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Characterization of modified monosodium titanate - an improved sorbent for strontium and actinide separations

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Abstract: High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove ^{134,137}Cs, ^{90}Sr, and alpha-emitting radionuclides (i.e., actinides) prior to disposal onsite as low level waste. An inorganic sorbent, monosodium titanate (MST), is currently used to remove ^{90}Sr and alpha-emitting radionuclides, while a caustic-side solvent extraction process is used for removing ^{134,137}Cs. A new peroxotitanate material, modified MST, or mMST, has recently been developed and has shown increased removal kinetics and capacity for ^{90}Sr and alpha-emitting radionuclides compared to the current baseline material, MST. This paper describes recent results focused on further characterization of this material.

Key words: ion exchange, peroxotitanate, plutonium, neptunium, uranium, alkaline waste, iodometric titration

Short Title: Modified Monosodium Titanate

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INTRODUCTION

Monosodium titanate (MST) is an inorganic sorbent material that exhibits high selectivity for strontium and actinide elements in the presence of strongly alkaline and high sodium containing salt solutions. This material currently serves as the baseline sorbent for the removal of ^{90}Sr and alpha-emitting radionuclides from HLW at the Savannah River Site (SRS).[1-5] Efforts to increase efficiency and rapidly remove alpha-emitting radionuclides to increase operational throughput led to the identification of a peroxotitanate material with improved strontium and actinide removal characteristics.[6]

Compared to the baseline MST material, the new peroxotitanate material, referred to as modified MST, or mMST, exhibits higher batch (short-term) capacities and kinetics for the separation of strontium and actinides from alkaline waste solutions.[6-8] Consequently, this material offers the opportunity to reduce sorbent use and increase throughput in processing facilities. Previous publications described the optimization of synthetic conditions and performance testing under a variety of conditions.[6-9] This paper describes recent results focused on further characterization of the material, including gas release during synthesis and storage, settling characteristics, peroxide content, and solid phase transformations upon heating to elevated temperatures.

EXPERIMENTAL

Preparation of MST and mMST

The MST used in these studies was prepared using a sol-gel process developed at the Savannah River National Laboratory (SRNL) and supplied by Optima Chemical Group LLC (Douglas, GA, Lot #00-QAB-417) as a 15 wt % suspension in water containing 0.10-0.15 M NaOH and 100-150 mg L^{-1} $NaNO_2$.[4] Modified monosodium titanate (mMST) used in these studies was prepared by the post-synthesis treatment of MST with hydrogen peroxide. The details of this procedure have been previously published.[6] Bench-scale quantities of mMST were prepared using 25 grams of the Optima-supplied MST. Optima Chemical Group LLC (Douglas, GA) also produced a pilot-scale quantity (15 kg) of mMST, Lot #06-QAB-0139, as a 15 wt % suspension in water using the same conditions as used for the bench-scale preparations.

Six small-scale batches of mMST were also synthesized with varying hydrogen peroxide:Ti ratios, 0.25:1, 0.5:1, 1:1, 2:1, 3:1, and 4:1, for characterization of peroxide content. Earlier development of mMST lead to the choice of 3:1 as the optimal H_2O_2:Ti ratio,[6] and this ratio was used for the synthesis of the commercial scale batch of mMST (Optima 06-QAB-0139), and other larger, bench-scale (25-gram) prepared samples. These mMST samples were synthesized by adding the appropriate amount of a 30 wt % solution of hydrogen peroxide dropwise to approximately 10 g of a 15 wt % suspension of baseline MST (Optima 00-QAB-417). The MST had been previously isolated and washed, and the washed MST was then dispersed in water. The pH of the MST suspension was adjusted to 7 before the addition of peroxide. After the peroxide addition was complete, the reactions were stirred at room temperature for 24 hours. The products were then isolated by centrifuging (1400 x g for 15 min) and were washed six times with distilled water. After the final wash, the mMST samples were dispersed in water, and the pH of each suspension was adjusted to 4 with 1 M nitric acid. The suspensions were diluted to a final mass of approximately 10 g, and the weight percentage solids were determined.

Gas Release Measurements

During the synthesis of a 25-g batch of the mMST two gas samples were collected during the addition of the hydrogen peroxide. Gas samples were collected by locating a glass sampling bulb between the reactor and the bubbler such that any gases formed pass through the sample bulb before venting to the atmosphere through the bubbler. The glass sampling bulb was then isolated from the system. Identification and quantification of the gas composition utilized gas chromatography.

To evaluate the quantity and time-dependent behavior for the formation of gases after the synthesis, a test chamber was constructed consisting of a cylindrical plastic tube, a glass U-tube filled with ultrapure water and a gas-tight syringe. The cylindrical plastic tube was filled with a freshly prepared 25-g batch of mMST as a 15 wt % suspension in water. The system was closed to the atmosphere so that any gas produced and released to the vapor space displaced water in the attached U-tube. The volume of displaced liquid was measured periodically by pulling the released gas into a gas-tight 1.0-mL syringe, which returns the liquid level to the original position in the U-tube. After recording the volume, the system was vented to the atmosphere and then closed again. Time intervals were recorded between each set of measurements.

Over the course of the experiment, gas accumulated in the slurry resulting in an overall increase in the height of the suspension. Periodically, the walls of the cylindrical tube were gently tapped to release this trapped gas. In addition to releasing trapped gas, tapping also suspends some fraction of the settled solids. Over the course of the experiment, the system was opened once and the contents of the cylindrical tube were mixed with a stainless steel rod to re-suspend the solids. After mixing, the system was again closed and gas release measurements continued.

