 10). The 1.8 meg/g of strontium adsorption after 24 hours is about 30% of the estimated capacity of the material.

Samples of extrusion pelletized sodium titanate were prepared both in this laboratory and at the Bonnot Co., Kent, Ohio. Water, a water solution of PVA, Cerzma-Bind 542 (a commercial product found to be a solution of aluminum phosphate), and bentonite clay were evaluated as binders. The

water - PVA binder was discarded as the PVA was slowly leached out of the material by the salt cake simulant resulting in particle degradation and the formation of foam.

A sample of pelletized material containing 2% by weight of bentonite clay was prepared by Bonnot by extruding through 0.093" diameter holes and drying at 200°F for two hours. The pellets were found to disintegrate into powder almost immediately after contact with 6 N NaNO_3 - 0.6N NaOH solution. Heating of the pellets increased their physical stability in solution; only slight attrition occurred in pellets heated in the 150°-250°C range and none was observed in material heated in the 300°-900°C range. In capacity tests, none of the materials, some of which were pre-soaked prior to contact with Sr^{++} solution, exhibited sorption rates or capacities considered to be satisfactory in this application. The results are given in Table 11.

The pellets containing the Ceram-Bind 500 binder appeared to have excellent stability in water and in the dissolved salt cake simulant during 24 hour tests. Strontium adsorption ranged from 5 to 7 meq/g in the simulant after 24 hours on 1/8" diameter pellets prepared using 2.5 - 20% by weight of the liquid binder (the binder contained ~ 50% solids). However, after soaking for 5 days or longer in the simulant, the pellets became very soft and disintegrated into powder during column preparation or operations such as backflushing.

Pellets prepared by extruding a water slurry of sodium titanate had a reduced Sr capacity (Table 12), but retained their physical integrity in the salt cake simulant. The lower capacity probably results from the difference in pellet porosity, as these pellets appear to have a higher packing density than any of the other materials.

Samples of both 1/16" and 1/8" diameter pellets were ground and -40 to +140 mesh fractions of each were included along with the same size fraction of ST powder. The results of Sr sorption experiments are given in Table 12.

The ground pellet material is superior to the powder with respect to ease of column preparation and also allows a column to be backwashed as it does not tend to stick together as does the powder. The high Sr capacity of the pellets as opposed to the ground pellets after 24 hours equilibration is not understood.

Samples of the pellets which were pre-soaked prior to contact with the Sr solution showed higher sorption rates in the first hour of contact and higher capacity after 24 hours. An argon atmosphere was used in some of the samples to insure that the loss of Sr from solution was the result of sorption on the titanate and not from precipitation of strontium carbonate due to absorption of atmospheric carbon dioxide.

A column experiment was done using the 1/16" pelletized material consolidated with the water binder. Two columns of the material were prepared and run in series. The first, a 14 cc bed 1 cm in diameter, contained the as-received pellets in lengths ranging from approximately 1/16" to 1/4", and the second was a 5.5 cc bed, one centimeter in diameter, containing the same material which was crushed and sieved to a -40 +140 size range. The packing efficiency of the first column was very poor, as the column contained large voids (estimated to be ~ 40% of the bed column) which could readily result in channeling. It was included in the test to get a qualitative indication of how the pelletized material would perform in removing tracer level Sr from a high salt matrix under column conditions.

The effluent from the first column flowed directly into the second column, which was prepared in the same way as ST powder columns. The feed

solution was a dissolved salt cake simulant containing 1μ Ci/ml ^{85}Sr and was pumped through the columns at a rate of two column volumes per hour based on the volume of the second column. Samples (5 ml) of effluent from both columns were taken at various intervals and counted along with a "feed" sample on a NaI scintillation crystal detector. The "feed" solution blank was counted each time so as to eliminate the need for correcting for decay of ^{85}Sr .

The experiment was terminated after ~ 17 liters or ~ 3000 column volumes (based on the volume of the powder column) were run through the system. The results are plotted in Figure 11 where C/Co is the activity of the sample either from the pellet column or powder column divided by the activity of feed solution. The C/Co for the pellet column increased sharply after ~ 400 column volumes and continued to increase slowly to the end of the experiment, while the C/Co for the powder column appeared to remain fairly constant ($1-2 \times 10^{-4}$) until ~ 2400 column volumes throughput. The overall decontamination factor and total column throughput of the two columns in series is equivalent to or better than a single ST powder column.

C. Sodium Titanate in Macroreticular Ion Exchange Resin

This material is prepared by introducing an anionic titanium species into a strong base anion exchange resin. This is done by soaking the resin in an aqueous solution of a quaternary ammonium titanate compound to load the resin by an ion exchange process. The resin is thoroughly washed with water until Ti is not detected by addition of H_2O_2 to the filtrate and then put into 3 M NaNO_3 solution for in situ conversion of the sorbed titanium to sodium titanate.

