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Alternate Sorbents for the Pretreatment of Tank Waste

Attached is the final technical report submitted by Dr. Abraham Clearfield of the Texas A & M University for work performed under Task Order Agreement # KF92338-O, ERDA Subcontract # C001571-O. This report is the final deliverable required under the task order agreement.

TAMU researchers synthesized three different types of sorbents; sodium nonatitanate ($Na_4Ti_9O_{20}{\cdot}xH_2O$), sodium titanosilicate of the ideal composition $Na_2Ti_2O_3SiO_4{\cdot}2H_2O$ and a pharmacosiderite of general formula, $M_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$, where M = Na, K. Strontium and actinide removal characteristics indicated that the sodium nonatitanate and pharmacosiderite materials performed as well as or better than the current Salt Processing facility baseline material, monosodium titanate (MST). The titanosilicate material exhibited relatively poor strontium and actinide removal characteristics under the strongly alkaline conditions.

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Development of Strontium and Actinide Specific Ion Exchangers for Nuclear Waste Remediation

ERDA Grant No. C001571-O

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Executive Summary

Several different types of sorbents have been synthesized and submitted to WSRC for testing in the removal of Sr and several actinides from Savannah River nuclear waste solutions. The samples include several forms of sodium nonatitanate, $Na_4Ti_9O_{20}{\cdot}xH_2O$, a semi-crystalline sodium titanosilicate (CST) of ideal composition $Na_2Ti_2O_3SiO_4{\cdot}2H_2O$ and pharmacosiderites of general formula $M_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$, $M = Na^+, K^+$. Results of screening tests at the Savannah River Site showed that the nonatitanate samples exhibited as good, or better, performance than the monosodium titanate samples (MST) proposed for the treatment process. The sodium pharmacosiderite achieved very high sorption of strontium and actinides and should be examined in greater detail. None of the CST samples, whether crystalline (UOP preparations) or semi-crystalline (submitted in this study), were particularly effective in removal of the radioactive species, although the semi-crystalline product out-performed the crystalline samples.

It is recommended that the final removal process take advantage of the kinetics of the sorption reactions. The vast bulk of the uptake of strontium and the actinides occurs in the first two to three hours after the addition of the sorbents to the waste solution. By utilizing a double precipitation method on smaller batches, the first filtration may take place after a 2-3 hour hold time followed by a second addition of sorbent and a 3-4 hour hold time to reach acceptable levels of removal of the radioactive species in place of 168h equilibration or the 24h baseline. Such a procedure should increase the throughput of treated waste.

Objectives:

1. Synthesize inorganic ion exchangers directed towards the removal Sr^{2+} from Savannah River (SR) supernatant high-level wastes.
2. Examine the structures of the ion exchangers and relate the structures to the ability to sequester the strontium and actinide ions in the waste systems.

Introduction

Three groups of compounds were chosen for synthesis, determination of ion exchange behavior in waste simulants and testing. They are sodium titanium silicate popularly designated as CST, titanium silicates with pharmacosiderite structure, and semi-crystalline sodium nonatitanates, $Na_4Ti_9O_{20}$. All three have been previously shown to exhibit a high selectivity for strontium. A brief description of the three exchangers follows:

CST: The ideal formula for this compound is $Na_2Ti_2O_3(SiO_4) \cdot 2H_2O$. The crystals are tetragonal: a = 7.8082(2), c = 11.9735(4)Å, space group $P4_2/mcm$ and Z = 4. The titanium atoms occur in clusters of four grouped about a 4_2 axis, two up and two down, rotated by 90°. Each titanium is octahedrally coordinated, sharing edges in such a way that an inner core of four oxygens and four Ti atoms form a distorted cubane-like structure (**Figure 1**).[1] These cubane-type structures are bridged to each other through silicate groups along the a- and b-axis directions. The titanium-oxygen clusters are 7.81Å apart in both the a- and b-axis directions with the Si atoms at c = ¼ and ¾. In the c-axis direction, the Ti atoms are bridged by oxo-groups. The c-axis is approximately 12Å long, which is twice the distance from the center of one cubane-like cluster to its neighbor in the c-axis direction. These two views of the framework are shown in **Figures 2** and **3**.

The net result of this framework arrangement is that tunnels which form are one-dimensional, running along the c-axis direction. Perpendicular to the tunnels are vacancies in the faces of four sides of the tunnels. These cavities are just the right size to enclose sodium ions. Four silicate oxygens bond to the sodium ion at a distance of 2.414(5)Å (**Figure 3**). The sodium ion coordination is completed by bonding to two water molecules in the tunnels at a bond distance of Na-O of 2.765(1)Å. Half the Na^+ ions are thus accounted for in the framework sites, as there are two sodiums in each face, over one c-axis cell length for a total of four out of the eight required per unit cell. The remaining sodiums reside within the tunnels along with the water molecules.

The Na-O bond distances within the tunnels are longer than the sum of the ionic radii (2.42Å) [2] at 2.76(1)Å. This bond distance measurement was made with only 64% of the sodium ion sites occupied.[1] The deficiency of sodium arises from hydrolysis during washing, so that the actual formula was $Na_{1.64}H_{0.36}Ti_2O_3(SiO_4)\cdot 1.8H_2O$. Because of the deficiency of Na^+, the sodium ion positions were found to be disordered with partial occupancy by water (or hydronium ions). It is possible to obtain the fully occupied sodium phase by not washing the product of the hydrothermal reaction with water or using NaOH to replace the protons.

Ion Exchange Properties. One of the principal interests in the sodium titanium silicate under discussion is its ability to remove Cs^+, Sr^{2+} and actinides from highly basic nuclear waste solutions.[3] In fact, the X-ray structure work described here, very neatly explains the ion exchange behavior of this exchanger. **Figure 4** presents the potentiometric titration curves for alkali metals on the titanium silicate exchanger.[4] The selectivity is clearly seen in acid solution as $K^+ > Cs^+ >> Na^+ >> Li^+$. In fact, it turns out that the true sequence is $Cs^+ > Rb^+ >> K^+ >> Li^+$, as shown by logKc versus uptake curves.[5] However, the situation is not that simple. There are three exchange sites in this titanosilicate, the framework site, the near framework site and the center tunnel site. To obtain thermodynamic selectivities, it is necessary to determine to which site the ion locates so as to be able to describe the phase involved. This site determination can only be revealed by X-ray structural studies, and this study has been partially carried out in the case of Na^+, K^+ and Cs^+. The very high selectivity for Cs^+ is explained by the fact that Cs^+ just fits in the center of the tunnel at $c = ¼, ¾$. The Cs^+ ion is bonded to eight framework oxygens as shown in **Figure 5** at a distance of 3.183(5)Å. This distance is very close to the sum of the ionic radii for Cs^+ and O^{2-}. In fact, the selectivity sequence determined by ion exchange [5] is for the center tunnel site.

Titanium Silicate Pharmacosiderites. Pharmacosiderite is a mineral of composition $KFe_4(OH)_4(AsO_4)_3$ that has a framework structure with tunnels similar to those described above.[6] Chapman and Roe reported the synthesis of a titanium silicate analogue with a composition close to $K_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$.[7] We prepared this compound as a highly crystalline solid and determined its structure from X-ray powder diffraction data.[8] The crystals are cubic with a = 7.7644(3)Å, space group $P\bar{4}3m$ and Z = 1. The structure is similar to that of the previously described titanium silicate in that the $(TiO)_4$ cubane-like clusters exist in this compound also. The difference lies in the cubic nature of this compound that requires bridging of the TiO clusters by silicate groups in the c-axis direction as well as the a and b directions. This arrangement results in identical tunnels that are mutually perpendicular and parallel to the three unit cell directions. The K^+ ions reside exactly in the cube face centers and are 12-coordinate being bonded to eight silicon oxygens at 3.234(4)Å and four water molecules at 3.17(1)Å (**Figure 6**). According to Prewitt and Shannon [2], the radius for 12-coordinate K^+ is 1.60Å making the sum of the radii 3.0Å, somewhat smaller than the observed bond values.

Exchange of Cs^+ for K^+ was carried out by a titration procedure and the product structure determined by X-ray diffraction procedures for $K_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$.[8] The positioning of Cs^+ ions is interesting. They locate in a disordered site at ½ ½ ½ ± 0.0587 or ± 0.459Å from the face centers. This siting produces four short bonds (3.14Å) and four long bonds (3.41Å) to the silicate oxygens and similarly two short (2.82Å) and two long (3.62Å) bonds to the water molecules within the tunnels. One may wonder why the cesium ion did not locate at the face centers. According to the ionic radii provided by Prewitt and Shannon, Cs^+ in C.N. 12 has a radius of 1.88Å. Therefore, the Cs-O bonds should be of the order of 3.24Å or very close to those exhibited by potassium in the face centers. Thus, it would appear that Cs^+ could fit in the face centers, but is more stable slightly outside this position.

<u>Ion Exchange and Structure Modification</u>. The alkali metal selectivity series for $K_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$ is $Cs^+>K^+>Na^+>Li^+$.[8] The channel openings are not large enough to allow hydrated ions to diffuse into the tunnels. Thus, the ions must dehydrate to diffuse down the channels followed by water molecules to partially rehydrate the ions. Apparently, Cs^+ ion is just able to negotiate through the channel openings but may do so by repelling the oxygen atoms to a small extent. It occurred to us that if the Cs^+ resided within the face centers, it would have a more stable bonding environment, eight strong bonds to silicate oxygens instead of four and in addition four strong bonds to water molecules. For this to occur, it was felt that a slight expansion of the unit cell would allow for this siting. To accomplish the desired expansion, we replaced all or parts of the silicate by germanate groups, and indeed, the K_d for Cs^+ increased from ~10,000 to 50,000 ml/g. The titanium pharmacosiderite is even more selective for Sr^{2+} than for Cs^+.[9] A comparable study to optimize the selectivity for Sr^{2+} has not been carried out nor has an X-ray mechanism been established. Strontium exchange in several waste systems will be presented at the end of this section.

Sodium Nonatitanate, $Na_4Ti_9O_{20}{\cdot}nH_2O$. This compound was prepared by treatment of titanium hydroxide hydrothermally with different concentrations of NaOH.[10] The product is semicrystalline with the degree of crystallinity varying with the strength of the NaOH solution and time and temperature of hydrothermal treatment. Because of the non-descript nature of this exchanger, only partial information on its structure is available. The compound is definitely layered, as the layers may be expanded by soaking in water. This is revealed by the shift of the first peak in the X-ray pattern to higher d-spacings. The behavior of the solid as a Sr^{2+} sorber depends upon the structure with samples such as 67B and 64B (see *Experimental Section*), yielding extremely high Kd values and more crystalline samples such as 11B, yielding much lower Kd values. This compound has been highly effective in removing Sr^{2+} from a simulated Savannah River tank waste solution. A deeper look into structural aspects is required to understand this variation in selectivity.

Strontium Ion Exchange. In previous studies, we examined the Sr^{2+} sequestration and removal from several waste solutions at the Hanford site. The exchangers used and their designations follow[10]: (1) a highly crystalline sample of sodium titanium silicate, $Na_2Ti_2O_3(SiO_4){\cdot}2H_2O$, with no Nb substitution [1,9] designated as NaTS; (2) a highly crystalline pharmacosiderite from which K^+ was removed by acid washing to yield $H_4(TiO)_4(SiO_4)_3{\cdot}8H_2O$ designated HTiSi; (3) a semi-crystalline pharmacosiderite made by the sol-gel method, $K_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$ designated $KTiS_{sol}$; and (4) a sodium titanate with an interlayer spacing of ~10Å. The X-ray patterns of these exchangers are shown in **Figure 7**. These exchangers were tested for Sr^{2+} removal from several Hanford waste solution whose compositions are given in

Table **1**. "N-springs" is a ground water, while the remaining three are tank waste simulants. Although the NCAW and DSSF-7 indicate little or no Sr^{2+}, we added Sr^{2+} to a level of 0.024mg/L. The 101SY-Cs5 contained significant amounts of Sr^{2+} complexants. The results are summarized in a series of Tables **2-5**.

All of the exchanger samples proved satisfactory for removal of Sr^{2+} from the N-Springs simulant. This was particularly so for the V:m (volume to mass) ratio 1000:1. The poorest exchangers are the zeolites, which are normally used for mildly basic waste solutions. The sample with the highest affinity was the NaTS sample and the poorest was the pharmacosiderite, HTiSi. The low Kd value for this sample is probably the result of its high acid character. The sodium nonatitanate was also very selective, especially at the high V:m value. The same two exchangers, NaTS and NaTi performed very well with the NCAW and DSSF-7 simulants. All the exchangers performed poorly in the 101SY-Cs5 solution because they were unable to remove Sr from the complexants. We subsequently showed that addition of Ca^{2+} frees up the Sr^{2+} and then removal by NaTS proceeds smoothly.[11] For NaTi to remove ^{90}Sr, one needs to use a cation other than Ca^{2+} such as non-radioactive strontium to free up sufficient ^{90}Sr for removal since the presence of excess added Ca^{2+} interfered with uptake of Sr^{2+} by NaTi.

Experimental Section

Because the CST (NaTS) and NaTi samples showed the highest affinity for Sr^{2+}, we initiated this study with these samples.

Synthesis of Sodium Titanates. Two general methods were used to prepare the sodium titanate. In both cases, titanium isopropoxide, $Ti(i\text{-}OC_3H_7)_4$, TiIP, was used as the source of titanium.

Method I: A solution of TiIP was prepared and added to a pre-determined concentration of NaOH. After stirring for 15-30 minutes, the gel was transferred to a teflon-lined pressure vessel and heated at temperatures ranging from 150-200°C for different lengths of time.

Method II: In this method, the gel was refluxed in the NaOH solution before adding it to the pressure vessel.

Table 6 lists the conditions for several preparations and the type of X-ray diffraction patterns produced. The products group themselves into three structure types labeled T1, T2 and T3 in Table 6, based upon their X-ray diffraction patterns. The T1 types were obtained under mild conditions, low ratios of Na:Ti or if this ratio exceeds 4, temperatures of 170°C. These preparations are the least crystalline, but with a sharp initial diffraction peak. Higher mol ratios of Na:Ti and temperatures of 190-200°C yield T2 type as marked on the X-ray patterns of **Figures 8a** and **8b**. These compounds are also poorly crystalline, but all the peaks are broad. Still higher NaOH:Ti ratios and temperatures of 190-200° yield the most crystalline products labeled T3.

Table 7 presents the analysis of Na and Ti for several of the samples. The theoretical Ti:Na mole ratio for $Na_4Ti_9O_{20}$ is 1:0.444. We note that the sodium content is high for the first four samples. The reason for this imbalance was traced to the presence of Na_2CO_3, which showed up in the X-ray pattern for 23B and the IR spectra. Those samples containing Na_2CO_3 exhibited bands at ~1450 and 1400cm^{-1}, indicative of the presence of CO_3^{2-}. Some NaOH may also be present. Initially, these samples were washed in methanol to prevent hydrolysis, but after washing in water, it is observed that the ratios approach the theoretical much more closely. However, the T3 sample, 23BW2 (W2 meaning it was washed with water twice), is still high in sodium content. Selectivities were determined as K_d values where $K_d = (\frac{C_i - C_e}{C_e})$ v/m, C_i, C_e are the initial and final solution concentrations for a given ion, v/m is the solution volume to exchanger mass utilized.

