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ION EXCHANGE MATERIALS

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ION EXCHANGE MATERIALS

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ABSTRACT

Sodium titanate and sodium titanate loaded macroreticular resin are being considered as ion exchangers to remove ^{90}Sr and actinides from the large volume of defense waste stored at Hanford Site in Washington. Preliminary studies to determine the radiation effect on Sr^{+2} and I^- capacity of these ion-exchange materials were conducted. Samples of sodium titanate powder, sodium titanate loaded macroreticular resin, as well as the nitrate form of macroreticular anion resin were irradiated with up to 2×10^9 Rads of ^{60}Co gamma rays. Sodium titanate cation capacity decreased about 50% while the sodium titanate loaded macroreticular resin displayed a dramatic decrease in cation capacity when irradiated with 10^8 - 10^9 Rad. The latter decrease is tentatively ascribed to radiation damage to the organic portion which subsequently inhibits interaction with the contained sodium titanate. The anion capacity of both macroreticular resin and sodium titanate loaded macroreticular resin exhibited significant decreases with increasing radiation exposure. These results suggest that consideration should be given to the potential effects of radiation degradation if column regeneration is to be used.

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INTRODUCTION

The greater part of the current inventory of stored radioactive waste in the United States has resulted from the production of nuclear materials for military applications. At the Hanford Reservation near Richland, Washington, there now are 4×10^7 liters of sludge (primarily iron and aluminum precipitates), 1×10^8 liters of salt cake (primarily 60-80% sodium nitrate and 2-20% NaOH) and 4×10^7 liters of liquid (high concentrations of NaOH, NaNO_3 , $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$).^{1,2} The bulk of the radionuclides are contained in the sludge; however, significant quantities of ^{137}Cs , ^{90}Sr , other fission products and some actinides are present in the salt cake and liquid.^{1,2} Since the radioisotopes in the liquid and the water soluble salt cake are considered mobile, 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 these radionuclides by aqueous separation techniques with subsequent incorporation into a suitable waste form. The large volumes of residual salts would be stored as nonradioactive chemical waste. Standard ion exchangers can be employed to remove ^{137}Cs ; however, the high pH/salt content of these solutions severely limits the application of commercial ion exchangers for removing the ^{90}Sr and the actinides.

Recent studies by Dosch^{2,3} and Schulz⁴ have demonstrated that sodium titanate (empirical formula $\text{NaTi}_2\text{O}_5\text{H}$) is well suited to remove various fission products, including ^{90}Sr , and actinides from the high pH, high salt concentration waste at Hanford. Other work

with sodium titanate in a -40 +140 mesh powder form (to be denoted as sodium titanate powder) has demonstrated its use for solidification of actual high level liquid waste,^{5,6} but the question of radiation stability was not specifically addressed. A new form of sodium titanate, sodium titanate loaded macroreticular resin (to be denoted as sodium titanate resin), has been developed and no prior work concerning radiation stability on this material has been done. Therefore, the present work was initiated to determine if radiation from absorbed ⁹⁰Sr (or other radionuclides) would decrease the ion exchange capacity or reactivity for strontium of either sodium titanate powder or resin forms.

This report is divided into four sections: 1) a description of the titanate material, 2) an estimation of the radiation dose expected from absorbed ⁹⁰Sr, 3) the experimental procedures, and 4) the results and discussion of this work.

I. TITANATE MATERIALS

The development of hydrous oxide ion exchange materials for the solidification of liquid nuclear waste has been a continuing effort at Sandia Laboratories.^{3,5-8} The materials studied have the general representation, $M^{+n}(M'_xO_yH)_n$, where M^{+n} can be any cation and M' is Ti, Nb, Zr or Ta. Sodium titanate^{5,6} has received the most attention because it appears to be the most attractive economically, although recent studies⁹⁻¹¹ have shown that sodium zirconate may also be economically viable. These materials were initially prepared as fine powders^{3,4} and, as such, could present