The anionic titanium species is prepared by reaction of an anhydrous

solution of tetramethylammonium hydroxide in methanol with titanium isopropoxide. The solid compound is obtained by adding the methanol reaction mixture to acetone and slowly adding H_2O until the precipitate flocculates or adding the mixture directly to an acetone-water solution. The precipitate is a grainy solid, easily filterable, which can be dried to a constant weight in vacuum at temperatures up to $100^\circ C$. The dried compound is highly water soluble and remains so indefinitely if it is stored in a closed container. Prolonged contact with air results in conversion to a water insoluble material due to absorption of CO_2 resulting in the formation of carbonates. A molar ratio of titanium to base of 2 is generally used and results in a compound with an empirical stoichiometry of $(R_4)_2H^+ Ti_2O_5H^-$ which is adequate for predicting the chemistry of the material. Alternatively, the aqueous titanium solution can be prepared by adding water directly to the methanol reaction mixture and boiling to remove the alcohol. Mole ratios of titanium to base of less than 2.8 result in complete solubility in water solution.

The resins used in this work were AGL-X8 (100-200 mesh) and AG MP-1 (20-50 mesh) from Bio-Rad Laboratories, Richmond, CA. They were converted to hydroxide form from the as-received Cl^- form to minimize Cl^- addition to the waste stream. The titanium exchange rate or capacity was not dependent on the initial ionic form of the resin. The AGL-X8 resin was included in the initial stages of the work and no major differences in the titanium sorption characteristics of the two materials was observed. The macroreticular resin (AG MP-1) showed a slightly higher Ti capacity and was chosen as a baseline for material used in the remainder of the work described in this report.

In the titanium sorption step, excess titanium is kept in solution as the resin will not sorb 100% of the titanium. In column experiments, where the titanium is loaded onto the resin by flowing a solution of tetramethylammonium titanate through a resin bed representing a large excess of exchange

capacity, as much as 87% of the titanium was sorbed. In batch loading, it appears that about 70% of the titanium is exchanged (Table 13). The reason for this behavior is not understood, but the presence of an equilibrium mixture of two or more species of titanium, some of which do not exchange on the resin is suggested. Also surprising is that the percentage uptake increased with a decreasing ratio of resin capacity to titanium content (Table 13).

The temperature of the titanium solution during the sorption step effects the rate of sorption. Increasing the temperature results in an increased rate of sorption. However, over a period of 20 hours, the total titanium sorbed by the resin from solutions at 23°C and 90°C did not differ significantly.

After the sorption, the titanium is converted to sodium titanate by soaking in a solution of 3 M NaNO_3 . This probably occurs due to replacement of the titanate anion by the nitrate ion followed by interstitial precipitation of sodium titanate. Na_2CO_3 and NaOH were also used in the conversion step. The use of Na_2CO_3 resulted in lower sodium uptake and lower ^{85}Sr Kd's. Similar results using NaOH are discussed later. The differences resulting from the use of several sodium compounds, all of which were used at the same sodium concentration on the same titanium loaded resin, suggest the importance of the anion in the conversion process.

From the results of these initial experiments, a baseline preparation technique was established and is given in detail below along with the results of Sr capacity and ^{85}Sr distribution coefficients measurements made on the product after various drying procedures.

One hundred and fifty grams of tetraisopropyl titanate were added to 120 g of tetramethylammonium hydroxide (20% solution in methanol) and the

mixture stirred and added to 600 ml H_2O . Fifty grams of "damp" AG MP-1 resin in the OH form were added and the solution was boiled to remove the alcohol. The solution was stirred on a hotplate during this operation to prevent bumping, and the liquid volume was kept at 700 ml or greater during boiling by addition of deionized water. The resin was allowed to remain in the titanate solution for 20 hours at ambient temperature, thoroughly washed with water, and added to 400 ml of 3 M $NaNO_3$. The temperature of the $NaNO_3$ solution was increased to 90°C and then cooled to ambient. After 20 hours, the resin was filtered, washed with water, and removed from the filter while still damp. Portions of the batch were dried for 20 hrs. in flowing air at ambient temperature, in vacuum at ambient temperature, and in air at 100°C. As it is difficult to determine the water content of the hydroxide form of the resin, the point of reference used in determining the ST content is the weight percent of residue remaining after 700°C firing of a ST loaded resin which has been previously dried at 100°C. The damp resin lost 37.4% by weight after drying at 100°C and the dry resin contained 40.6% (by weight) residue after firing at 700°C. Air drying resulted in 28.1% weight loss and the dry material contained 35.4% residue after firing at 700°C. The vacuum drying of the damp resin resulted in 36.9% weight loss and the dry material contained 40.3% residue after 700°C firing.

The ash obtained by firing AG MP-1 resin in the OH form at 700°C was < 0.1%. The residue obtained from firing the loaded resin contained 86.0 w/o TiO_2 and 14 w/o Na_2CO_3 . Standard sodium titanate calcined at 700°C has a stoichiometry of $Na_2Ti_4O_9$, containing 83.8% TiO_2 and the remainder Na_2O .