Table 8 presents the K_d values for Sr^{2+} for several of the samples listed in **Table 6**. It is seen that the T1 samples have the lowest K_d values, T2 the highest, and the one T3 sample, a high K_d value. This latter value may be influenced by the high Na_2CO_3 content of 23B. This sample was submitted to SR for testing because of its high K_d value, but would need further examination as the washed sample gave a K_d value of ~40,000ml/g. Examples of actual sample preparations follow.

Preparation of $Na_4Ti_9O_{20}$ (Sample 23B). 15.1g of titanium isopropoxide (Aldrich 97%, *d*=0.9711) $Ti(OC_3H_7)_4$ (51.5mmol) was added to a plastic beaker, followed by addition of 43.0 g of a 50 wt % NaOH solution (537 mmol NaOH). The mixture was stirred vigorously during the addition and for 15-20 minutes after the addition was complete. The mixture was then transferred to a teflon-lined pressure vessel with 12 ml of distilled, deionized water (ddi). The vessel was placed inside a preheated oven at 190°C and allowed to cook for 22 hours. The bomb was cooled rapidly in cold water, the solid recovered by filtration and washed five times with ethanol and air-dried. Centrifugation may be required to separate the solid from the liquid in the latter washings, yield 6.05 g, essentially quantitative: found: Na, 16.16%; Ti, 37.82%; Ti:Na = 1:0.89, theoretical ratio 9/4 = 0.444. The high sodium level is due to incomplete removal of NaOH and sodium carbonate. Washing with water (see **Table 7**) removed most, but not all of the excess sodium. More thorough water washing of the nonatitanates is required.

A second preparation (64B) represents a variation in the procedure in that the gel was preheated before being subjected to hydrothermal treatment. 9.1g (32 mmol) titanium isoproxide was added to a solution of 50 wt % NaOH (22.2g) slowly with stirring. Then 10ml of ddi H_2O

was added and stirring continued. The mixture was then refluxed in a plastic round bottom flask, fitted with a condenser. Refluxing was continued for 3.4 hours. The refluxed mixture was then transferred to a teflon-lined pressure vessel using two 8ml portions of ddi (80ml capacity) and heated at 193±3°C for 20 hours. The product was washed as before, but this time with a 50-50 mixture of water and alcohol. The air-dried sample gave 9.55% Na, 39.70% Ti; ratio Ti:Na = 1:0.501. This sample is very much closer to the theoretical stoichiometry than 23B. We note that most of the samples in **Table 6** were prepared by the reflux method.

The deviation of the stoichiometry is very serious in the case of sample 23B and much less so for sample 64B. The excess Na was traced to the presence of Na_2CO_3 and NaOH. There was much less excess Na in 64B because of the mixed water-alcohol wash used. The reason for avoiding the use of water was to prevent hydrolysis, which incorporated protons in place of Na^+. In actual use in highly basic solutions, Na^+ would replace the H^+ in the sodium nonatitanate resulting from hydrolysis. The IR spectra showed the presence of carbonate ion in 23B by the bands at 1450 and 1400 cm^{-1} and sodium carbonate was also present in the X-ray powder pattern (XRPD). A water wash removed the major portion of Na_2CO_3 as evidenced by the absence of the carbonate bands in the IR spectrum and diffraction peaks in the XRPD. Therefore, it is recommended that thorough water washing is in order, as the presence of H^+ due to hydrolysis would do no harm, when used in strongly basic media.

Ion Exchange Behavior. The K_d values for the two samples submitted for testing to S.R.S. were obtained in a simulant consisting of 5M $NaNO_3$, 1M NaOH and 90 ppm of Sr^{2+} as

$Sr(NO_3)_2$ and traced with ^{89}Sr. The results are given below. The V/m = 200.

Sample No.	K_d Sr (ml/g)
23B	40,000
64B	>131,000
23BW*	>131,000
64BW	>134,000

*Water washed samples

These results show that the presence of Na_2CO_3 and/or NaOH lower the K_d values of sodium nonatitanate. From the analytical data, it is estimated about four additional moles of sodium were present in the unwashed sample of 23B. Even accounting for this mass as lowering the amount of nonatitanate present, the K_d is still lower than for 64B. If all the excess Na^+ was present as NaOH, it would constitute an increase in mass of 160g for 1023g of $Na_4Ti_9O_{20}\cdot 10H_2O$ or 13.5%. This would increase the K_d to 46,240 ml/g, i.e., 40,000/.865. Similarly for Na_2CO_3, the K_d would increase to 48,000 ml/g. Removal of the Na_2CO_3 + NaOH in the washing resulted in a much larger K_d as shown in the above table.

Sodium Titanium Silicate, $Na_2Ti_2O_3SiO_4\cdot 2H_2O$, CST. We realized from earlier work that the titanosilicate could be prepared in semi-crystalline as well as crystalline form. Our objective was to obtain a product optimized for Sr^{2+} uptake, rather than Cs^+ selectivity. Furthermore, we felt that a less crystalline solid would be more effective in the removal of actinides since they may be present as anions. As a result, it was less likely that they would exchange Na^+ in narrow tunnels, but might still be adsorbed onto the surface of a poorly crystalline product.

Two preparative methods were utilized. One using $TiCl_4$ as the source of Ti and the second, titanium tetra isopropoxide, $Ti(O_3C_3H_7)_4$. We varied time, temperature and concentration.

In our first series of sample preparations, we examined the effect of time on crystallinity and resultant affinity for Sr^{2+}. The preparations utilized titanium isopropoxide and were heated at 180°C for different lengths of time from 1h to 7d. The ratio of ingredients Ti:Si:NaOH was 1:2:12.8. The results are shown in **Table 9**. The K_d values were determined at V/m = 250 and spiked with ^{89}Sr. The values in the first K_d column indicate an increasing selectivity for Sr^{2+} as the crystallinity increases. The only exception is the sample obtained after 1h. This sample had an initial d-spacing of 9.70Å (**Figure 9A**). The titanosilicate has an initial d-spacing of 7.90Å and this peak first appears in the 10h sample (**Figure 9B**). Thus, the phase obtained in one hour is not CST, but a precursor of unknown structure. The product obtained in 10h is a mixture of the unknown phase and CST. This accounts for the variation in K_d values.

When the concentration of the supporting electrolytes is increased 100-fold, the K_d values decrease, but now we clearly see that the K_d values increased with increase in crystallinity (**Table 9**, last column).

An important factor is the concentration of NaOH in the final mix of ingredients. Above a concentration of 2.5M, a major impurity of composition $Na_2TiOSiO_4$ (See PDF No. 181261) is obtained as shown in **Figure 10**. It is easily identified by the peaks at 5.1Å and 2.74Å mixed with the CST. This phase has no ion exchange ability, and therefore, is inert and would add to the bulk solid waste. Another important factor is that the silica needs to be present in excess in the reactant mix. For example, we note that the mole ratio of Ti to Si is 1:2 in this preparation, but the ratio in CST is 2:1. Ratios of Ti:Si as low as 1:1 have been used with good results.

Temperatures have been varied from 170° to 210°C with higher crystallinity obtained at the higher temperatures. However, the factors as to NaOH concentration, ratio of ingredients and temperature are all correlated and need to be adjusted experimentally. Two preparations, one for a highly crystalline sample and another semi-crystalline, are given at the end of this section.

While we have seen that the K_d values increase with increased crystallinity, we intuitively felt that the highly crystalline product might exhibit slow kinetics. Therefore, we carried out kinetic experiments on a highly crystalline CST DMI-13-2 and a semi-crystalline sample DMI-13-1. The results are shown in **Figure 11**. It is seen that the K_d values for the crystalline sample are much lower as a function of time than the semi-crystalline sample. However, the uptake of Sr^{2+} after 2h of equilibration for the crystalline sample is about 91% or close to the initial measured value of sample 13-1 at 2 min. time. Based on these results, we decided to submit a sample for testing at SRTC similar to DMI-13-1, i.e., DMI-11-1. This sample preparation is described below and its performance in Sr^{2+} uptake is shown in **Figure 12**. The increase in K_d and uptake with time is very close to that of DMI-13-1, but the curve extends over a much longer time period.

Preparation of Sodium Titanium Silicate, sample DMI-11-1. We prepared a sample of sodium titanium silicate (CST) that showed a high selectivity for Sr^{2+} uptake. Reagants: 32.08 ml of $Ti(OC_3H_7)_4$ (Alfa Aesar, 97%, density = 0.971); 16.58g Silicic Acid (Fisher Chem., 99.7% SiO_2 as determined by TGA), 51ml, 10M NaOH solution. The SiO_2 was dissolved in 30ml of the sodium NaOH followed by addition of the $Ti(OC_3H_7)_4$ with continuous stirring. To this mixture was added the remainder of the sodium hydroxide, followed by 162 ml of ddi H_2O. This mixture was added to a teflon-lined pressure vessel and heated at 180°C for 3.5 days. The solid was recovered by filtration, washed with dilute sodium chloride solution to prevent hydrolysis and finally washed twice with a minimum of water. The ratio of Si to Ti in the reaction mix was 2.50:1 and the concentration of the diluted reaction solution was Ti, 0.435; Si, 1.12M; NaOH, 2.09M. An X-ray diffraction pattern of the solid phase is shown in **Figure 13**, where it is seen to be poorly crystalline. Weight loss to 500°C measured 20.5%. This is equivalent to a formula of $Na_{1.6}H_{0.4}Ti_2O_3SiO_4 \cdot 3.6H_2O$. The highly crystalline samples contain $2H_2O$ indicating a higher absorption of water in the semi-crystalline products.

Preparation of CST from TiCl₄. To 30ml of a freshly prepared 2M $TiCl_4$ solution ($TiCl_4$ Aldrich) was added 40ml of a 30 wt % H_2O_2 solution, 150ml of ddi and 40ml of NaOH (10M). The peroxide forms a soluble complex with Ti that does not precipitate in NaOH. Then 4.3g silicic acid (Aldrich, 99.9%) was dissolved in 200ml of 1M NaOH and added dropwise with stirring to the reaction mixture. The mix was transferred to a 1L teflon-lined pressure vessel and heated at 200°C for 10 days. This procedure leads to a highly crystalline product. Filtration and extensive water washing results in partial replacement of Na^+ by H^+ to yield a product, $Na_{1.6-1.7}H_{0.3-0.4}Ti_2O_3SiO_4 \cdot 1.8H_2O$.

Pharmacosiderites. Because the time for carrying out tests on our samples at S.R., before the expiration of our grant period, was short we did not have time to optimize the samples of pharmacosiderite to be submitted. We, therefore, merely duplicated syntheses we had carried out earlier that exhibited high K_d values for strontium. These are described in what follows.

Synthesis of pharmacosiderite, sample EAB-II-23. Reagents: fumed SiO_2 (Sigma, 99.8%); titanium tetraisopropoxide (Aldrich, 97%); KOH (Fisher, 5.055M). 20.02 g fumed SiO_2 (0.322 M) was added to 170 ml of ddi H_2O in a plastic beaker with stirring, followed by addition of 45.75 g (0.161 M) of the titanium isopropoxide. The resultant gel was stirred for 6 hours. The mol ratio of reactants Si:Ti:H_2O was 2:1:58.6. The gel was centrifuged and the supernatent liquid poured off. The gel was then washed twice by centrifugation and then transferred to a 500 ml plastic beaker using 115.2g ddi H_2O. To this gel was added 70.5g (57.8 ml) of the KOH solution with constant stirring. The mol ratio of reactants was Ti:Si:KOH:H_2O, 1:2:1.8:58.3. The mixture was then added to a 1L teflon-lined pressure vessel and heated at 200°C for 47 hours. The pressure vessel was quenched in cold water and when cooled, the solid was filtered, using 0.2µ FP membrane. It was washed with absolute ethanol and dried in an oven at 55°C. The X-ray diffraction pattern is shown in **Figure 14**. Yield was 28.3g (97.2%) based on the formula $K_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$.

Preparation of $Na_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$. A new preparation of $K_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$ was carried out as before, but at a level of 40% of the reagents used for EAB-23. The yield was 9.26g or 82% conversion to the sodium phase. Sodium tetraphenylborate, $NaB(C_6H_5)_4$, was utilized to substitute Na^+ for K^+. A mixed solution of 0.2M in $NaB(C_6H_5)_4$, Na-TPB, (Aldrich, 99.5%) 1.0M in NaCl and 0.01M in EDTA (Fisher Chem.) was prepared by adding 6.84g Na-TPB, 5.846g NaCl and 0.305g EDTA to 100ml ddi H_2O. To this mixture was added 3.526g of $K_3H(TIO)_4(SiO_4)_3 \cdot 4H_2O$ prepared previously. A yellow precipitate was observed to form. The mixture was shaken for one hour, then centrifuged and the supernatant decanted. The solid was then extracted with three 50ml portions of acetone to remove the K-TPB. The sodium phase was then treated with 40ml of 2M HNO_3 to remove the Na^+ followed by a second treatment with 30ml of 2M HNO_3. This treatment ensured the complete removal of K^+. Two grams of the proton phase was converted to the sodium phase by treatment with 15ml of 0.1M NaOH + 0.1M $NaNO_3$. The final pH was 6.7, indicating some protons may still be present. Therefore, a second treatment with 15ml of NaOH was carried out and the excess NaOH washed out with 15ml H_2O. This sample is TAMU DMI-25.

Test Results

Derived at the Savannah River Technology Center [12,13]. In addition to the samples described here, several other types of samples, as enumerated below were examined by WSRC.

1. Amorphous monosodium titanates; MST #33180, run at different time periods, MST 33470, MST #TNX.
2. SrTreat - A version of the monosodium titanate prepared by Fortnum Engineering in Finland; SrTreat #48, #49, #8.
3. Sodium nonatitanate (ST), two samples from Honeywell, ST-39287-5A and ST-39287-5B and two samples from Texas A&M University RC-4-23B and RC-4-64B.
4. Sodium titanium silicate, ideal formula $Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$. Two crystalline commercially available phases CST-IE-910 and CST-IE-911 were obtained from UOP and a semi-crystalline sample optimized for Sr^{2+} removal, TAMU DMI-11-1 from Texas A&M University.
5. Pharmacosiderites: TAMU EAB-II-23 is a potassium ion phase of composition $K_3H(TiO)_4(SiO_4)_3\cdot 4H_2O$ and DMI-25 a semicrystalline sample of composition $Na_3H(TiO)_4(SiO_4)_3\cdot 4H_2O$.

Sample performance. Sample performance is judged on the basis of two criteria, the Decontamination Factor (DF) or the distribution coefficient, K_d, which is an indication of removal capacity, and the kinetic factor, which is best revealed by graphs of total Sr^{2+} remaining in solution as a function of time. Data were obtained not only for uptake of strontium, but also of plutonium, uranium and neptunium. (see **Figures 15** and **16** for solution compositions.)

A. <u>Decontamination Factors, Table 10</u>. For Sr removal - The MST sample, labeled MST-33180, exhibited DF values of greater than 100 in a 24h time period in three of four different trials. Two other samples of MST performed less well than MST-33180. The variability of the MST samples may reflect differences in preparation or in post-preparation treatment, which could include sodium content, degree of hydration or aging.

SrTreat. Two samples of SrTreat #49 and #8 exhibited high DF values and one, #48, much lower DFs. Since this material is a form of monosodium titanate, the same comments apply as for the MST samples.