difficulties from an engineering standpoint for use in flow through columns. However, Dosch^{2,3,12} has developed a simple preparation scheme whereby the sodium titanate material is formed within the porous structure of commercially available macroreticular anion exchange resin, e.g., Bio-Rad AG MP-IV (nominal composition: 21.7 weight % sodium titanate, 39.2 weight % nitrate form of quaternary ammonium styrene macroreticular resin, 39.1 weight % water). These resin "beads" are nominally 0.3-0.84 mm diameter and would be quite amenable to standard engineering practices for working with ion exchange columns. Although loaded with sodium titanate, the macroreticular resin retains ca. 90% of its original anion capacity. Sodium titanate in any form has a Sr^{+2} capacity of approximately 5 meq/gm sodium titanate in acidic solution and 10 meq/gm sodium titanate in basic solution.

In laboratory scale experiments, with simulated defense waste, Dosch^{2,3,12} has observed that most of the strontium is absorbed in the upper portions of the column. Several thousand column volumes of feed were passed through the column before Sr^{+2} appeared in the effluent.

One possible modus operandi for processing the Hanford waste is to use two columns of sodium titanate in the resin bead form (183 cm diameter and 305 cm long) placed in parallel and to replace them every three months over a two year period.⁴ A total of 16 columns would be used for the total strontium inventory (ca. 31 kgm Sr of which ca. 18 kgm is ⁹⁰Sr), which translates into approximately 1.5×10^5 Ci ⁹⁰Sr for each column.

II. EXPECTED RADIATION LEVELS

An estimate of the radiation levels to be expected during actual column operation must be calculated in order to define the maximum radiation boundary conditions for radiation effect studies. Since radiation effects are directly related to the quantity of energy deposited per unit mass, it is necessary to know both the time related number of radioactive decays per unit mass and the energy released per decay.

The radioactive decay of ^{90}Sr proceeds by emission of a beta particle only (maximum beta energy, $E_{\text{Sr}} = 0.546$ MeV; half life = 28.9 years), thereby forming ^{90}Y which is also radioactive and subsequently decays to stable ^{90}Zr by beta emission (maximum beta energy, $E_{\text{Y}} = 2.27$ MeV; half life = 64 hours), viz. $^{90}\text{Sr}(\beta^-) \rightarrow ^{90}\text{Y}(\beta^-) \rightarrow ^{90}\text{Zr}(\text{stable})$. This decay sequence is in secular equilibrium* in the storage tanks, i.e., disintegrations of ^{90}Sr per unit time equals the disintegrations of ^{90}Y per unit time.¹³ The pH of the liquid waste dictates that any yttrium formed in solution prior to ion exchange would precipitate as a hydroxide and become part of the sludge rather than being available in ionic form for absorption on ion exchange resin. However, ^{90}Y produced in solution within the column should be absorbed or precipitated and therefore remain entrapped within the column.

In beta decay, the average energy associated with the beta particle is $0.3-0.4 E_{\text{max}}$ with the remaining $0.6-0.7 E_{\text{max}}$ being associated with a neutrino^{14,15} which does not contribute to energy

*If fresh ^{90}Sr is added, a period of time equal to several ^{90}Y half-lives is required for secular equilibrium to be reestablished.

deposition in materials.¹⁶ Less than 5% of the beta energy is converted to external bremsstrahlung.¹⁵ Therefore, it is assumed in this work that $E_{avg} = 0.4 E_{max}$. Assuming the existence of secular equilibrium, the estimated energy release per unit mass in an ion exchange column loaded to capacity with ^{90}Sr (and associated ^{90}Y) is

$$E_R \text{ (MeV/day-gm)} = \frac{\Lambda_{90}}{\rho V} (E_{\text{Sr,avg}} + E_{\text{Y,avg}}) \quad (1)$$

where Λ_{90} is the disintegrations per unit time of either ^{90}Sr or ^{90}Y , ρ is the density of the sodium titanate material (0.693 gm/cm³ and 0.35 gm/cm³ for the resin bead and powder, respectively), and V is the volume occupied by the sodium titanate material containing ^{90}Sr and ^{80}Y .