Strontium capacities obtained by one and twenty-four hour soaks in 6 M $NaNO_3$ -0.6 M $NaOH$ -0.075 M Sr^{++} solution are given in Table 14. These results indicate that all the drying techniques used result in a decrease

in total capacity. The strontium capacity of AG MP-1 resin in the OH form was found to be 0.1 meq per gram of damp resin, which is of the same order as the uncertainty in the analytical technique used to determine strontium.

Distribution coefficients for ^{85}Sr between the various dried forms of the resin and a 6.0 M NaNO_3 -0.6 M NaOH solution containing $\sim 1 \mu\text{Ci/ml}$ of ^{85}Sr are given in Table 15. These results show the damp resin to have slightly lower K_d 's than the other materials. Based on the results of both the capacity and distribution coefficient experiment, either air drying or vacuum drying appear to be the most satisfactory drying techniques.

To further optimize the preparation of the loaded resin, a group of materials was prepared using varying conditions as listed below:

1. One-hour soak in quaternary ammonium titanate versus a 24-hour soak;
2. A four-hour soak in NaNO_3 versus a four-hour soak in NaOH for conversion to the sodium titanate form;
3. Air-drying the resin prior to contact with the sodium solution versus using the damp resin directly after the titanate loading step;
4. Omitting the sodium conversion step prior to contact with dissolved salt cake simulant and the effect of air drying on this material prior to use.

The methods of preparation for samples labeled #1 - #12 are given in Table 16. Table 17 lists the sodium titanate, or in the case of those materials not contacted with sodium, the titanium dioxide content of samples 1-12. The weight percents given are based on a sample weight

obtained by drying each material in air to constant weight prior to analysis. In Table 18, distribution coefficients for ^{85}Sr in dissolved salt cake simulant containing $1 \mu\text{Ci/ml}$ of ^{85}Sr are given. The K_d 's are given for both the actual weight of "damp" or air-dried material used and for the amount of sodium titanate or titanium dioxide actually contained in the sample.

A number of conclusions can be drawn from the data in Tables 17 and 18: 1) Conversion of the titanate to the sodium form prior to contacting the salt cake simulant results in higher K_d values after both 15 minute and 24 hour equilibrations; 2) the material converted with NaNO_3 appears to be superior to that converted with NaOH ; 3) air drying the titanate form prior to sodium conversion results in material with higher K_d values; 4) the K_d 's based on the weight of Sr or TiO_2 in resin are higher in all cases for those materials which were contacted for only 1 hour with the titanate solution. This may be the result of "plugging" of the available pores in the case of the higher loaded materials. The final judgment as to the efficiency of the higher loaded material versus the lower will have to be based on column performance. Air drying prior to sodium form conversion and the use of NaNO_3 for the conversion appear to be preferable.

The completion of the initial characterization of the loaded resin material coincided with the end of the funding period for this project. Column testing was limited to a single material, prepared in the same manner as #8 in Table 12. A 1 cm diameter bed with a height of 10 cm was used to decontaminate dissolved salt cake simulant doped with approximately $1 \mu\text{Ci/ml}$ of ^{85}Sr . A flow rate of 1.25 bed volume per hour was used. The effluent was sampled after 30, 120 and 180 bed volumes showing decontamination factors of 770, 370, 316, respectively, which are satisfactory for a column of that

size containing 20-50 mesh material. The initial results indicate that two or more columns of the titanate-loaded resin in series may be necessary to achieve the decontamination and column lifetime desired for process use. However, the ease of preparation and application of the material may more than offset the need for multiple columns.

Another interesting aspect of this material is the fact that the resin retains its anion exchange characteristics even after it is loaded with titanate. Ion exchange capacities for I^- of 4.2 meq/dry gram of the chloride form of the resin and 4.0 meq/dry gram of resin containing 36.4% by weight of sodium titanate were observed. Titanium was not detected by the peroxide test in the iodide solution after equilibration which indicates that titanium was not displaced from the resin.

Scanning electron microscope examination of both the external surface and cross sectional area of the resins showed no differences in morphology as a result of the titanate loading. Elemental dispersion photographs showed homogenous distribution of Ti throughout the resin bead at magnifications as high as 5000X.

IX. Summary

An investigation into the use of an inorganic ion exchanger, sodium titanate, for removal of strontium from Defense Waste typified by caustic, near-saturated solutions of sodium nitrate has been completed. Comparison of Sr decontamination factors achieved with ST with those reported for other co-precipitation processes and ion exchange materials indicated that the titanate was superior in all cases.

Sodium titanate has a Sr capacity of approximately 9 meq/gram of dry material and the sorption kinetics are favorable for a column ion

exchange process. In simulant solutions containing excess Sr, over two-thirds of the total capacity is sorbed during the first ten minutes of contact and in solutions containing ^{85}Sr at the tracer level, decontamination factors of 50 are seen after ten minutes and >500 after one hour of contact. Cation impurities added to the simulant had little or no effect on Sr distribution coefficients on ST, but were shown to reduce the useful lifetime of a ST column by about a factor of two. The presence of EDTA in the simulant at concentrations approximating or less than the Sr concentration had a negligible effect on distribution coefficients, but at concentrations much higher than those of Sr, the EDTA solution can be used to elute Sr from the exchanger.