The behavior of the nonatitanate samples can be explained on the basis of the factors described in this study. Sample 64B gave a T2 X-ray diffraction pattern and contained no, or very little, excess Na_2CO_3. It performed extremely well for Sr^{2+} uptake. Sample 23B exhibited a T3 X-ray diffraction pattern, indicating a higher degree of crystallinity and an excess of Na, yet it performed better than many of the tested samples. The samples submitted by Honeywell were not as good, but we do not have X-ray patterns for comparison. However, sample 5B performed better than most other samples for Sr^{2+} uptake as shown in **Figure 15**.

A surprise is the evident failure of the CST samples to rank in the highest levels. The Texas A&M product was the best of the CST samples, but even it is not nearly as effective as the titanates. The pharmacosiderites produced interesting results. The K^+ phase was moderately effective in Sr uptake, but the sodium phase was much better. What is notable is that this potassives phase sample, DMI-1-25, had the highest DF for Pu uptake, 247. As detailed in the introduction, the K^+ pharmacosiderite is cubic with K^+ in the face centers (see **Figure 6**). Sodium ion being much smaller than K^+ would not be tightly held in the face centers. The positioning of Na^+ in the lattice is not known, but it is less strongly held than K^+. Another factor to consider is the fact that the sodium phase was somewhat less crystalline than the K^+ phase.

Actinide Removal. (a) *Plutonium.* TAMU sample DMI-25 exhibited, by far, the highest K_d and DF for Pu after 7d equilibration. However, the 24h values were quite low. SrTreat #8 showed the same type of behavior, a very low DF at the 24h point, but a much higher one after 7d. The other SrTreat samples exhibited among the lowest DF values. Three sodium nonatitanate samples exhibited relatively high DF values for Pu after 24h with considerable increase in DF over the 7d period. Only sample 23B did not conform to this behavior and yielded low DF values for Pu. This may stem from the increased crystallinity of this compound. For the monosodium titanate, only some trials with sample MST#33180 gave reasonable DF values, but generally lower than those for the nonatitanates. (b) *Uranium.* None of the sorbent exhibited respectable values of DF or Kd for uranium. This may stem from the fact that uranium is present in the waste simulants at a much higher level than the other actinides. Still, it should be noted that several thousand ppb of U were sorbed. Interestingly, the sodium pharmacosiderite did sorb more than two-thirds of the uranium [13]. The double precipitation method, suggested below, may reduce the U level even further. (c) *Neptunium.* None of the samples gave particularly high DF or K_d values. The sodium pharmacosiderite had the highest 7d DF at 20.9 and had the highest uptake after the 7d equilibration [13]. Relatively speaking, this value is quite good. Several other samples had values between 10 and 20 [three nonatitanates, one trial of MST#33180 and SrTreat#8].

Kinetics of Exchange

The rates of uptake of Sr^{2+} and the actinides in simulants approximating the composition of the S.R. wastes were carried out by WSRC [12,13]. Some of the results are reproduced in **Figures 15** and **16.**

Strontium Uptake. **Figure 15** is a summary of some of the results for Sr^{2+} uptake. At the 24h level of equilibration, three samples, ST-RC-4-64B, SrTreat #8 and ST-RC-4-23B, fell below the 1ppb level. At the 7 d (168h) point, the samples below 1ppb remaining in solution were in the order 64B > SrTreat #8 > 5B > 23B. All other samples were between 1 and 8 ppb. The nonatitanate 64B consistently outpaced the other samples and at the 2h equilibration point, had sorbed all but 1ppb of Sr^{2+}. It should be noted that five other samples were below the 10ppb level at the 2h point. Therefore, the major portion of time, 166h, is utilized to sorb 1-8 ppb. It is surprising that the CST samples did not perform well.

Actinides. (a) Plutonium - **Figure 16A** shows that the nonatitanates 64B and 5B achieved the highest Pu uptake, but that the fastest rate, up to the 24h equilibration time, was achieved by 5B. The MST 33180 sample was somewhat slower, and also exhibited a slightly lower capacity. In a subsequent additional test [13], in which sample 5B was not included, the potassium pharmacosiderite EAB-II-23 exhibited the fastest rate for 24h and achieved a level of uptake of close to 99%. The sodium pharmacosiderite was initially much slower, but eventually achieved the highest uptake, closely followed by SrTreat #8 and the K-pharmacosiderite and then 64B and MST. It is quite possible that the potassium pharmacosiderite exhibited initial fast kinetics by forming an insoluble potassium plutonium hydroxide with the K^+ on the surface of the sorbent. If this is the case, then a higher surface area sample should exhibit faster kinetics.

(b) *Uranium.* This element is present in much higher levels, 12,000-14,000 ppb than the other actinides. There is an initial rapid uptake of perhaps 4,000 ppb by MST 33180 and EAB-II-23 in less than an hour [Ref. 13, Figure 4.4.3]. However, the rate of uptake of 64B surpasses that of the MST sample, while the sodium pharmacosiderite, DMI-25, equals it at the 24h point. Sample 64B has taken up ~6,000 ppb, MST somewhat less and the sodium pharmacosiderite

(DMI-25) about 5,000 ppb. After 168h, TAMU DMI-25 has taken up slightly more than 10,000 ppb of U, sample 64B ~9,000 ppb and SrTreat #8, about 8,000 ppb followed by MST at ~7,000 ppb. In an earlier test [12, Figure 8], other nonatitanates 5A and 5B, as well as 64B, were shown to sorb ~9,000 ppb U after 168h equilibration.

(c) *Neptunium.* In an early test, MST 33180 outperformed two SrTreat samples #48, #49 and the CST 910, 911 samples [12, Figure 9]. Comparison of this MST sample with the nonatitanates is shown in **Figure 16B**. Two samples, ST-39287-5A and 5B exhibited rates equivalent to that of the MST, but ST-RC-64B was somewhat slower. However, at the 168h time, all three of the nonatitanate samples had achieved the same Np uptake as had the MST.

In the latest series of tests with ~600 ppb Np, which included many more samples [13, Figure 4.4.4], the fastest rates (to the first 24h) were exhibited by RC-4-23B, RC-4-64B and MST 33180. However, the order of loading at the highest equilibration time (168h) was the sodium pharmacosiderite TAMU-DMI-25 (580 ppb) followed by SrTreat #8 (555 ppb), TAMU-RC-4-64B (540 ppb), MST 33180 (520 ppb) and TAMU-RC-4-23B (500 ppb). The fact that the sodium pharmacosiderite sample DMI-25 achieved the highest uptake of U, Pu and Np over the 7d equilibration in competition with the MST and nonatitanate sample indicates that further work with this material is desirable.

Conclusions

1. The results indicate that a combination of monosodium titanate such as MST-33180 and a nonatitanate such as 5B and/or 64B would effectively achieve acceptable levels of radioactive species containment. Standardized products of both types of exchangers need to be developed so as to avoid variability in performance.

2. Sodium titanium pharmacosiderite should also receive additional study as it shows promise of being effective in strontium removal as well as high levels of actinide uptake.
3. Because the bulk of the radioactive species are taken up within a 2-hour time period, it would appear prudent to develop a process utilizing this behavior. A possible strategy would be to use smaller batches of waste, filter or centrifuge after 2-3 hours, and add a second portion of sorbent for perhaps a 3-4 hour hold and filter. The amount of sorbent used can be adjusted to be no more than would be used for a single in-tank 7d procedure. The time saved by taking advantage of kinetic factors would allow the processing of far more waste than achievable in longer hold times.
4. The nonatitanate has been scaled up to the 5kg level by Honeywell and could be made available commercially.
5. CST performed poorly, as did most of the SrTreat samples. However, the latest SrTreat sample #8 did perform well. Fortum Oy should be able to determine why this sample performed well, whereas the earlier samples did not. If consistency in preparation is achieved, further study is warranted.
6. In summary, these screening tests indicate that sodium nonatitanates and the pharmacosiderites exhibit as good, or better a performance than MST. Therefore, somewhat larger scale tests are in order with these materials and perhaps including SrTreat and sodium pharmacosiderite.

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Table 1. Simulant profiles for N-Springs, NCAW, DSSF-7 and 101SY-Cs5.

Species	**N-Springs**	**NCAW**	**DSSF-7**	**101SY-Cs5**
	Concentration (M)			
Al	0	0.43	0.72	0.42
Ba	1.12E-07	0	0	0
Ca	7.27E-07	0	0	4.20E-03
Cs (inactive)	0	5.00E-04	7.0E-5	4.19E-05
Fe	0	0	0	1.96E-04
K	0	0.12	0.945	0.034
Mg	2.16E-04	0	0	0
Mo	0	0	0	4.20E-04
Na	2.61E-04	4.99	7.0	5.1
Ni	0	0	0	2.50E-04
Rb	0	5.00E-05	0	4.20E-06
Sr (inactive)	1.48E-06	0		2.90E-07
Zn	0	0	0	5.00E-04
carbonate	1.25E-04	0.23	0.147	0.038
chloride	4.51E-05	0	0.102	0
fluoride	1.05E-05	0.09	0	0.092
hydroxide	n/a	3.4	4.634	3.78
hydroxide (free)	1.66E-03	1.68	1.75	2.11
nitrate	1.94E-04	1.67	3.52	1.29
nitrite	0	0.43	1.512	1.09
sulfate	2.16E-04	0.15	0.008	4.75E-03
phosphate	0	0.025	0.014	0.02
citric acid	0	0	0	5.00E-03
tetrasodium EDTA	0	0	0	5.00E-03
N-(2-hydroxyethyl) EDTA	0	0	0	3.75E-3
iminodiacetic acid	0	0	0	0.031
nitriloacetate	0	0	0	2.50E-04
sodium gluconate	0	0	0	0.013
Theoretical pH	11.2	14.5	14.56	14.4

Table 2. ^{89}Sr Distribution Coefficients (Kd) and Percent Removal for the N-Springs.*

Sample	V:m = 200:1		V:m = 1000:1	
	K_d(ml/g)	% Sr Removed	K_d (ml/g)	% Sr Removed
Chabazite	30,650	99.35	10,400	91.04
Clinoptilolite	27,190	99.34	4,400	81.71
HTiSi	7,900	97.54	28,800	99.89
KTSsol	57,610	99.69	121,500	99.20
NaTi	25,300	99.24	322,400	99.69
NaTS	>326,000	>99.94	863,400	99.89

* As in Table 1 traced with ^{89}Sr for Tables 2-5.

Table 3. ^{89}Sr Distribution Coefficients (Kd) and Percent Removal for NCAW.

Sample	V:m = 200:1		V:m = 1000:1	
	K_d(ml/g)	% Sr Removed	K_d (ml/g)	% Sr Removed
NaTS	269,500	99.93	225,800	99.56
NaTi	235,100	99.92	39,600	97.52
HTiSi	44,800	99.55	3,700	78.09
KTSsol	20,200	98.80	5,000	83.85

Table 4. ^{89}Sr Distribution Coefficients (Kd) and Percent Removal for DSSF-7.

Sample	V:m = 200:1		V:m = 1000:1	
	K_d(ml/g)	% Sr Removed	K_d (ml/g)	% Sr Removed
NaTS	111,000	99.82	134,700	99.29
NaTi	54,800	99.64	38,400	97.48
HTiSi	22,800	99.14	7,000	87.63
KTSsol	6,400	97.00	4,800	82.38

Table 5. ^{89}Sr Distribution Coefficients (Kd) and Percent Removal for 101SY-Cs5.

Sample	V:m = 200:1	
	K_d(ml/g)	% Sr Removed
NaTS	231	54.66
NaTi	295	61.12
HTiSi	164	45.60
KTSsol	31	13.20

Table 6. Reaction conditions for sodium titanate preparation.

Sample No.	CONC Ti Soln(M)	CONC NaOH Soln(M)	Ti:Na	Reflux Time (R)	Temp. °C	X-ray Type
11A	1.0	4.0	1:4	3	200(20h)	T1;T2
11B	1.0	2.0	1:2	3	200(20h)	T1
13B	0.9	9.0	1:10	3.2	190(21h)	T3
23B	0.92	9.7	1:10.5	0	190(22h)	T3
48A	0.63	3.1	1:5	2	170(22.5h)	T1
48B	0.70	3.3	1:4.7	0	170(23h)	T1
67A	0.43	0.87	1:2	3.5	145(4d)	Amorph.
67B	0.75	5.1	1:6.8	1	200(4d)	T2
62A	1.6	2.5	1:1.56	3	190(20h)	T1
64A	0.65	4.5	1:69	3.2	193(19.7h)	T2
64B	0.58	5.1	1:8.9	3.2	193(19.7h)	T2
71A	0.69	1.4	1:2.1	3	200(7d)	T1
90A	0.44	8.35	1:19.4	16.5	200(1d)	T3
92A	1.1	1.5	1:1.37	3.25	200(20h)	T1

Table 7. Chemical analysis of the three types of titanates formed from hydrothermal treatment.

Sample	wt % Na	wt % Ti	Ti:Na mole ratio
92A(T1)	12.47	43.23	1:0.623
67B(T2)	12.04	40.36	1:0.622
64B(T2)	9.55	39.70	1:0.501
23B(T3)	16.16	37.82	1:0.890
92AW2(T1)	11.37	50.08	1:0.473
67BW(T2)	9.33	47.20	1:0.412
23BW2(T3)	12.26	48.40	1:0.528

Table 8. Sr^{2+} K_d's for titanate samples in the presence of 5 M $NaNO_3$, 1 M NaOH, and 91-95 ppm Sr^{2+} (solution to sample ratio was 200:1).

Sample No.	Structure Type	Sr K_D (ml/g)
11A	T1, T2	27,300
11B	T1	7,310
92A	T1	4,350
67B	T2	58,700
62A*	T1	16,100
51D*	T1	4,600
48A	T1	≥131,000
48B	T1	29,100
64A	T2	229,000
64B	T2	≥131,000
23BW	T3	≥131,000

*The solution to exchanger ratio was 250:1.

Table 9. K_d **values for sodium titanosilicate as a function of time. V/m = 250, pH = 10**

Sample No.	Temp. °C	Time (h)	X-ray	$K_d(\frac{ml}{g})^b$	$K_d(\frac{ml}{g})^c$
DMI-6-1	180	1	Semi-cryst, d=9.78Å See figure	49,700	1540
DMI-6-2	180	10	Semi-cryst, d=9.78Å See figure	27,700	3114
DMI-6-3	180	24	Like X-ray Figure 9	48,500	4670
DMI-6-4	180	72	Almost crystalline	50,800	7785
DMI-6-5	180	168	crystalline[a]	51,800	10,840
DMI-2a*	190	120	crystalline[a]	51,900	9440
DMI-2b	190	120	crystalline[a]	54,500	10,100

* Using $TiCl_4$ as source of Ti, otherwise similar to DMI-2b.

a. Similar to Figure 7a.

b. Solution contained 10^{-4}M $NaNO_3$ and 10^{-5}M $Ca(NO_3)_2$ spiked with ^{89}Sr.

c. Solution contained 0.04M $NaNO_3$, 0.025M KNO_3, 7.5 x 10^{-3}M $Ca(NO_3)_2$.