The unit commonly used for studies involving radiation absorption by materials is the Rad which is defined as the deposition of 100 ergs of energy by any radiation in one gram mass of any material. To establish both the anticipated dose rate and a maximum dose rate for this work, two cases were considered. Case I: For the anticipated dose rate, it is assumed that 80% of E_R resulting from one gram of sodium titanate materials is absorbed within the one gram; it is estimated that 20% of E_R will escape the volume represented by the one gram. Case II: The maximum dose rate was chosen to be a factor of 17 greater than the anticipated dose rate.

Table I summarizes the estimated radiation absorption by sodium titanate material for both Case I and Case II. Figure 1 illustrates the integrated Rad dose for one gram of sodium titanate material assuming that it contains ^{90}Sr (and associated ^{90}Y) from time zero and continuously absorbs the calculated radiation dose.

TABLE I
ESTIMATED RADIATION ABSORPTION BY SODIUM TITANATE MATERIALS*

	Case I	Case II
MeV/day-gm	7.5×10^{13}	1.3×10^{15}
Rad/day	1.2×10^6	2.1×10^7
Total Rad (90 days)	1.1×10^8	1.9×10^9

*Beta radiation resulting from decay of the ^{90}Sr - ^{90}Y secular equilibrium.

III EXPERIMENTAL

The experimental effort was comprised of two parts: the first dealt with the gamma irradiation of materials in the Sandia Gamma Irradiation Facility and the second quantified the ion exchange capacities of the irradiated materials. These and associated subjects are discussed separately below.

Ion Exchange Materials. Three forms of material were used in this study: sodium titanate powder, sodium titanate resin and a nitrate form of 50-100 mesh AG MP-1 macroreticular anion resin. One to five gram samples of the materials were placed in screw top glass vials for the irradiations in the Gamma Irradiation Facility. Non-irradiated samples of the three materials were included in this study to obtain the zero Rads data points.

Gamma Irradiation. The ^{60}Co gamma source chosen for this work has the following characteristics: 107 kCi ^{60}Co , 5.27 year half life, 1.17 and 1.33 MeV gamma rays essentially 100% abundant. This source provided 1.2×10^5 Rads/min at the irradiation point used for the samples. A detailed description of the Gamma Irradiation Facility is given elsewhere.¹⁷ The irradiations were for times ranging from three hours to 11 days which corresponded to absorbed radiation doses ranging from 10^7 to 2×10^9 Rads. The gamma absorption coefficients for the materials used in this study do not vary more than 10-15% from each other and no corrections were deemed necessary. The ^{60}Co source and samples are in close proximity in an air environment during irradiation. This results in the samples experiencing a thermal environment with temperatures ranging up to 100°C .

Solutions. Analytical solutions of EDTA (0.0200 N) and AgNO_3 (0.100 N) were made from Acculut standards. A 0.243 N iodide solution was made and standardized by normal means.¹⁸ A simulated liquid waste solution was prepared containing 6 N NaNO_3 , 0.6 N NaOH, and 0.600 N Sr^{+2} .

Ion Exchange Capacities. Cation capacities of the powder and resin forms of sodium titanate were determined by equilibrating for one hour 1.25 gm samples of the resin and 0.25 gm samples of the powder with 70 mL volumes of the simulated liquid waste solution. Following equilibration, five mL aliquots of the simulated waste solution were removed from each sample by filtration, diluted with 100 mL deionized water and the Sr^{+2} contents were determined by titration with EDTA. Capacities were calculated on the basis of

sodium titanate ($\text{Na}_2\text{Ti}_4\text{O}_9$) fired at 800°C .

Anion capacities of both sodium titanate resin and the macroreticular anion resin were determined by equilibrating for 18 hours 0.5 gm titanate resin samples and one gm anion resin samples with 50 mL volumes of standard iodide solution. Subsequently, five mL aliquots were removed from each sample by filtration, diluted with 50 mL of deionized water, and the iodide concentrations were determined by titration with standard silver nitrate solution. Capacities were calculated on the basis of the resin forms dried at 103°C for one hour.