The sodium titanate has also been shown to be extremely efficient in sorbing actinides from a dissolved salt cake simulant. A decontamination factor of $\approx 5 \times 10^5$ was obtained by passing simulant containing 2.4×10^6 dpm/ml of ^{238}Pu activity through a ST column, producing an effluent in which Pu was not detected above background using liquid scintillation counting techniques. In column experiments with ^{85}Sr doped dissolved salt cake simulant, decontamination factors of > 500 were observed in the first 2000-3500 bed volumes of effluent, depending on the presence or absence of other cations in the simulant. The decontamination factor was not affected by flow rate in the range of 1 to 14 column bed volumes per hour.

Column experiments and distribution coefficients measurement were done in related experiment at the Rockwell Hanford Operations facility near Richland, Wash., using salt cake which had been taken from their storage tanks. No significant deviations from the results obtained in simulant solutions were reported.⁽⁸⁾

A potential commercial supply of sodium titanate powder was developed as an integral part of this study. Two vendors prepared small quantities of ST using preparation techniques, acceptance criteria, and analytical methods supplied by Sandia. Cerac, Inc. of Milwaukee, Wis. subsequently supplied a 200 Kg batch of material which met the established criteria.

The baseline material used in this work was a sodium titanate powder in the -40 to +140 mesh range. Although the material performed satisfactorily in columns of up to 4 inches in diameter, there remains concern as to how a powder material would perform in larger column and in the area of material handling and column preparation. An investigation to identify and produce an alternate form of the titanate with more favorable handling characteristics was done in parallel with the powder work. This resulted in two materials which appear promising which include an agglomerated form produced by extrusion pelletization using water as a binder and a macroreticular organic anion exchange resin loaded with 30-40% by weight of sodium titanate.

The pelletized material was tested in a column experiment using two columns in series; one containing the 1/16" pellets in lengths up to 1/4" and the other containing crushed pellets in the size range of -40 to +140 mesh. An overall decontamination factor for ^{85}Sr in salt cake simulant of 3×10^3 was obtained in 300 column volumes of effluent. Based on initial experiments, similar results are expected for the loaded resin material.

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Table 1

Composition of Dissolved Salt Cake
Simulant Used at Sandia

NaNO_3	6.0 M
NaOH	0.6 M
NaAlO_2	0.14 M
NaNO_2	0.11 M
Na_2CO_3	0.10 M
Na_3PO_4	0.026 M
$\text{Na}_2\text{S}^{2-}_4$	0.0036 M
Na_2CrO_4	0.01 M
$^{85}\text{Sr}^{(1)}$	$\sim 1 \mu\text{Ci/ml}$

- (1) 3-30 Ci/g Sr - Analytical Sr concentration in the range of 3.9×10^{-6} to 3.9×10^{-7} M.

Table 2
Comparison of Materials Used for Sr Decontamination
in a Batch Process

Concentration of Scavenger, <u>M</u>	$\text{Fe}_2\text{O}_3 \times 10^{(1)}$	^{85}Sr Decontamination Factors $\left(\frac{C_s}{C_o - C_s} \right)$		
		$\text{Sr}_3(\text{PO}_4)_2^{(1)}$	$\text{Ca}_3(\text{PO}_4)_2^{(1)}$	ST
0.080	---	---	--	235 ⁽²⁾
0.029	139	110	58	850 ⁽²⁾
0.015	91	57	32	357 ⁽³⁾
0.0075	54	36	30	179 ⁽³⁾
0.0037	35	16	29	87 ⁽³⁾

(1) Data taken from ARHCO Report #ARH-ST-110C.

(2) Values calculated from K_d obtained for 0.08 M ST equilibration.

(3) Values calculated from K_d obtained for 0.016 M ST equilibration.

Table 3
Effect of $\text{CO}_3^{=}$ in ST on Strontium Removal
from Dissolved Salt Cake Simulant

<u>sample</u>	<u>$\text{CO}_3^{=}$ wt. %</u>	<u>D.F. (1)</u>	<u>$K_d^{(1)}$</u>
Sandia ST-2A Vacuum Dried	0.25	2×10^3	1×10^5
G.F. Smith ST-2A Sample	3.54	2.7×10^3	1.35×10^5
Sandia ST-2A Air Dried, 528 hrs	4.93	5.4×10^3	2.8×10^5

(1) Determined by 24 hr equilibration of 1 g of ST with 50 ml of dissolved salt cake simulant doped with ~ 1 mCi/lite of ^{85}Sr .