Table 10

Decontamination Factor

Sorbent	Sr 24 h	Sr 7d	Pu 24 h	Pu 7d	U 24 h	U 7d	Np 24 h	Np 7d
MST #33180	1.51E+02	3.05E+02	1.13E+01	3.23E+01	1.14E+00	1.36E+00	3.47E+00	8.08E+00
SrTreat #48	4.20E+00	4.08E+01	1.40E+00	1.81E+00	9.33E-01	9.97E-01	9.37E-01	1.33E+00
SrTreat #49	1.07E+02	5.91E+02	1.74E+00	2.90E+00	9.31E-01	1.02E+00	1.06E+00	1.73E+00
CST IE-910	1.06E+01	1.59E+01	1.28E+00	1.16E+00	9.58E-01	9.56E-01	1.00E+00	1.16E+00
CST IE-911	5.81E+00	1.97E+01	1.95E+00	3.39E+00	1.00E+00	1.12E+00	1.13E+00	2.00E+00
MST #33180	3.23E+01	4.31E+01	4.93E+00	1.44E+01	1.12E+00	1.22E+00	1.98E+00	2.47E+00
SrTreat #8	8.74E+01	1.96E+02	2.01E+00	8.20E+01	1.20E+00	2.26E+00	1.43E+00	1.13E+01
TAMU DM1-11-1	2.61E+01	4.76E+01	1.30E+00	1.82E+00	1.17E+00	1.24E+00	1.23E+00	1.45E+00
MST #33180	1.58E+02	1.90E+02	1.03E+01	2.96E+01	2.08E+00	1.36E+00	5.56E+00	1.34E+01
ST-RC-4-23B	1.09E+02	9.91E+01	3.54E+00	9.11E+00	1.50E+00	1.52E+00	3.47E+00	7.04E+00
ST-RC-4-64B	2.91E+02	4.73E+02	7.69E+00	5.69E+01	1.80E+00	2.71E+00	2.81E+00	1.24E+01
ST-39287-5A	7.60E+01	1.78E+02	1.09E+01	2.56E+01	2.92E+00	2.43E+00	4.19E+00	1.31E+01
ST-39287-5B	2.55E+01	6.07E+01	3.08E+01	5.81E+01	2.04E+00	2.23E+00	5.44E+00	1.72E+01
MST #33180	1.07E+02	1.41E+02	9.21E+00	2.11E+01	1.40E+00	1.74E+00	2.02E+00	6.42E+00
MST #33470	3.62E+00	2.81E+01	2.36E+00	1.29E+01	1.14E+00	1.34E+00	1.37E+00	3.68E+00
MST #TNX	1.14E+01	3.17E+01	3.87E+00	1.37E+01	1.15E+00	1.18E+00	1.50E+00	3.02E+00
TAMU DM1-25	8.73E+01	1.53E+02	4.21E+00	2.47E+02	1.27E+00	3.20E+00	1.61E+00	2.09E+01
TAMU EABII-23	2.91E+01	7.73E+01	1.69E+00	1.91E+01	1.13E+00	1.34E+00	1.27E+00	3.01E+00

Distribution Constant (mL/g)

Sorbent	Sr 24 h	Sr 7d	Pu 24 h	Pu 7d	U 24 h	U 7d	Np 24 h	Np 7d
MST #33180	3.75E+05	7.61E+05	2.58E+04	7.85E+04	3.48E+02	9.06E+02	6.18E+03	1.77E+04
SrTreat #48	6.97E+03	8.67E+04	8.80E+02	1.77E+03				7.19E+02
SrTreat #49	2.22E+05	1.23E+06	1.54E+03	3.97E+03		4.52E+01	1.34E+02	1.52E+03
CST IE-910	8.82E+03	1.37E+04	2.57E+02	1.46E+02			4.46E+00	1.45E+02
CST IE-911	4.34E+03	1.68E+04	8.60E+02	2.15E+03		1.08E+02	1.15E+02	9.00E+02
MST #33180	7.83E+04	1.05E+05	9.85E+03	3.36E+04	3.08E+02	5.62E+02	2.45E+03	3.69E+03
SrTreat #8	3.52E+05	7.95E+05	4.10E+03	3.30E+05	8.05E+02	5.14E+03	1.76E+03	4.20E+04
TAMU DM1-11-1	5.42E+04	1.01E+05	6.47E+02	1.76E+03	3.73E+02	5.11E+02	4.97E+02	9.82E+02
MST #33180	3.92E+05	4.72E+05	2.33E+04	7.14E+04	2.71E+03	8.88E+02	1.14E+04	3.11E+04
ST-RC-4-23B	2.23E+05	2.03E+05	5.25E+03	1.68E+04	1.03E+03	1.08E+03	5.11E+03	1.25E+04
ST-RC-4-64B	5.53E+05	9.01E+05	1.28E+04	1.07E+05	1.53E+03	3.27E+03	3.46E+03	2.18E+04
ST-39287-5A	9.56E+04	2.26E+05	1.26E+04	3.13E+04	2.45E+03	1.83E+03	4.06E+03	1.55E+04
ST-39287-5B	4.70E+04	1.15E+05	5.72E+04	1.10E+05	1.99E+03	2.36E+03	8.52E+03	3.12E+04
MST #33180	2.65E+05	3.51E+05	2.06E+04	5.04E+04	1.01E+03	1.86E+03	2.56E+03	1.36E+04
MST #33470	6.57E+03	6.80E+04	3.41E+03	2.98E+04	3.47E+02	8.52E+02	9.38E+02	6.71E+03
MST #TNX	2.59E+04	7.63E+04	7.14E+03	3.16E+04	3.64E+02	4.51E+02	1.25E+03	5.01E+03
TAMU DM1-25	9.13E+04	1.60E+05	3.40E+03	1.60E+05	2.88E+02	2.33E+03	6.45E+02	2.11E+04
TAMU EABII-23	3.37E+04	9.14E+04	8.22E+02	2.16E+04	1.56E+02	4.13E+02	3.21E+02	2.41E+03

Appendix I

Table AI. Chemical Composition of Salt Solution Simulant

Component	Concentration
$NaNO_3$	2.60 M
NaOH	1.33 M
Na_2SO_4	0.521 M
$NaAl(OH)_4$	0.429 M
$NaNO_2$	0.134 M
Na_2CO_3	0.0260 M
Total Na	5.6 M
Total Sr	86.7 ± 3.77 μg/L
Total Pu	190 ± 5.83 μg/L
Total U	9040 ± 986 μg/L
^{237}Np	416 ± 20.7 μg/L

Strontium and actinide removal testing utilized the same experimental method previously reported using the MST sorbent. * We added approximately 0.030 grams of the ST to 125 mL of the salt solution equilibrated at 25°C. This quantity of ST provides the equivalent titanium content obtained upon addition of the current baseline material, MST, at 0.4 g/L. Researchers pulled samples from the test bottles after 5, 24, 48, 144, 170 and 244 hours of contact at 25°C.

*D.T. Hobbs, M.S. Blume and H.L. Thacker, "Phase V Simulant Testing of Monosodium Titanate Adsorption Kinetics" Report WSRC-TR-2000-00142, Rev. 0, May 24, 2000.

Figure Captions

Figure 1. Cubane type $(TiO)_4$ portion of sodium titanium silicate, $Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$ (CST). The oxygen atoms in black bond to Si, the lined oxygens bond to 3Ti and the stippled oxygens are oxo-groups that connect the cubane groups in the c-axis direction.

Figure 2. Representation of CST looking down the c-axis. The cubane groups are at the corners and the tunnel is parallel to the c-axis direction. Sodium ions (black) and water molecules occupy the tunnel.

Figure 3. Ball and stick representation of CST structure in the ac (or bc) plane. Note the sodium ions held within the framework in addition to those in the tunnel. The structure is best visualized by holding **Figure 2** horizontally and **Figure 3** vertically.

Figure 4. Ball and stick representation of Cs^+ exchanged CST showing the position of the Cs (black circle) in the tunnel center.

Figure 5. Uptake of alkali metal cations as a function of pH. The low uptake of Cs^+ results from its size. Cs^+ uptake is 25% of the total exchange capacity and these ions occupy only half the tunnel sites and none of the framework sites.

Figure 6. Ball and stick representation of $K_3H(TiO)_4(SiO_4)_3\cdot 4H_2O$. The corners of each unit cell have $(TiO)_4$ cubane-like groups and the K^+ are in the face centers within the tunnels. Because the lattice is cubic, there are three intersecting tunnels.

Figure 7. Inorganic ion exchangers examined for removal of Sr^{2+} from nuclear waste solutions. The exchangers are identified on the figure.

Figure 8. Representative X-ray powder patterns of sodium nanotitanates. The structure types are indicated to the right of the X-ray patterns.

Figure 9. X-ray powder patterns of solids obtained during examination of heating time in preparation of the CST, $Na_2Ti_2O_3SiO_4\cdot 2H_2O$, (A) Unknown precursor phase formed after one

hour at 200°C, and (B) After ten hours heating a mixture of the precursor phase and CST is obtained as shown by the narrow peak at 7.89Å.

Figure 10. X-ray powder pattern of $NaTiOSiO_4$, a non-ion exchange phase obtained at high base concentrations in the synthesis of CST.

Figure 11. Kinetic curves for strontium exchange from a simulant for a highly crystalline CST sample DM1-13-1, and a poorly crystalline sample DM1-13-2.

Figure 12. Kinetics of Sr^{2+} uptake by a poorly crystalline CST sample DM1-11-1 submitted for testing at WSRC.

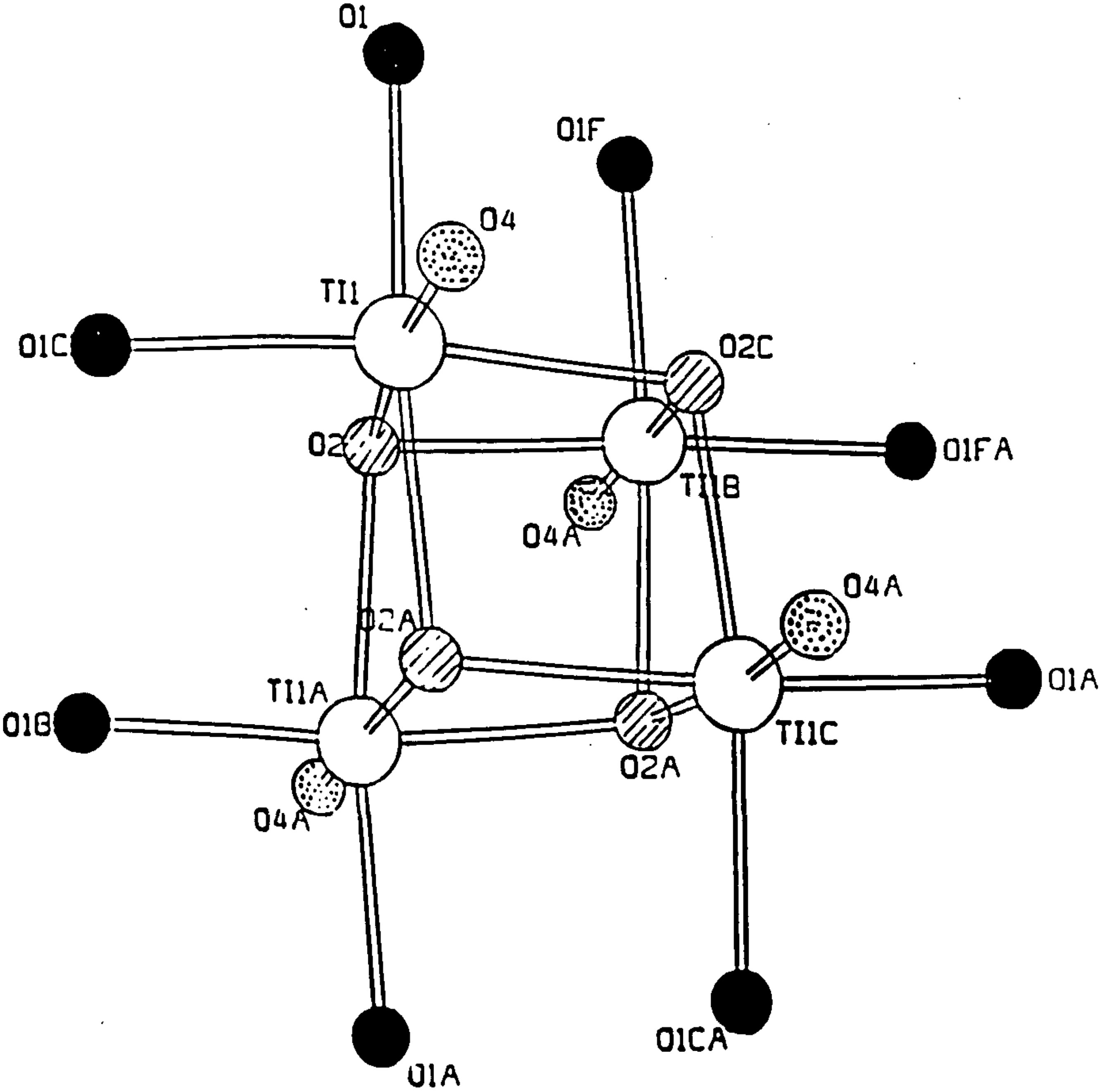
Figure 13. X-ray Diffraction powder pattern of the semi-crystalline CST sample DM1-11-1.

Figure 14. X-ray Diffraction pattern of a potassium titanium pharmacosiderite, of intermediate crystallinity, $K_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$.

Figure 15. Kinetics of exchange of Sr^{2+} at WSRC for several inorganic ion exchangers in a simulant waste solution developed to duplicate Savannah River waste.