IV RESULTS AND DISCUSSION

Figure 2 illustrates the cation capacities of sodium titanate resin and powder forms as a function of radiation absorbed dose (Rad). The anion capacities of sodium titanate resin and the macroreticular anion resin as a function of irradiation are also presented in the figure.

It is apparent that the anion capacity of sodium titanate resin and macroreticular anion resin are quite similar throughout; they steadily decrease and have lost over 85% of their capacity by 2×10^9 Rads. Further information would be required to determine if total loss of capacity occurs at higher doses. Scanning electron micrographs of nonirradiated and irradiated (2×10^9 Rads) sodium titanate resin do not reveal any morphological differences between the two materials (Figure 3). However, the physical appearance of these two materials (Table II) strongly suggests degradation of the organic due possibly to gamma-heating and/or to radiation damage.

TABLE II
 PHYSICAL APPEARANCE OF IRRADIATED SODIUM TITANATE
 RESIN AND MACRORETICULAR ANION RESIN

<u>Hours in Gamma Irradiation Facility</u>	<u>Rad Dose</u>	<u>Color of Resin*</u>
0	0	white-yellow
3.33	2×10^7	light straw
6.67	5×10^7	straw
13.3	1×10^8	yellow-tan
66.7	5×10^8	light ochre
133.2	1×10^9	red-brown
266.7	2×10^9	dark red-brown

*The color of temperature treated sodium titanate resin was beige in all cases

The cation capacity results appear to present an anomaly. The cation capacity of the sodium titanate resin, which is due entirely to sodium titanate within the ion exchange beads, exhibits little decrease until about 5×10^8 Rads at which point there is a sudden decrease. On the other hand, sodium titanate powder demonstrates a cation capacity that varies slightly up to ca. 5×10^7 Rads, then undergoes a 40% decrease over the next decade of radiation dose, and apparently becomes relatively constant at ca. 10^9 Rads. A possible explanation for this apparent anomaly between the two sodium titanate materials is the following. Previous work with sodium titanate powder has demonstrated that continued exposure to elevated temperature causes a continual decrease in cation capacity.^{5,7,19*} This was verified in the present

*Recent studies show this capacity loss to be true also when wet sodium titanate powder is autoclaved at 250°C for several hours.²⁰

work by comparing sodium titanate powder samples exposed in the Gamma Irradiation Facility (estimated sample temperature $90 \pm 10^\circ\text{C}$) with samples exposed to 100°C oven temperature for various times (see Figure 4). Although the results do not coincide because experimental conditions could not be exactly duplicated between the irradiation facility and the oven, they are essentially identical in shape. Therefore, the cation capacity decrease of the irradiated sodium titanate powder is probably due to gamma heating.

A similar comparison was made with sodium titanate resin. The results shown on Figure 5 indicate that temperature alone has little effect up to about 100 hours; however it appears that radiation eventually causes a significant decrease in capacity. A plausible explanation, then, is that increasing radiation damage of the organic resin portion finally becomes sufficient to physically and/or chemically inhibit ion-exchange reaction with the sodium titanate. This is given credence by the visible radiation effects on the organic portion (Table II) and the severe decrease in anion capacity (Figure 2) which may be associated with radiation damage.

Although the foregoing may be a reasonable explanation, the exact nature of any radiation damage in sodium titanate resin is not fully known and will be investigated further.

In summary, the initial results suggest that temperature affects the cation capacity of both sodium titanate powder and resin form. Radiation apparently affects both the cation and anion capacities of the sodium titanate resin form and the anion

capacity of the macroreticular resin. The removal of ^{90}Sr from defense wastes by these materials should produce minimal temperature effects and, therefore, no difficulty is foreseen in that respect. A problem may arise if the sodium titanate resin is exposed to a radiation level of $> 10^8$ Rads. Since the expected radiation level should be $\leq 10^8$ Rads, no serious degradation of cation capacity should be experienced. However, if the Sr is to be eluted from the column so the column can be reused, serious consideration must be given to the potential effects of radiation degradation.