Table 4
Cation Impurities Added to Salt Cake
Simulant Solutions

<u>Cation Impurities</u>	<u>Nominal, ppm</u> ⁽¹⁾	<u>Found, ppm</u> ⁽²⁾
Ni ⁺²	3.3	1.6
Fe ⁺³	3.5	2.4
Mn ⁺²	2.8	ND
Ba ⁺²	7.4	ND
Mg ⁺²	0.2	ND
Ca ⁺²	2.4	1.6

- (1) These concentrations represent estimated detection limits for analyses of these elements by atomic absorption in dissolved salt cake.
- (2) Concentrations found in a simulated salt cake solution after doping at the nominal concentrations and filtering.

Table 5
Effect of Cation Impurities on ^{85}Sr
Distribution Coefficients

Weight ST/25 ml Feed	Contact Time, hr	Control Feed		Cation Doped Feed	
		DF	Kd	DF	Kd
0.0005 g 25 ml	24	1.6	2.6×10^4	1.3	1.5×10^4
	48	1.6	2.7×10^4	1.3	1.5×10^4
	144	1.7	3.0×10^4	1.5	2.1×10^4
0.001 g 25 ml	24	2.3	3.0×10^4	1.8	1.9×10^4
	48	2.5	3.4×10^4	1.9	2.1×10^4
	144	3.1	4.3×10^4	2.4	3.1×10^4
0.002 g 25 ml	24	3.6	2.9×10^4	2.6	1.9×10^4
	48	4.2	3.5×10^4	3.7	3.0×10^4
	144	6.4	5.8×10^4	5.6	4.8×10^4
0.100 g 25 ml	24	No data	--	290	7.3×10^4
	48	260	6.1×10^4	380	9.1×10^4
	144	410	9.5×10^4	530	1.2×10^5
0.500 g 25 ml	24	1220	6.2×10^4	1620	8.1×10^4
	48	2780	1.3×10^5	1510	7.3×10^4
	144	2350	1.1×10^5	2630	1.2×10^5

$$K_d = \frac{[\text{Sr}]_{\text{solid}}}{[\text{Sr}]_{\text{liquid}}} \times \frac{\text{Vol (ml)}}{\text{Solid (g)}} \quad DF = \frac{[\text{Sr}]_{\text{liq. initial}}}{[\text{Sr}]_{\text{liq. final}}}$$

Table 6
Chelate Effects for Sr Sorption on ST and
Other Titanates

Material	Sr Kd Values			
	10^{-3} M EDTA $10^{-3} \text{ M Sr}^{++}$	10^{-3} M EDTA $3.9 \times 10^{-6} \text{ M } ^{85}\text{Sr}^{(1)}$	$5 \times 10^{-10} \text{ M EDTA}$ $3.9 \times 10^{-6} \text{ M } ^{85}\text{Sr}^{(1)}$	$3.9 \times 10^{-6} \text{ M } ^{85}\text{Sr}$
ST	5.5×10^3	1×10^3	7.7×10^3	8.9×10^3
Cu(II)T	1.9×10^4	6.6×10^2	4.0×10^3	4.3×10^3
Ca(II)T	8.0×10^3	2.7×10^2	--	2.8×10^3
Fe(III)T	4.3×10^3	3.9×10^2	5.7×10^3	5.0×10^3

- (1) The ^{85}Sr isotope solution contained 3-30 Ci/g of Sr.
The analytical Sr concentrations in the doped solutions
were in the range of $3.9 \times 10^{-6} \text{ M}$ to $3.9 \times 10^{-7} \text{ M}$.

Table 7

Residual Liquor: Composition and K_d 's for ^{85}Sr

Synthetic Residual Liquor (RL)

NaOH	5.0M
NaAlO ₂	2.5M
NaNO ₃	2.0M
NaNO ₂	2.0M
Na ₂ CO ₃	0.5M

<u>Solution, Volume Ratio</u>	^{85}Sr K_d (1)	
	<u>1 hour</u>	<u>24 hours</u>
Pure RL	1.4×10^2	3.7×10^2
3RL : 1 H ₂ O	2.4×10^2	6.1×10^2
2RL : 1 H ₂ O	2.7×10^2	6.4×10^2
1RL : 1 H ₂ O	5.7×10^2	1.6×10^3
0.5RL : 1 H ₂ O	1.7×10^3	4.8×10^3
0.25RL : 1 H ₂ O	2.8×10^3	1.9×10^4

1) 0.1 g Sr in 25 ml of solution containing $\sim 1 \mu\text{Ci/ml}$ of ^{85}Sr .