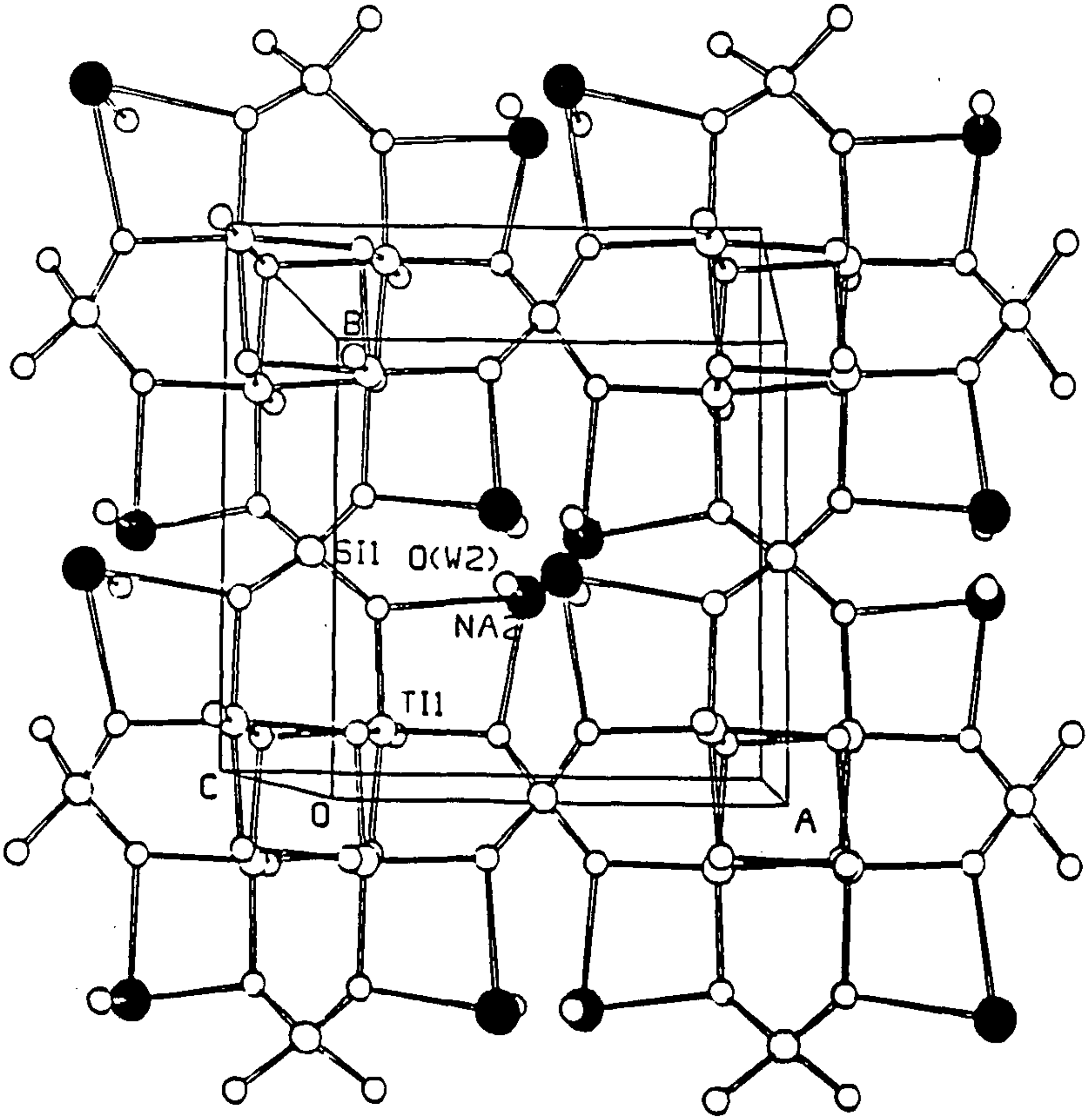
Figure 16. Kinetic measurements for (A) plutonium uptake and (B) Neptunium uptake as a function of time for several sodium nonatitanates in SR waste simulant. Work performed at WSRC.

Figure 1



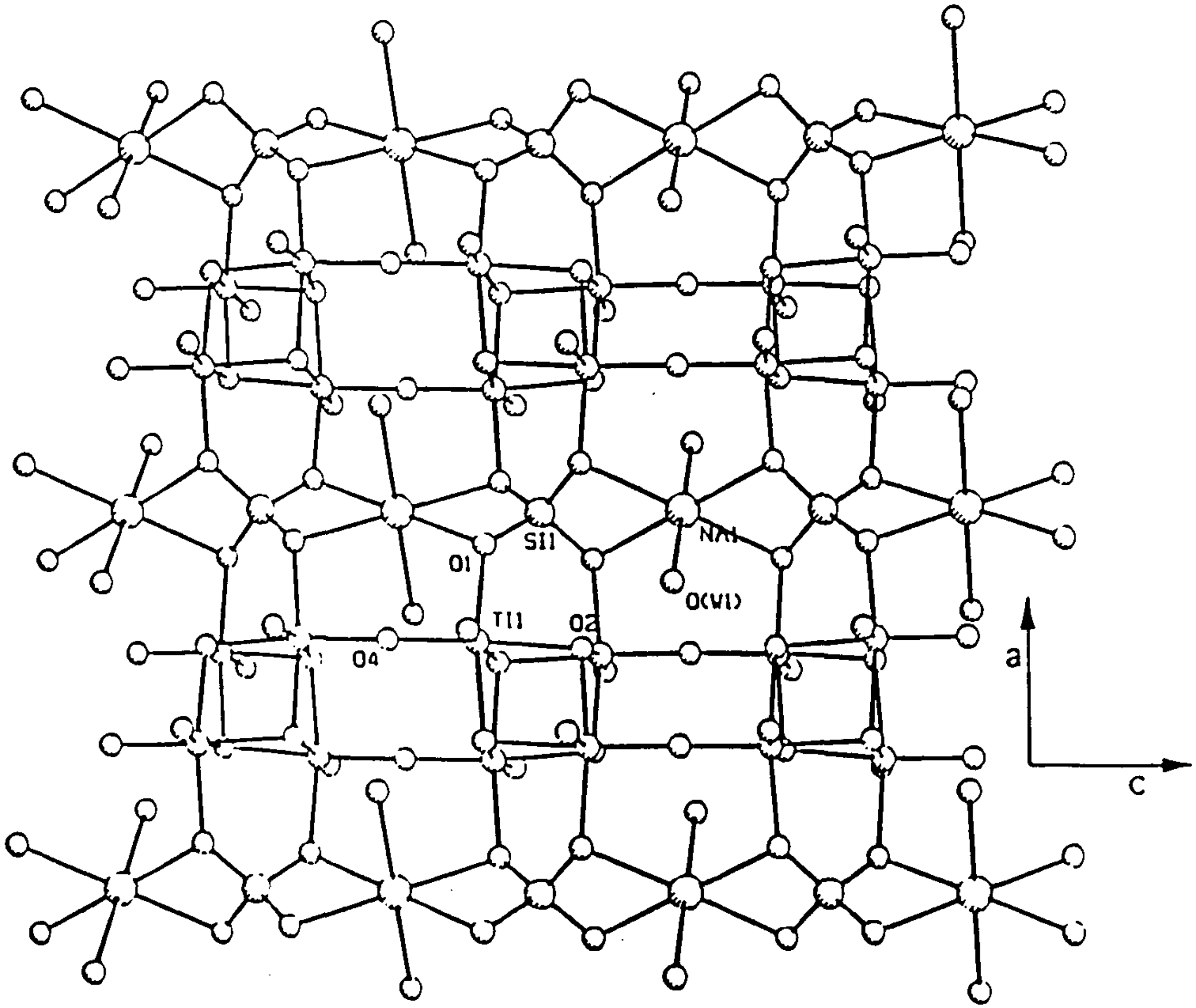
Cubane type $(TiO)_4$ portion of sodium titanium silicate, $Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$ (CST). The oxygen atoms in black bond to Si, the lined oxygens bond to 3Ti and the stippled oxygens are oxo-groups that connect the cubane groups in the c-axis direction.

Figure 2



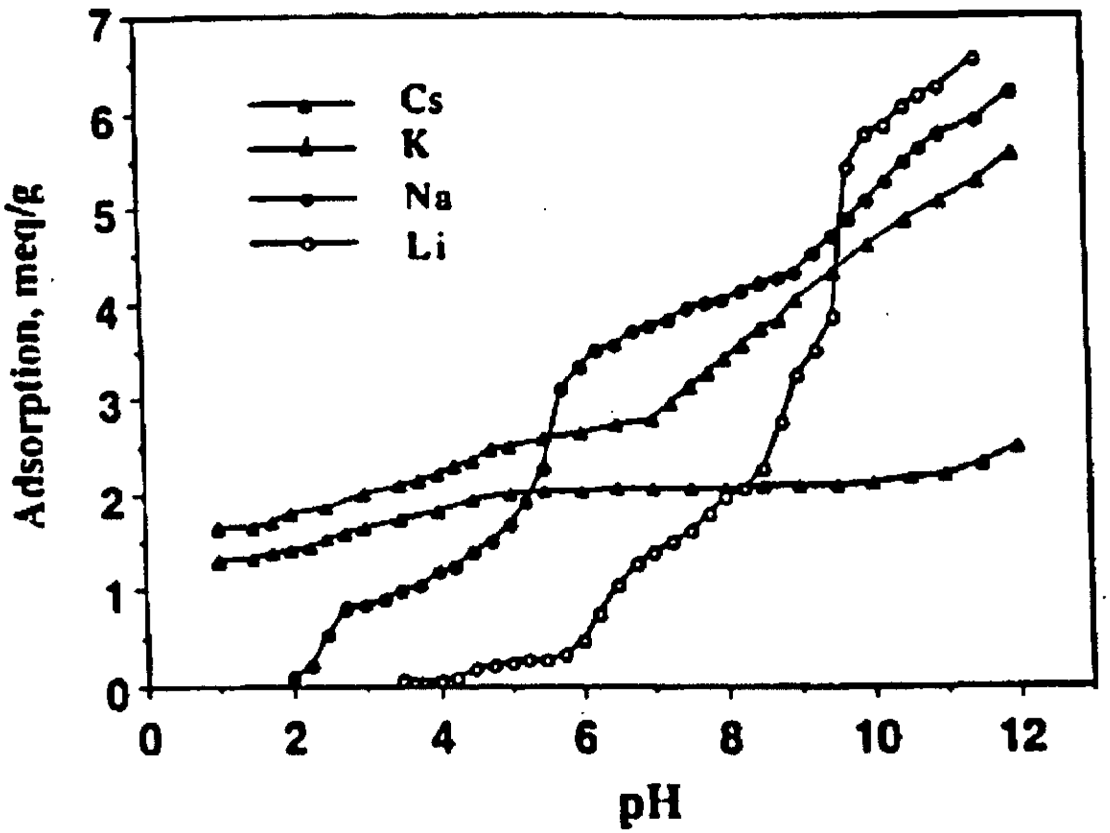
Representation of CST looking down the c-axis. The cubane groups are at the corners and the tunnel is parallel to the c-axis direction. Sodium ions (black) and water molecules occupy the tunnel.

Figure 3



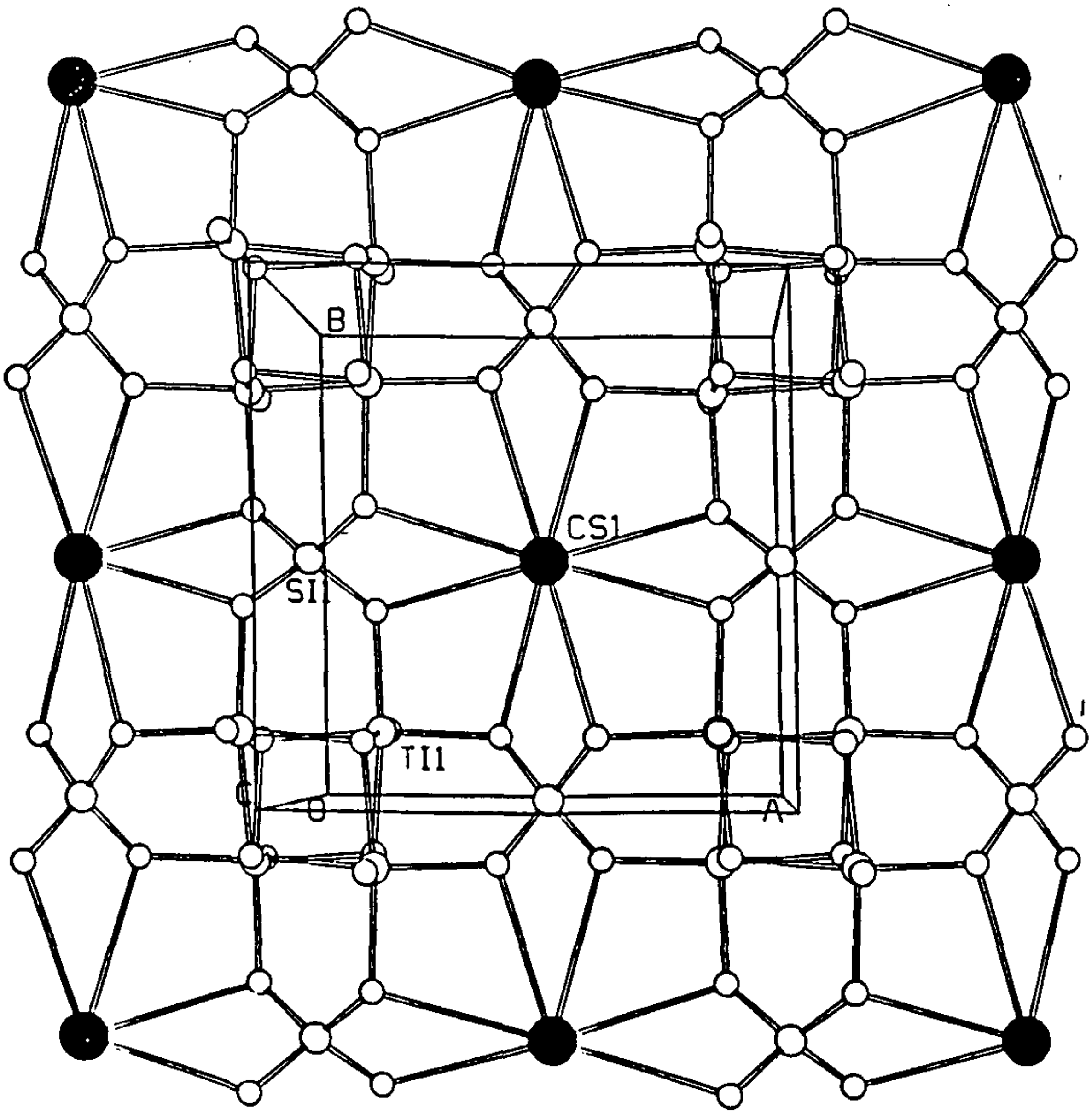
Ball and stick representation of CST structure in the ac (or bc) plane. Note the sodium ions held within the framework in addition to those in the tunnel. The structure is best visualized by holding **Figure 2** horizontally and **Figure 3** vertically.