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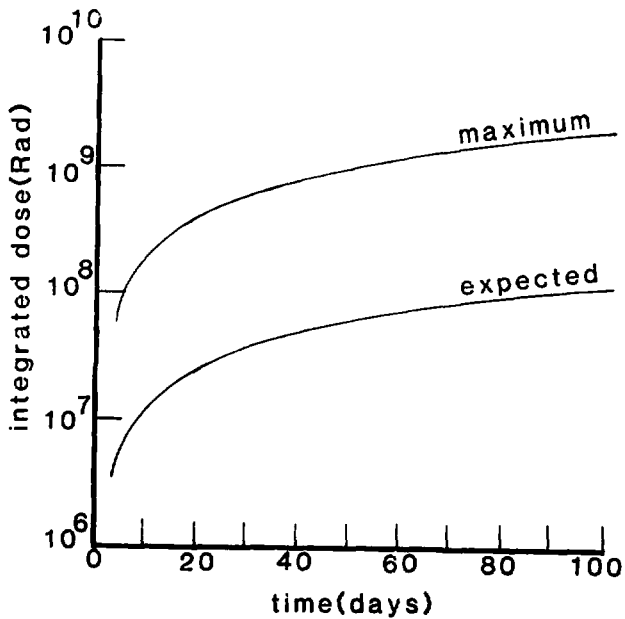


FIGURE 1. ^{90}Sr RADIATION ABSORPTION BY SODIUM TITANATE MATERIAL AS A FUNCTION OF EXPOSURE TIME.

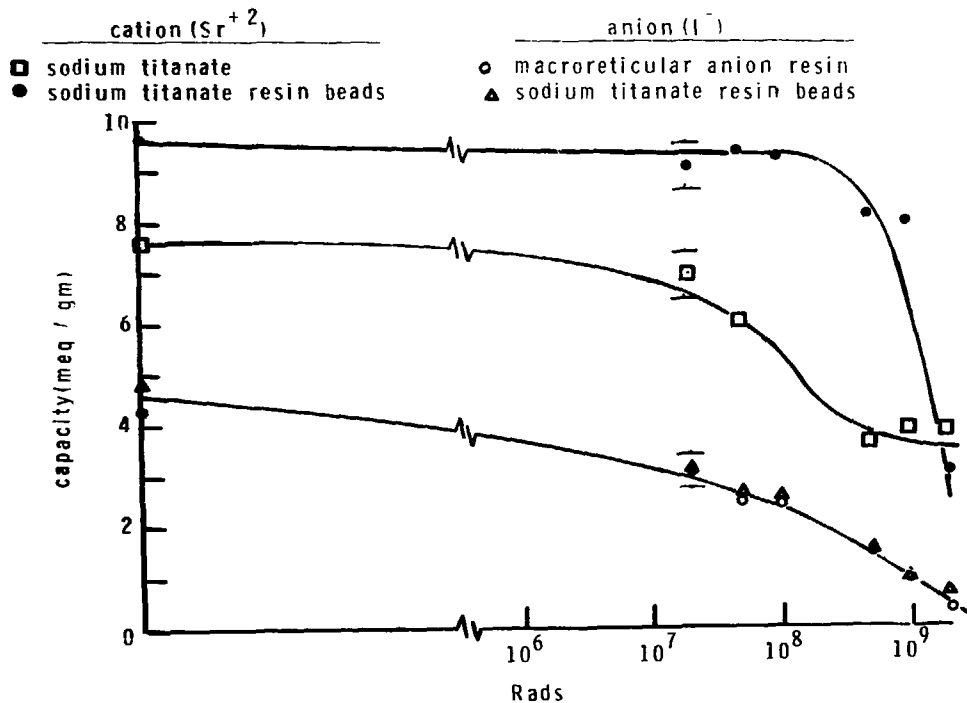


FIGURE 2. ION EXCHANGE CAPACITIES AS FUNCTION OF RAD DOSE.