Table 8

Sr Elution with EDTA

Weight ST or SN	Sr Content of Liquid Phase		Sr Content of Liquid Phase After EDTA Addition	Mole Ratio EDTA:Total Sr
	Initial	Final		
1 g ST	73.7 ppm	0.65 ppm	45.2 ppm	1.36
1 g ST	73.7 ppm	0.62 ppm	51.7 ppm	3.4
1 g ST	73.7 ppm	0.68 ppm	61.7 ppm	6.8
1 g SN	73.7 ppm	10.2 ppm	53.4 ppm	1.36
1 g SN	73.7 ppm	9.9 ppm	65.2 ppm	3.4
1 g SN	73.7 ppm	7.5 ppm	68.4 ppm	6.8

Table 9

Elution of Sr from Sodium Titanate

pH	NaNO_3 , moles/liter	% Sr Eluted ⁽¹⁾
7.5	6	98.3
8.4	6	98.2
8.9	0.5	>100
8.9	1.0	98.5
8.9	2.0	>100
8.9	4.0	99
9.0	6.0	>100
10.2	6.0	99.4
11.4	6.0	95.1
12.0	6.0	94.8
12.0	6.0	84.7
13.4	6.0	77

- (1) The results listed as >100 reflect an average of duplicate analyses which exhibited slightly greater than 100% recovery of the available Sr.

Table 10

Sr Capacity of ST Consolidated with Epoxy Binders

<u>Binder</u>	<u>Method of Resin Application</u>	<u>Pre-treat</u>	Sr ⁺⁺ Capacity, ⁽¹⁾ meq/g		
			<u>15 min.</u>	<u>1 hr.</u>	<u>24 hrs.</u>
EPON 828	Soak	None	---	1.1	1.8
EPON 828	Soak	Pre-soaked 4 hrs in 6 N NaNO_3 - 0.6 N NaOH	---	0.61	1.33
EPON 828	Sprayed	None	0.22	0.39	0.67
EPON 1001	Sprayed	None	0.30	0.29	0.64

- (1) 1.5 g sample equilibrated in ~100 ml of 6.0 N NaNO_3 -0.6 N NaOH -0.0762 N $\text{Sr}(\text{NO}_3)_2$

Table 11

Sr Capacity of ST with 2 w/o Clay Binder

<u>Heat Treatment</u> ⁽¹⁾	Sr Sorption, ⁽²⁾ meq/gram			
	<u>1 hr</u>	<u>5 hr</u>	<u>24 hr</u>	<u>96 hr</u>
150°C	---	1.11	2.27	---
200°C	---	0.82	1.63	---
210°C in vacuum	---	0.74	1.52	---
250°C	---	0.82	1.67	---
300°C ⁽³⁾	0.13	---	0.51	0.59
500°C ⁽³⁾	0.12	---	0.80	1.46
700°C ⁽³⁾	0.16	---	0.24	0.41
900°C ⁽³⁾	0	---	0.04	0.47

(1) Samples taken from ambient to given temperature and held one hour.

(2) Samples equilibrated in 6 M NaNO₃, 0.6 M NaOH, 0.0783 N Sr(NO₃)₂

(3) Samples pre-soaked 2 hours in hot 6 M NaNO₃-0.6 M NaOH.

Table 12

Sr Sorption on ST Extrusion Pelletized Using Water as a Binder⁽¹⁾

<u>Binder</u>	<u>Pretreatment</u>	<u>Particle Size</u> ⁽²⁾	<u>Sr Sorption (meq/g)</u>	
			<u>1 hour</u>	<u>24 hour</u>
H ₂ O	None	1/16"	1.7	4.0
H ₂ O	None	1/16" reduced to -40 to +140 mesh	2.2	3.0
H ₂ O	68 hr Presoak in 6 M NaNO ₃ (argon)	1/16"	2.8	5.7
H ₂ O	68 hr. Presoak in 6 M NaNO ₃ -0.6 M NaOH (argon)	1/16"	2.7	4.6
H ₂ O	68 hr Presoak in 6 M NaNO ₃ -0.6 M NaOH (air)	1/16"	3.8	5.5
H ₂ O	None	1/8"	1.5	3.6
H ₂ O	None	1/8" reduced to -40 to +140 mesh	1.5	3.0
None - Powder	None	-40 to +140 mesh	7.8	8.9

(1) All material was consolidated by Bonnot Co.

(2) Diameter of cylindrical pellet.

Table 13

Uptake of Titanium on AG MP-1 Resin

<u>Ti Concentration⁽¹⁾</u> <u>in Solution</u>	<u>Resin Capacity, meq/ Total Ti, meq⁽²⁾</u>	<u>% Ti Uptake on Resin⁽³⁾</u>
316 ppr	46 - 56	62.4
757 ppm	19 - 23.4	59.3
1264 ppm	11.4 - 14	61.6
2528 ppm	5.8 - 7	70.0
3792 ppm	3.8 - 4.6	71.0
7584 ppm	1.9 - 2.3	71.1

- (1) Analytical concentration of Ti in 20 ml of an aqueous solution of tetramethylammonium titanate.
- (2) Ratio of estimated capacity of 2 g of damp AG MP-1, OH form, to the total number of meq Ti assuming an empirical anionic species represented as $(Ti_2O_5H)^-$.
- (3) Per cent of total titanium in solution that was absorbed by the resin.