Figure 4



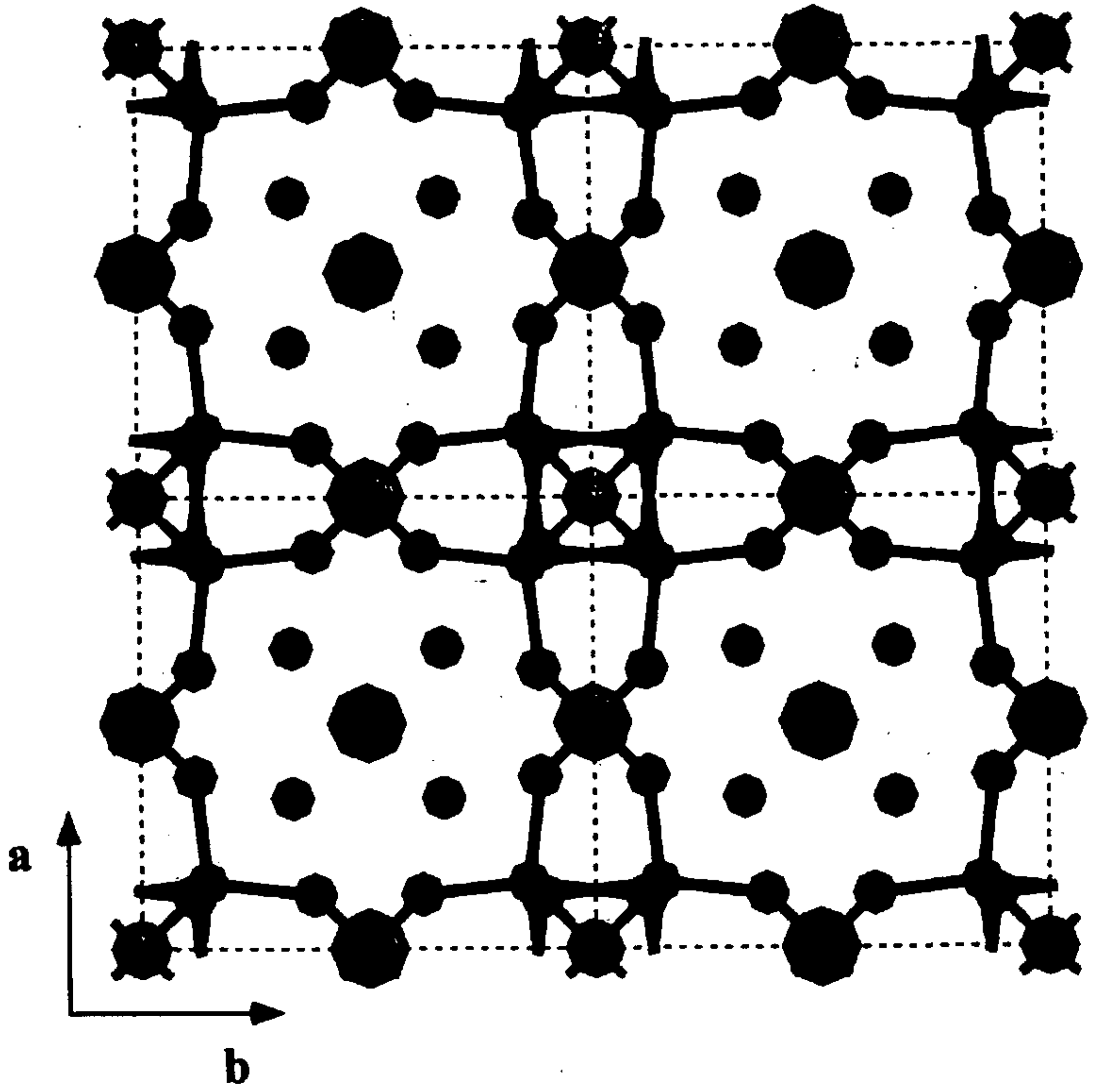
Uptake of alkali metal cations as a function of pH. The low uptake of Cs^+ results from its size. Cs^+ uptake is 25% of the total exchange capacity and these ions occupy only half the tunnel sites and none of the framework sites.

Figure 5



Ball and stick representation of Cs$^+$ exchanged CST showing the position of the Cs (black circle) in the tunnel center.

Figure 6



Ball and stick representation of $K_3H(TiO)_4(SiO_4)_3\ 4H_2O$. The corners of each unit cell have $(TiO)_4$ cubane-like groups and the K^+ are in the face centers within the tunnels. Because the lattice is cubic, there are three intersecting tunnels.

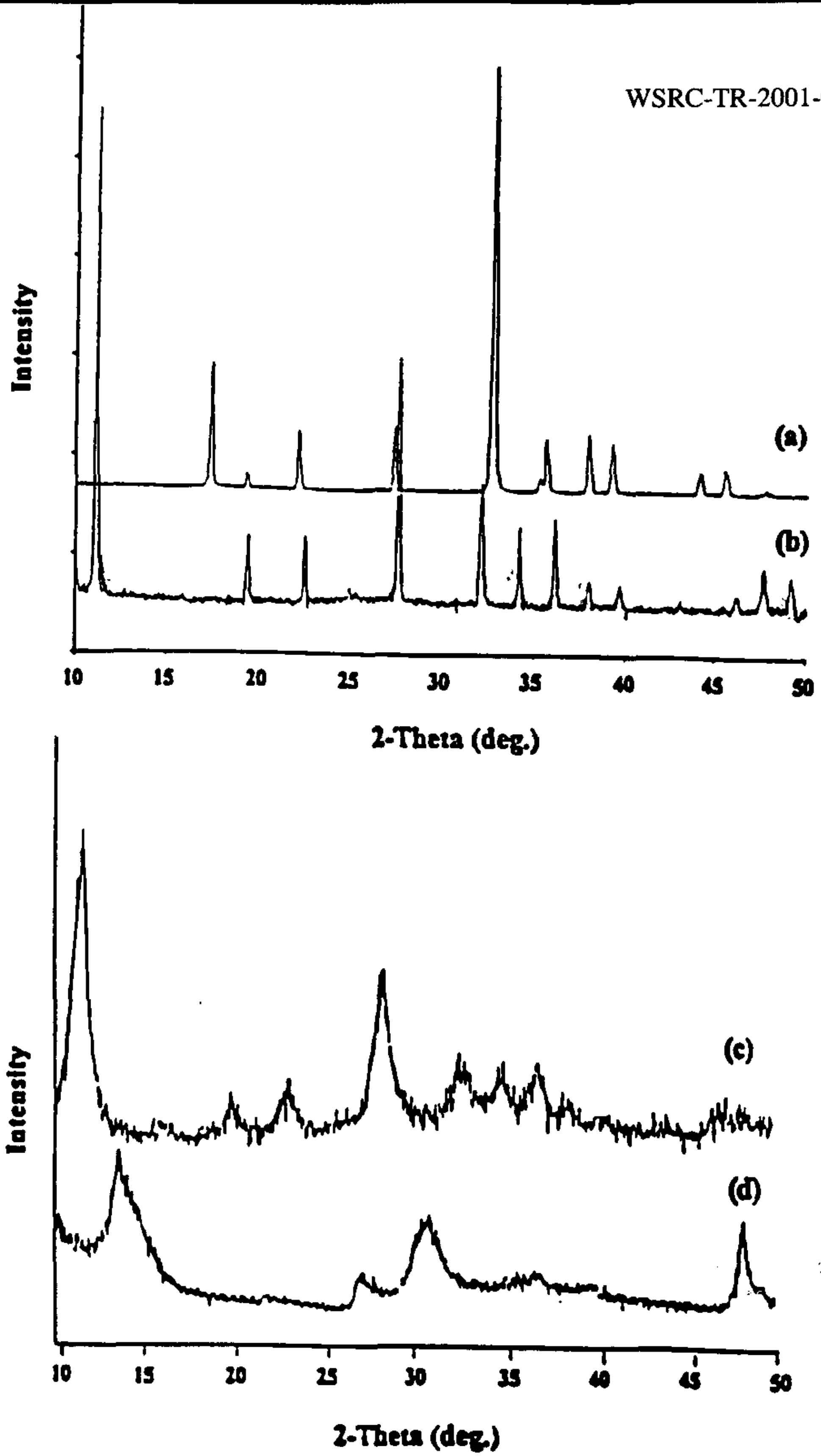


Figure 7

Inorganic ion exchangers examined for removal of Sr^{2+} from nuclear waste solutions. The exchangers are identified on the figure.

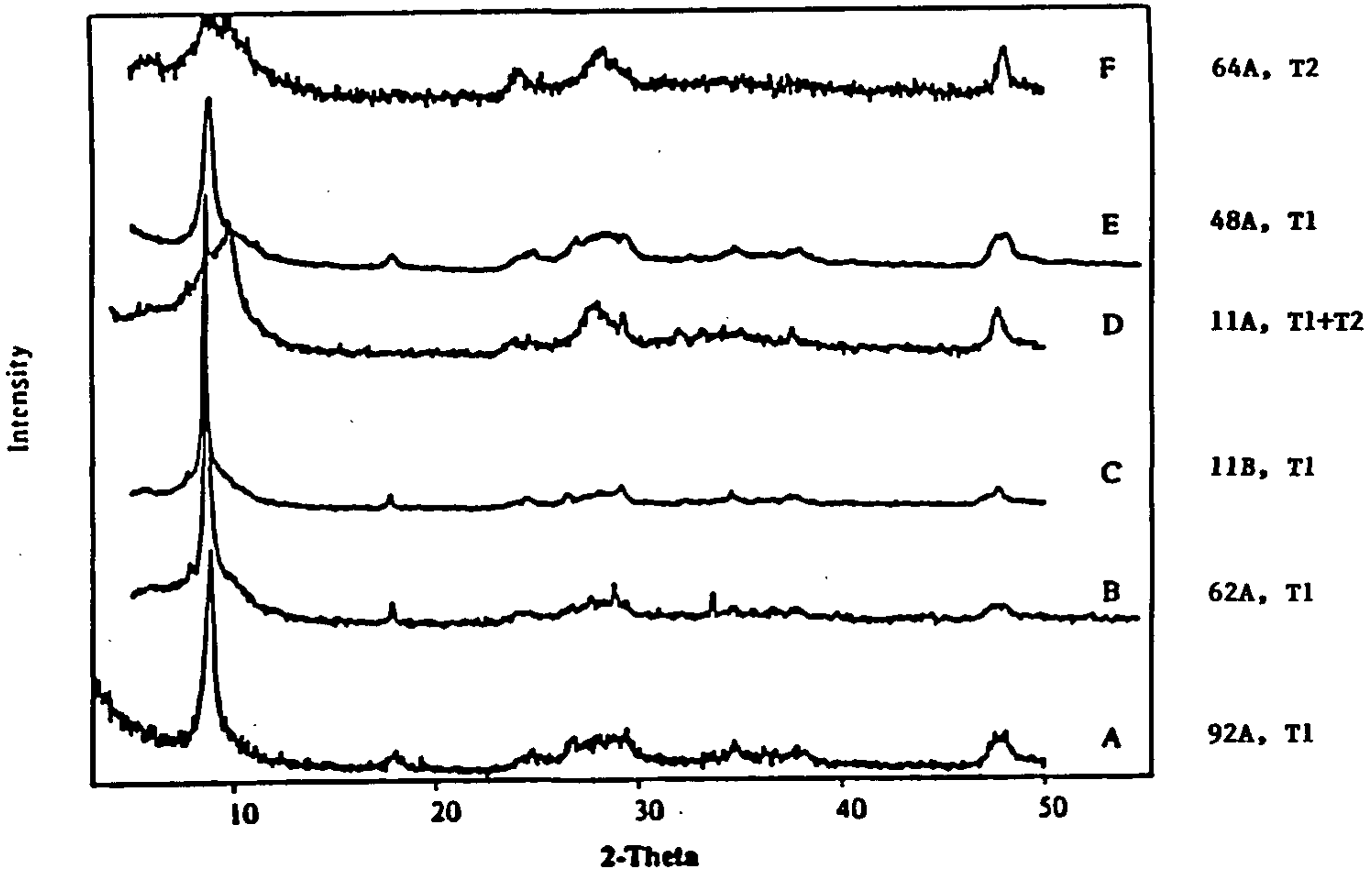


Figure 8a

Representative X-ray powder patterns of sodium nanotitanates. The structure types are indicated to the right of the X-ray patterns.

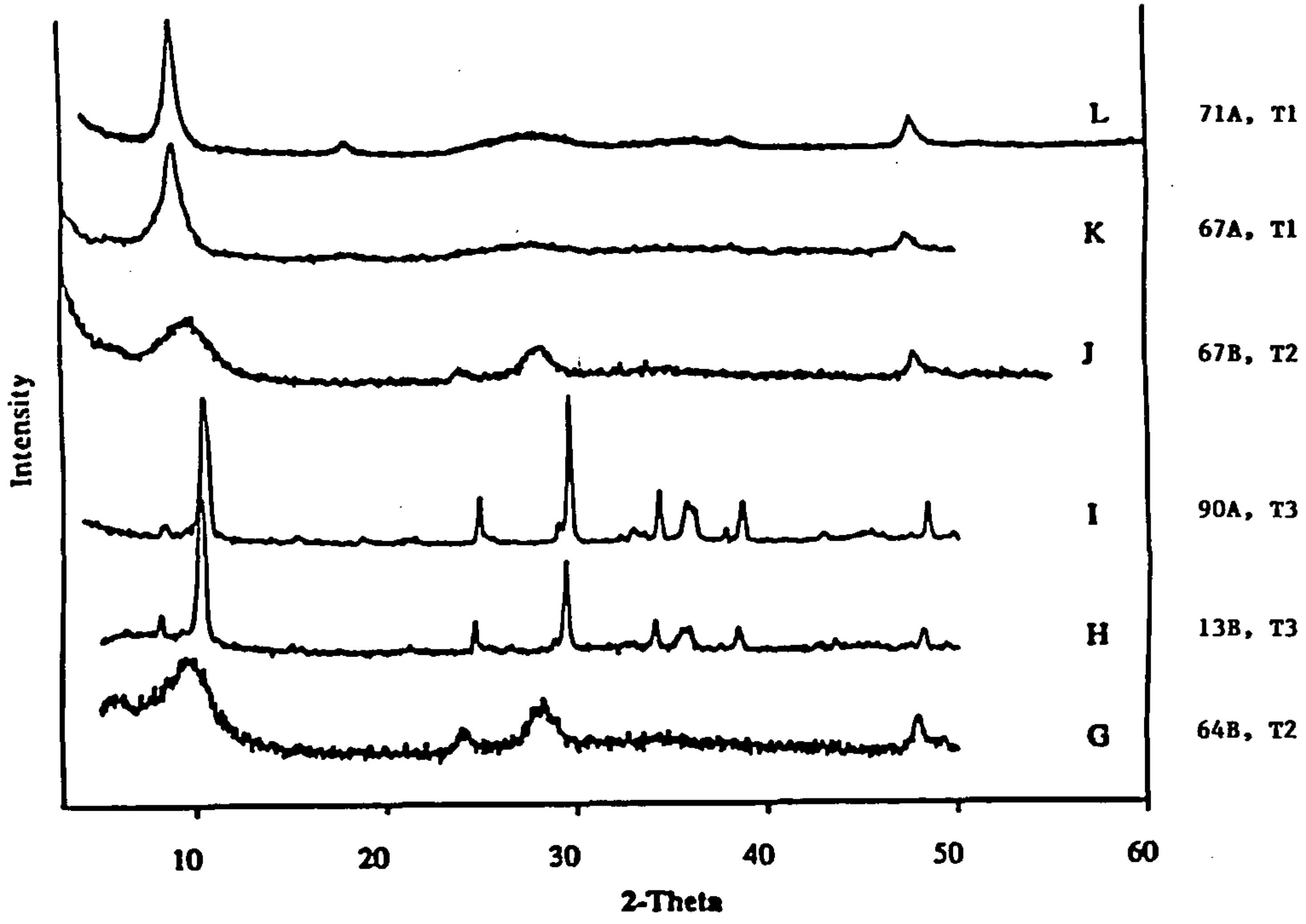
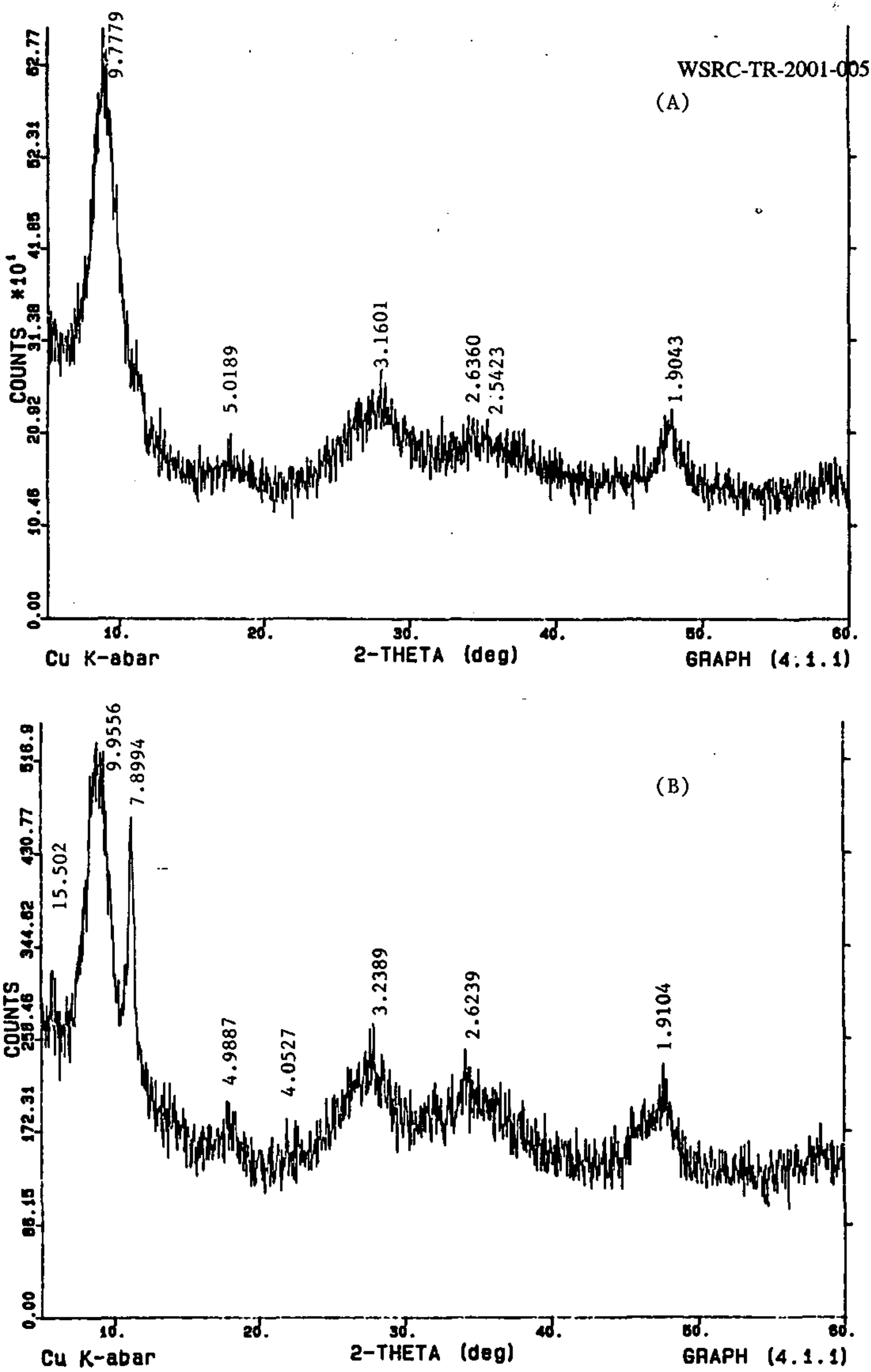