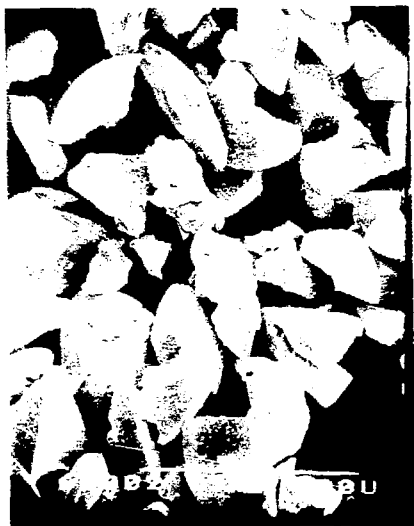


(a) 100X, unirradiated



(b) 600X, unirradiated

FIGURE 3. SCANNING ELECTRON MICROGRAPHS OF MRST.



(c) 100X, 2×10^9 rads



(d) 600X, 2×10^9 rads

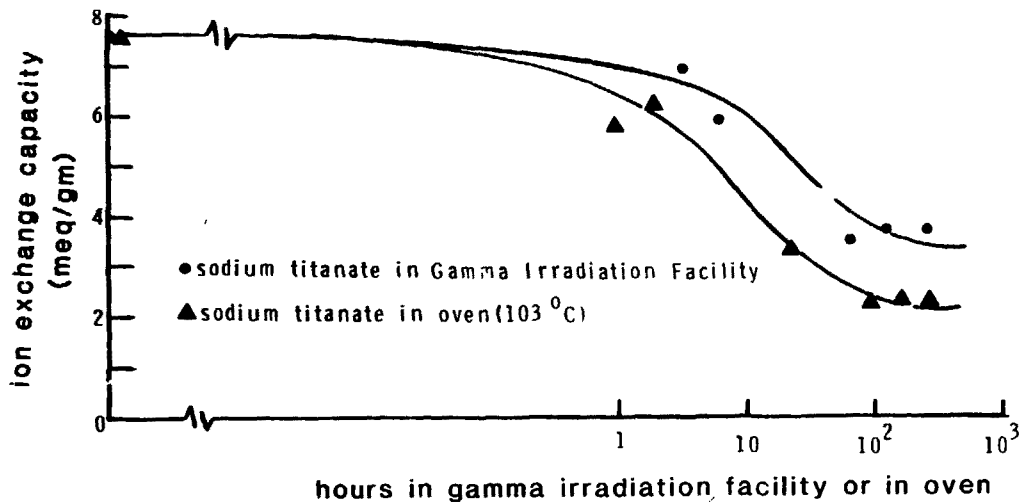


FIGURE 4. CHANGE IN CATION CAPACITY OF SODIUM TITANATE AS A FUNCTION OF TIME IN GAMMA IRRADIATION FACILITY OR IN OVEN.

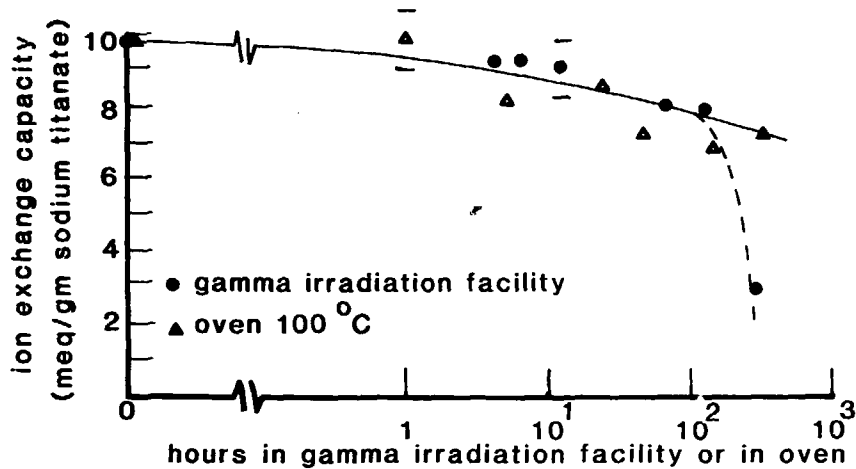


FIGURE 5. CHANGE IN CATION EXCHANGE CAPACITY OF SODIUM TITANATE LOADED RESIN AS A FUNCTION OF TIME IN GAMMA IRRADIATION FACILITY OR IN OVEN.