Table 14

Strontium Capacity of Titanate Loaded AG MP-1 Resin

<u>Material</u>	<u>1 hour</u>		<u>24 hours</u>	
	<u>meqSr/g resin¹</u>	<u>meqSr/g ST²</u>	<u>meqSr/g resin¹</u>	<u>meqSr/g ST²</u>
"damp" AG MP-1 Titanate loaded	0.7	2.7	1.6	6.2
"air-dried" AG MP-1 Titanate loaded	0.8	2.4	1.7	4.7
"vacuum-dried" AG MP-1 Titanate loaded	1.0	2.7	1.9	5.1
"100°C-dried" AG MP-1 Titanate loaded	0.9	2.2	1.8	4.4

1. Capacity per gram of the particular form of loaded resin used.
2. Capacity per gram of ST in the loaded resin used.

Table 15

⁸⁵Sr Distribution Coefficients on Titanate Loaded AG MP-1 Resin

<u>Material</u>	<u>1 hour</u>		<u>24 hours</u>	
	<u>Loaded Resin¹</u>	<u>ST in Resin²</u>	<u>Loaded Resin¹</u>	<u>ST in Resin²</u>
"damp" AG MP-1 Titanate loaded	8.3×10^2	3.2×10^3	3.5×10^3	1.1×10^4
"air-dried" AG MP-1 Titanate loaded	1.2×10^3	3.4×10^3	4.8×10^3	1.4×10^4
"vacuum-dried" AG MP-1 Titanated loaded	1.3×10^3	3.7×10^3	4.5×10^3	1.3×10^4
"100°-dried" AG MP-1 Titanate loaded	1.7×10^3	4.1×10^3	6.3×10^3	1.2×10^4
AG MP-1 OH Form	(Kd of 0.8 measured after 1 hour)			

1. Kd based on weight of loaded resin.
2. Kd based on weight of ST in loaded resin.

Table 16

Preparation of Titanate-Resin Samples

<u>Sample Nomenclature</u>	<u>Titanate Contact Time</u>	<u>Initial Drying</u>	<u>Sodium Conversion</u>	<u>Final Drying</u>
1. 1 d	1 hr	damp	--	--
2. 1 NO ₃ d	1 hr	damp	NaNO ₃	damp
3. 1 OHd	1 hr	damp	NaOH	damp
4. 1 AD	1 hr	air dried	--	--
5. 1 ADNO ₃ d	1 hr	air dried	NaNO ₃	damp
6. 1 ADOHd	1 hr	air dried	NaOH	damp
7. 24 d	24 hr	damp	--	--
8. 24 NO ₃ d	24 hr	damp	NaNO ₃	damp
9. 24 OHd	24 hr	damp	NaOH	damp
10. 24 AD	24 hr	air dried	--	--
11. 24 ADNO ₃ d	24 hr	air dried	NaNO ₃	damp
12. 24 ADOHd	24 hr	air dried	NaOH	damp

Table 17

Titanate Content of Titanate Resin Samples

<u>Sample Nomenclature</u>	<u>Wt.% ST or TiO₂</u>
1. 1 d	21.3 - TiO ₂
2. 1 NO ₃ d	22.9 - ST
3. 1 OHd	24.8 - ST
4. 1 AD	21.3 - TiO ₂
5. 1 ADNO ₃ d	21.9 - ST
6. 1 ADOHd	23.6 - ST
7. 24 d	36.7 - TiO ₂
8. 24 NO ₃ d	37.9 - ST
9. 24 OHd	46.2 - ST
10. 24 AD	36.7 - TiO ₂
11. 24 ADNO ₃ d	37.6 - ST
2. 24 ADOHd	43.1 - ST

Table 18
⁸⁵Gr Kd's in Titanate-Resin Samples

<u>Nomenclature</u>	<u>15 minutes</u>		<u>24 hours</u>	
	<u>Kd¹</u>	<u>Kd(ST)²</u>	<u>Kd¹</u>	<u>Kd(ST)²</u>
1. 1 d	7.3×10^1	7.2×10^2	3.8×10^2	3.8×10^3
2. 1 NO ₃ d	2×10^2	1.5×10^3	1×10^3	7.6×10^3
3. 1 OHd	7.1×10^1	6.7×10^2	6.9×10^2	6.5×10^3
4. 1 AD	1.9×10^2	9.2×10^2	1.1×10^3	5.3×10^3
5. 1 ADNO ₃ d	3.7×10^2	3.1×10^3	1.9×10^3	1.6×10^4
6. 1 ADOHd	1.3×10^2	1.2×10^3	1.6×10^3	1.5×10^4
7. 24 d	8.7×10^1	4.4×10^2	3.3×10^2	1.7×10^3
8. 24 NO ₃ d	2.6×10^2	1.1×10^3	1.2×10^3	5.2×10^3
9. 24 OHd	9.6×10^1	3.9×10^2	1.0×10^3	4.1×10^3
10. 24 AD	1.6×10^2	5.3×10^2	8.4×10^2	2.8×10^3
11. 24 ADNO ₃ d	4.1×10^2	1.8×10^3	2.6×10^3	1.2×10^4
12. 24 ADOHd	1.1×10^2	5.2×10^2	1.4×10^3	6.7×10^3

1. Kd based on total weight of solid phase.

2. Kd based on weight of ST in the solid phase.

FIGURE 1. COMPARISON OF DISTRIBUTION COEFFICIENTS FOR STRONTIUM ON SODIUM TITANATE WITH THOSE OBTAINED ON SOME COMMERCIAL ORGANIC ION EXCHANGERS AS A FUNCTION OF SODIUM ION CONCENTRATION.