Figure 8b

Representative X-ray powder patterns of sodium nanotitanates. The structure types are indicated to the right of the X-ray patterns.



X-ray powder patterns of solids obtained during examination of heating time in preparation of the CST, $Na_2Ti_2O_3SiO_4\cdot 2H_2O$; (A) Unknown precursor phase formed after one hour at 200°C, and (B) After ten hours heating a mixture of the precursor phase and CST is obtained as shown by the narrow peak at 7.89Å.

Figure 9

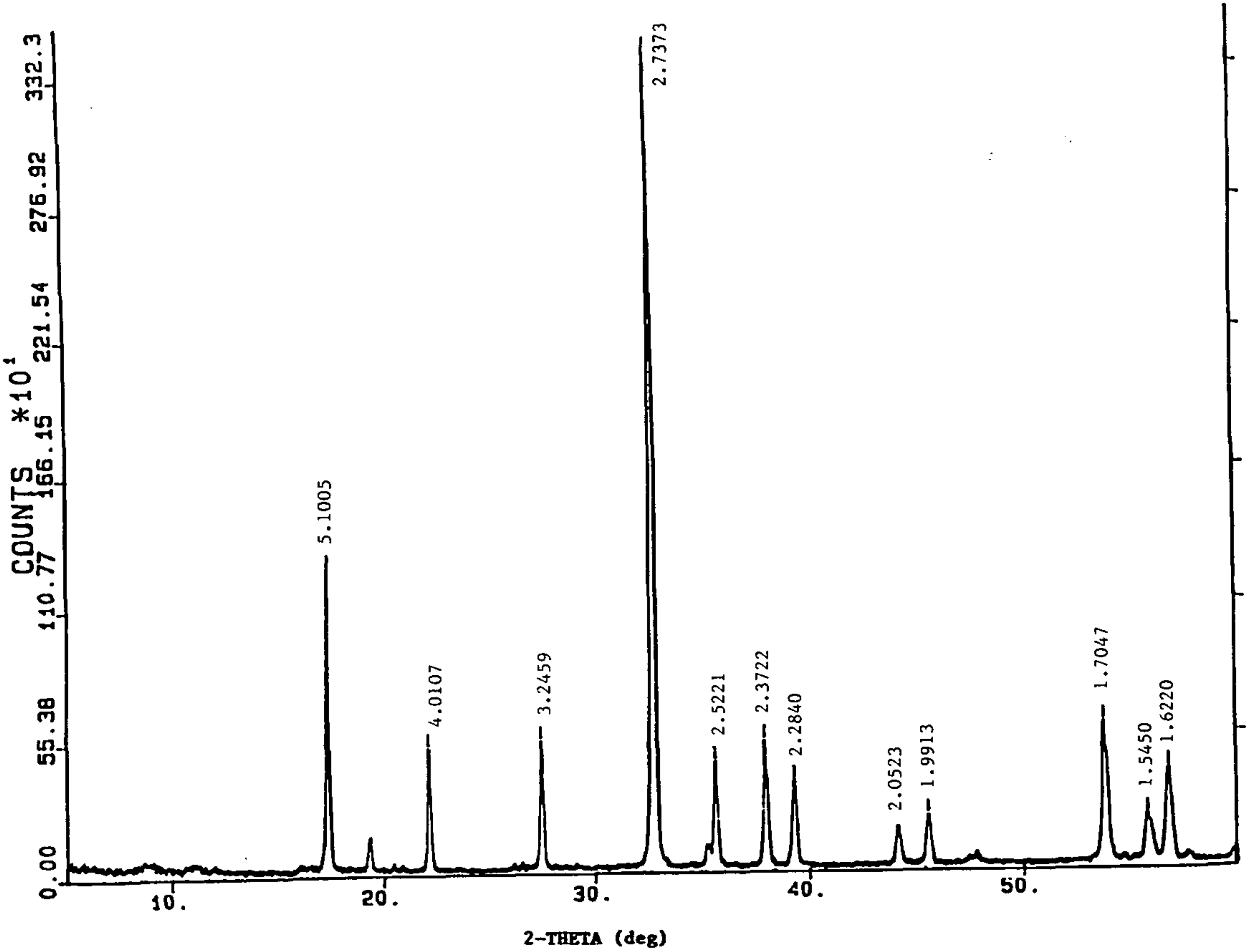
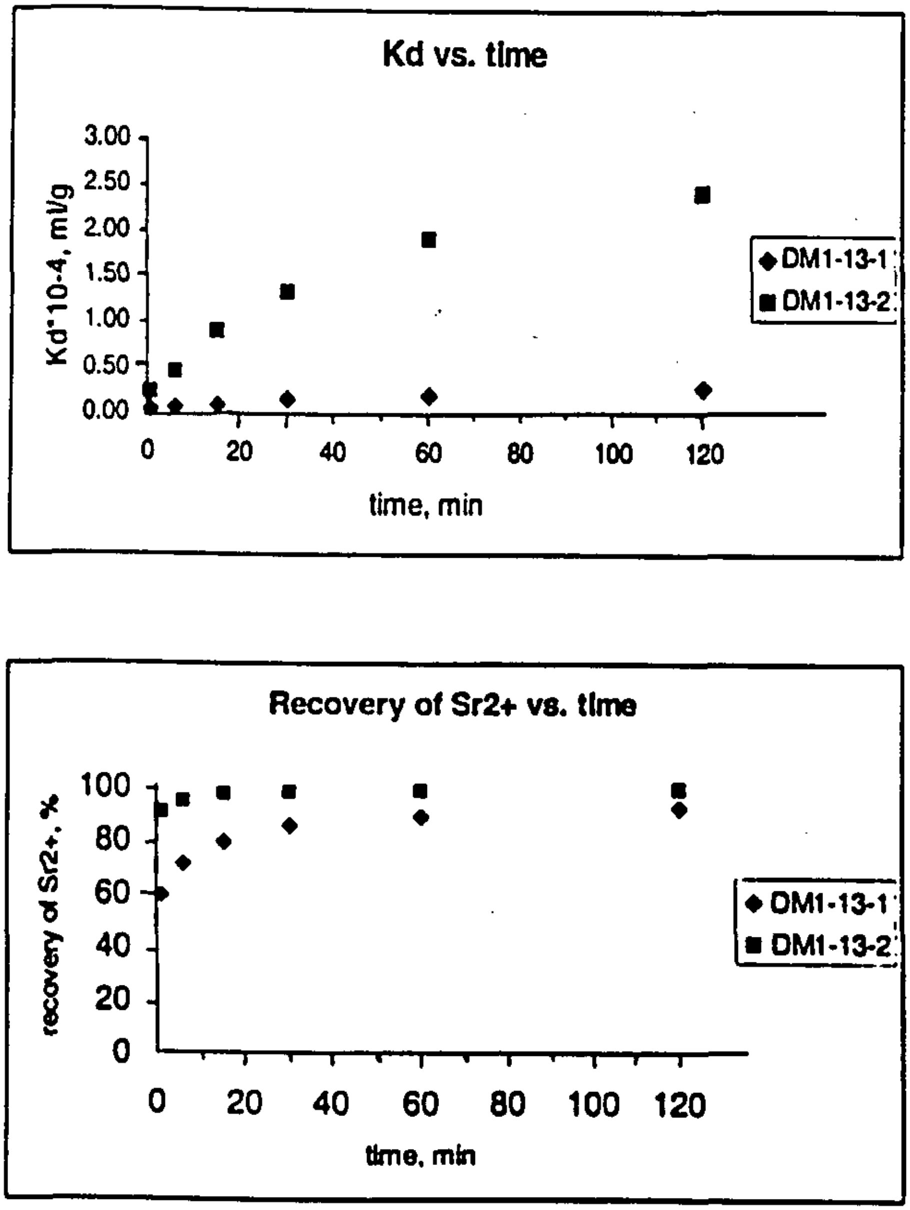


Figure 10

X-ray powder pattern of $NaTiOSiO_4$, a non-ion exchange phase obtained at high base concentrations in the synthesis of CST.

Figure 11

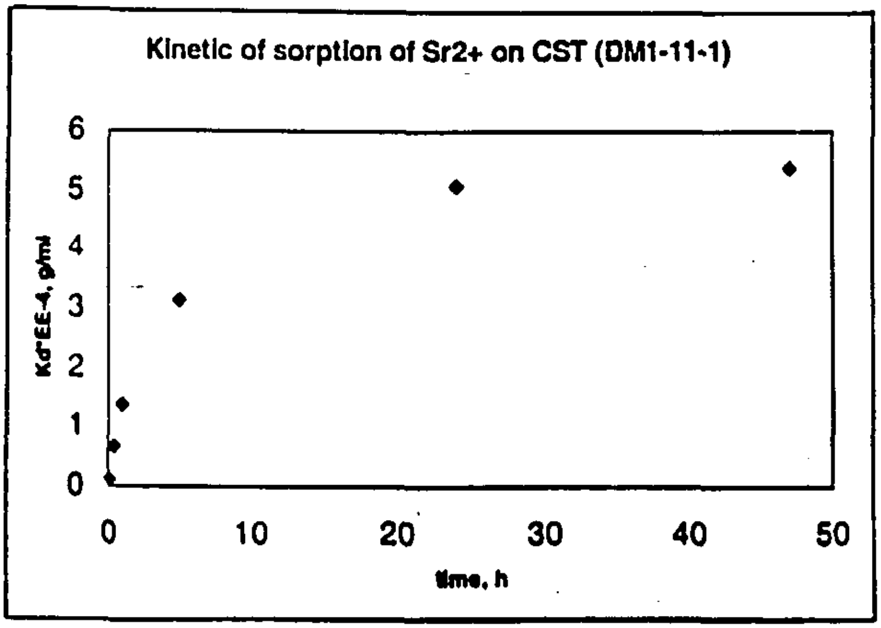
Kinetic studies of sorption of Sr^{2+} on TS DM1-13-1 and DM1-13-2.
Simulant: 0.0075M Ca^{2+}, 0.04M Na^{+}, 0.025M K^{+}, Sr^{2+} - traces



Kinetic curves for strontium exchange from a simulant for a highly crystalline CST sample DM1-13-1, and a poorly crystalline sample DM1-13-2.

Figure 12

time, h	$Kd \times 10^{-4}$, ml/g	recovery of Sr2+, %
0.083	0.1015	80.3
0.5	0.6669	96.43
1	1.372	98.21
5	3.1342	99.22
24	5.0874	99.52
47	5.3710	99.54



Kinetics of Sr^{2+} uptake by a poorly crystalline CST sample DM1-11-1 submitted for testing at WSRC.

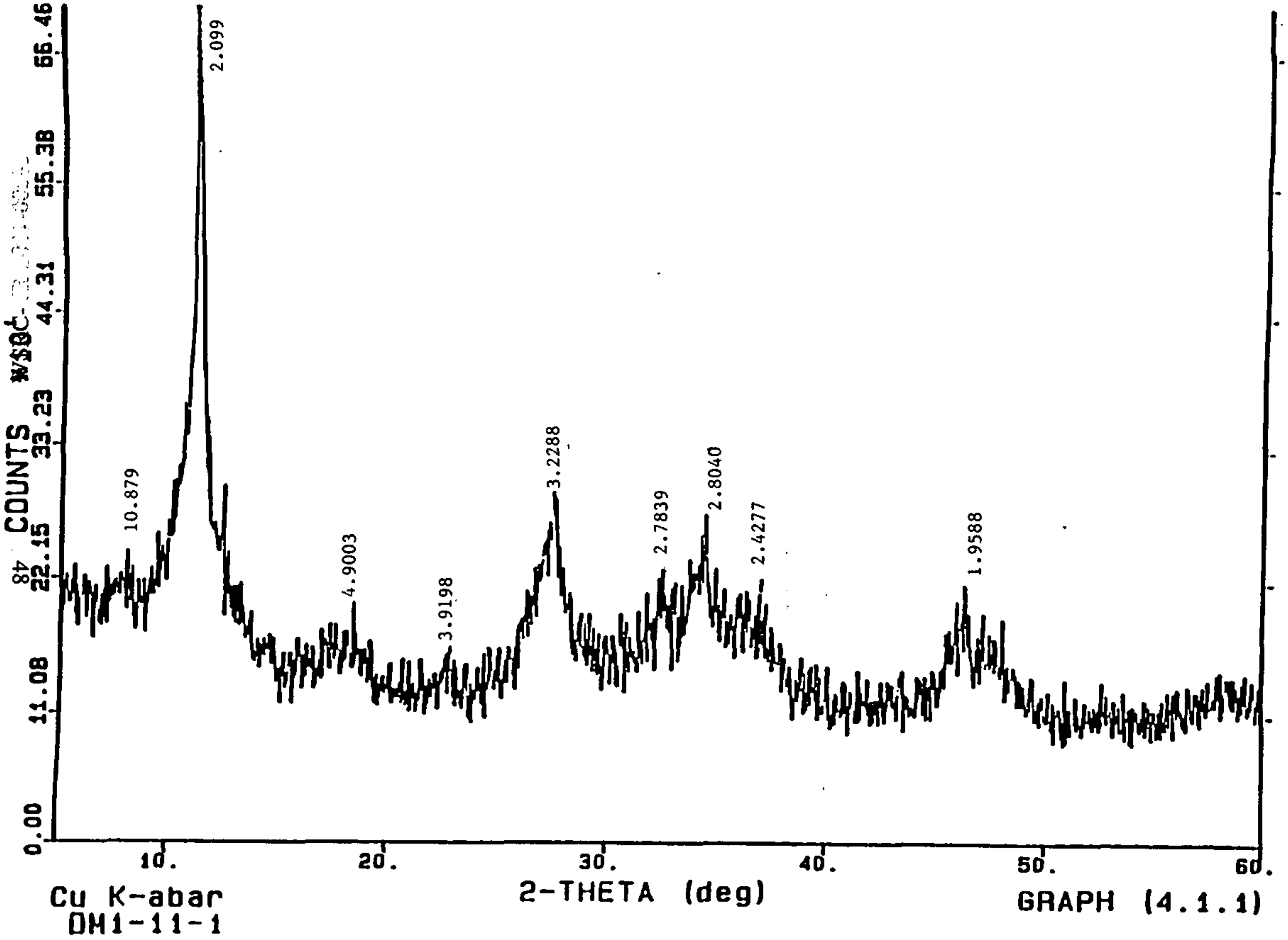
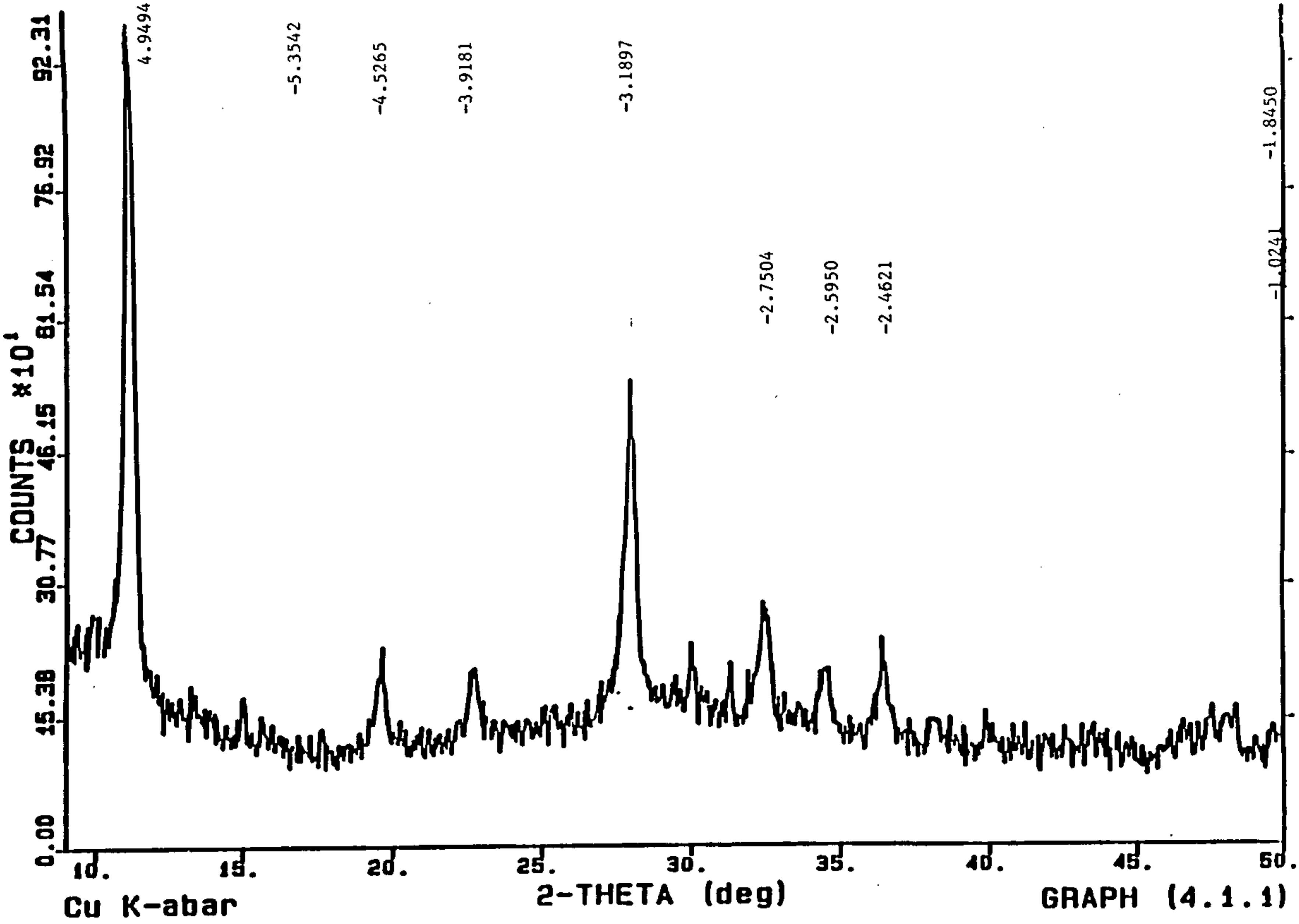


Figure 13

X-ray Diffraction powder pattern of the semi-crystalline CST sample DM1-11-1.

Figure 14



X-ray diffraction pattern of a potassium titanium pharmacosiderite, of intermediate crystallinity, $K_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$.

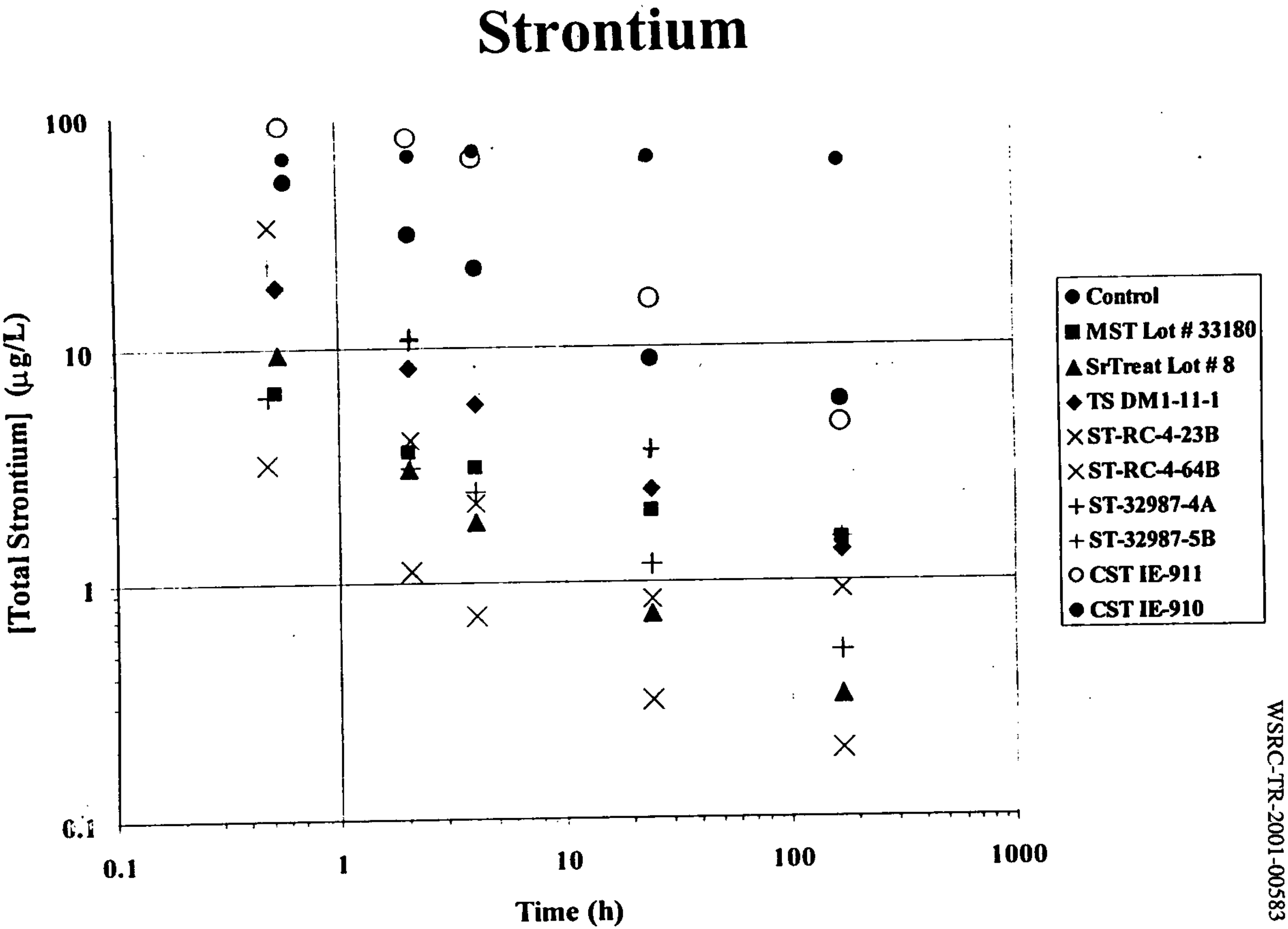


Figure 15

Kinetics of exchange of Sr^{2+} at WSRC for several inorganic ion exchangers in a simulant waste solution developed to duplicate Savannah River waste.

Figure 16a. Plutonium Removal with Sodium Nonatitanate and Monosodium Titanate Samples

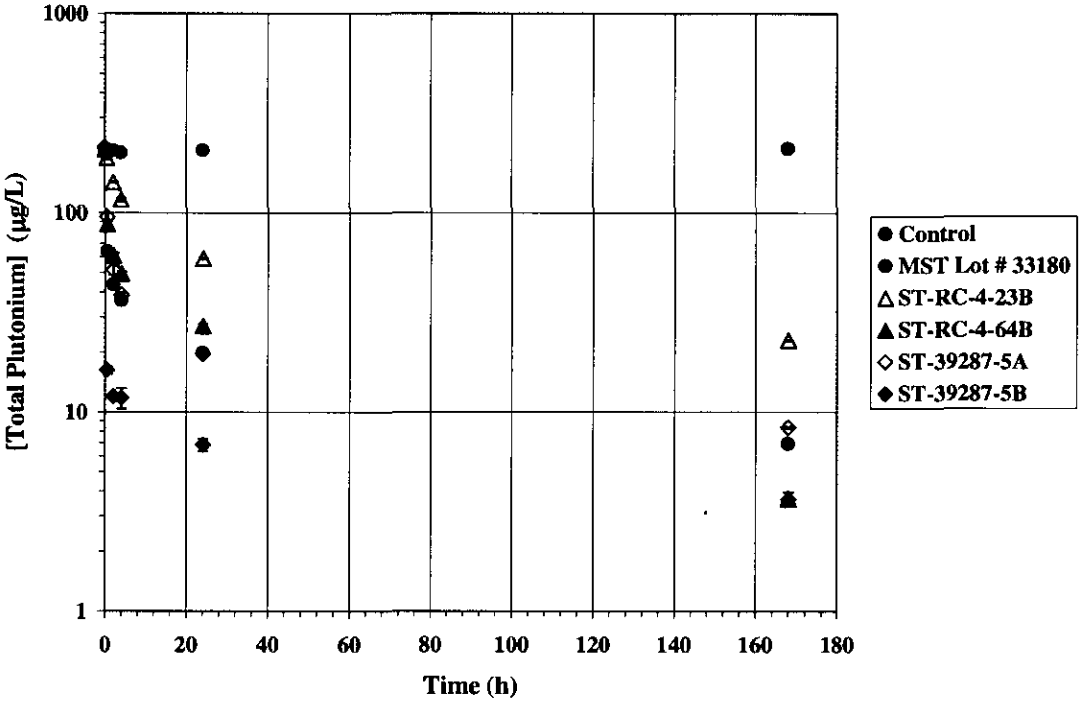
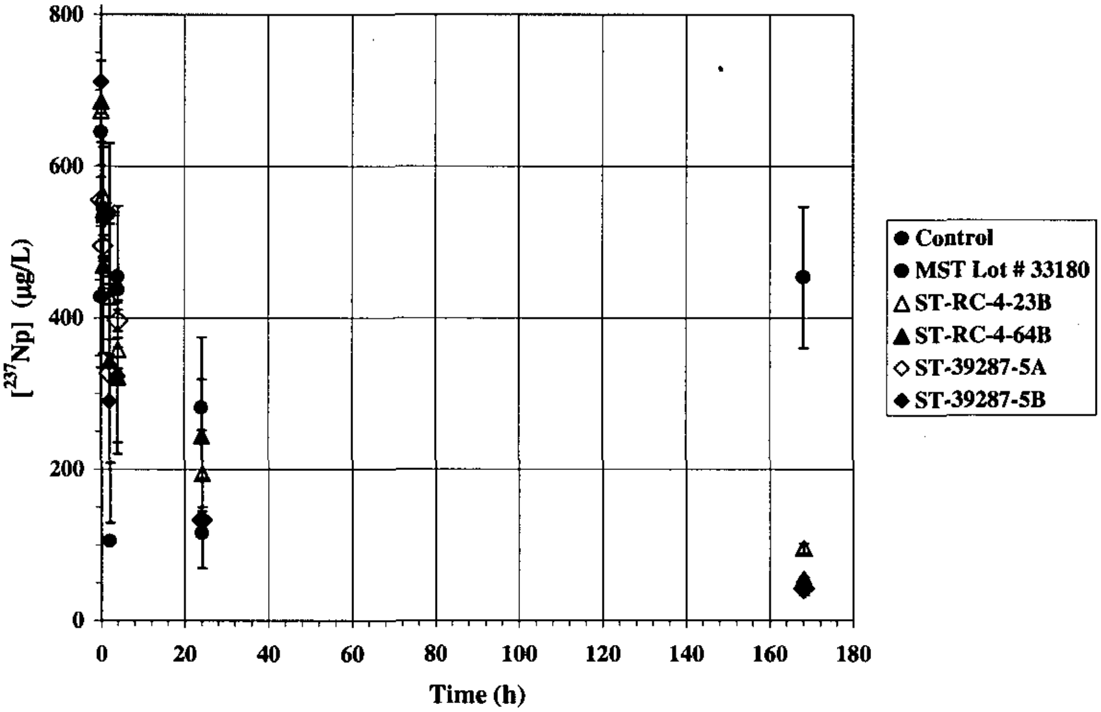


Figure 16b. Neptunium Removal with Sodium Nonatitanate and Monosodium Titanate Samples



Kinetic measurements for (A) plutonium uptake and (B) Neptunium uptake as a function of time for several sodium nonatitanates in SR waste simulant. Work performed at WSRC.

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