FIGURE 2. COMPARISON OF THE DECONTAMINATION FACTORS FOR STRONTIUM FROM SIMULATED SALT CAKE OR OTHER WASTE SOLUTIONS USING ION EXCHANGE COLUMNS CONTAINING SODIUM TITANATE, CHELEX 100, AND ARC - 350. FLOW RATES ARE GIVEN IN COLUMN VOLUMES PER HOUR.

FIGURE 3. ABSORPTION OF STRONTIUM ON SODIUM TITANATE POWDER IN AN ALKALINE MEDIA AS A FUNCTION OF TIME AND PARTICLE SIZE DISTRIBUTION.

FIGURE 4. ABSORPTION OF TRACER LEVEL STRONTIUM IN AN ALKALINE MEDIA ON SODIUM TITANATE POWDER AS A FUNCTION OF TIME. CATION IMPURITIES WERE ADDED TO THE SIMULANT SOLUTION TO DETERMINE THEIR EFFECT ON THE SORPTION RATE.

FIGURE 5. STRONTIUM BREAKTHROUGH CURVE FOR A SODIUM TITANATE ION EXCHANGE COLUMN. THE SOLUTION USED WAS A DISSOLVED SALT CAKE SIMULANT CONTAINING TRACER LEVEL STRONTIUM. THE FLOW RATE WAS VARIED DURING THE EXPERIMENT TO DETERMINE THE EFFECT ON THE DECONTAMINATION FACTOR.

FIGURE 6. STRONTIUM BREAKTHROUGH CURVE OF A SODIUM TITANATE ION EXCHANGE COLUMN. THE SOLUTION USED WAS A DISSOLVED SALT CAKE SIMULANT CONTAINING TRACER LEVEL STRONTIUM AND OTHER CATION IMPURITIES. THE FLOW RATE WAS VARIED TO DETERMINE THE EFFECT ON THE DECONTAMINATION FACTORS.

FIGURE 7. THE INITIAL PART OF THE STRONTIUM BREAKTHROUGH CURVE SHOWN IN FIGURE 6. A DEPENDENCE OF THE OBSERVED DECONTAMINATION FACTOR ON COLUMN FLOW RATE IS APPARENT.

FIGURE 8. COMPARISON OF THE STRONTIUM BREAKTHROUGH CURVES FOR SODIUM TITRATE COLUMNS USING A DISSOLVED SALT CAKE SIMULANT AND THE SAME SIMULANT WHICH CONTAINED SOME MULTIVALENT CATION IMPURITIES. THE COLUMN BREAKTHROUGH CHARACTERISTICS SHOW A DEFINITE DEPENDENCE ON THE PRESENCE OF THESE IMPURITIES ALTHOUGH THE OVERALL CAPACITY REMAINS SUFFICIENT FOR THE INTENDED APPLICATION.

FIGURE 9. ELUTION PROFILE ON STRONTIUM FROM A SODIUM TITANATE COLUMN. APPROXIMATELY 900 nCi OF Sr-^{85} WERE SORBED ON THE COLUMN AND THEN ELUTED WITH AN EDTA SOLUTION. SIXTY PER CENT OF THE SR WAS RECOVERED IN THE FIRST SIX AND ONE-HALF COLUMN VOLUMES OF ELUATE.

FIGURE 10. EFFECT OF THE THERMAL HISTORY OF SODIUM TITANATE ON THE STRONTIUM CAPACITY OF THE MATERIAL IN ALKALINE MEDIA. THE TEMPERATURES GIVEN WERE THOSE USED IN DRYING THE TITANATE PRIOR TO CONTACT WITH THE STRONTIUM SOLUTION, WHICH CONTAINED 0.02N SR IN A 6N NaOH - 0.6% NaOH SOLUTION.

FIGURE 11. STRONTIUM BREAKTHROUGH CURVES FOR COLUMNS CONTAINING PELLETIZED SODIUM TITANATE. A DISSOLVED SALT CAKE SIMULANT CONTAINING ^{85}Sr TRACER WAS FEEDING THROUGH TWO COLUMNS CONNECTED IN SERIES CONTAINING PELLETS AND CRUSHED PELLETS, RESPECTIVELY. THE OVERALL C/C_0 FOR 2200 COLUMN VOLUMES OF FEED WAS LESS THAN 0.3003.