Similar experiments were also performed using samples of mMST that were washed with acidic or basic solution during the work-up of the reactions. In contrast, the normal work-up involves isolation of the material by filtration followed by washing with distilled water.

An additional gas release experiment was also performed at elevated temperature, 49 °C, to determine the gas release rates that may be observed during shipping and storage of the material. For this experiment, the cylindrical plastic tube described above was replaced with a round bottom flask. The flask was then submerged in a temperature controlled water bath for the course of the experiment.

Solids Settling Characteristics

The settling characteristics of the baseline and modified MST were measured in aqueous solutions over a range of pH values. The baseline and modified MST suspensions used in this test were the commercially prepared Optima Batch #00-QAB-417 and Optima Batch #06-QAB-0139, respectively. The pH of the as-received baseline and modified MST suspensions measured 10.47 and 4.84, respectively. Suspensions of each MST sample were prepared at pH values of 6, 7, 8, 9 and 10 by adding 2 M nitric acid solution to the baseline MST suspension and 2 M NaOH solution to the modified MST suspension. After mixing for 30 minutes, aliquots of approximately 11 mL were transferred from each of the as-received and pH-adjusted suspensions into separate 15-mL glass centrifuge tubes. The suspensions then stood at ambient laboratory temperature undisturbed for 50 days. Each tube was periodically inspected and the height of the settled solids was measured.

Two tests were also performed to examine the settling characteristics of mMST in simulated salt solutions, with sodium concentrations of 0.5, 4.6, 5.6, and 6.6 M. The first test involved determination of the settled solids density. For this experiment, aliquots of mMST (Optima 06-QAB-0139) were added to 15-mL centrifuge tubes. The solids were washed once with the appropriate salt solution (5 mL), either SWS-11-2008 (5.6 M Na) or SWS-12-2008-2 (0.5 M Na), and were re-isolated by centrifugation at 1400 x g for 2 minutes. After decanting the solution, 10-mL aliquots of the salt solutions were added to the washed solids. The contents were then gently mixed to suspend all the solids. Each suspension was then centrifuged at either 6.3 x g or 1400 x g for 10 minutes. The volume of the settled solids was then measured. Without disturbing the settled solid plug in the bottom of the centrifuge tube, the tube was returned to the centrifuge, and was centrifuged for an additional 5 minutes at the appropriate speed. The tubes were removed and the volume of settled solids was again measured. This process was repeated until no additional change in the settled solids volume occurred.

The second set of tests examined the solid settling rate as a function of time in three salt solutions with Na concentrations of 4.6, 5.6, and 6.6 M. For these experiments aliquots of mMST and MST were placed in graduated cylinders along with 90 mL of the appropriate salt solutions, giving final mMST/MST concentrations of 0.53 g/L. Each cylinder was capped, and shaken to disperse the solids. The graduated cylinders were then placed on the bench top, and the level of the liquid-solid interface was monitored as a function of time. During the tests two interfaces were observed, one between the cloudy slurry and the clear supernate at the top which is indicative of the smallest, slowest settling particles (fines), and one between the concentrated slurry and cloudy slurry located at the bottom of the graduated cylinder. This bottom interface is indicative of the largest fastest settling particles.

High Temperature X-Ray Diffraction Analyses (HTXRD)

X-ray diffraction data (XRD) were collected on a theta-theta PANalytical X'Pert Pro X-ray diffractometer using an Anton Paar HTK 1200 high temperature attachment. Instead of fixing the sample on a resistively heated platinum strip, the sample cup was placed in a uniformly heated sample chamber in the camera. A type S thermocouple was inserted into the chamber near the sample cup to monitor the sample temperature. This configuration eliminates most of the sample temperature gradients observed in ribbon style high temperature attachments. The alumina sample cup has a well that is 0.4 mm deep. The instrument was scanned over a 5-70 ° 2θ range with a 0.0167 ° step size and a dwell time of 99.695 s/2.122 ° (2θ) for a total measurement time of ~25 minutes. The large dwell time with short analysis time was achieved using the X'Celerator™ detector that has a 2.122 ° (2θ) active length and operates as if there were an array of over a hundred detectors working simultaneously. High temperature X-ray diffraction scans were performed at seven temperatures, 25, 75, 125, 250, 300, 600, and 800 °C. All the HTXRD scans were performed under an ultra-pure (>99.999%) helium purge. After the powder sample had cooled to room temperature, the powder residue was ground into a fine powder and analyzed using a conventional XRD arrangement. A detailed compilation of all the instrument parameters is included in the Supplemental Information

Table 1S. Compound search-match identification was performed with Jade™ software (Version 9) from Materials Data Inc. using the latest inorganic PDF4™ powder diffraction database from the International Centre for Diffraction Data (ICDD).

A temperature calibration curve was generated for the helium atmosphere to correct for any temperature gradients in the high temperature attachment and any thermal lag between the measured and set-point temperatures. The phase transition temperatures and melting points for several recommended compounds routinely referenced by the X-ray diffraction community were used to construct calibration curves for He.[10-11] The observed temperatures were ~ 4 - 30 °C low in helium with the smallest ΔT at low temperatures. All the temperature data were corrected.

Two samples of both baseline and modified MST were analyzed. The first two samples were the commercially prepared materials as received (Optima 00-QAB-417 and Optima 06-QAB-0139). The second two samples were samples of these commercially prepared batches that had been pH adjusted. The baseline MST is received as a pH 10 slurry and the mMST is received as a pH 4 slurry. For the HTXRD experiments samples of MST were adjusted to pH 4 and samples of mMST were adjusted to pH 10. All samples were dried prior to analysis.

Iodometric Titrations

Iodometric titrations were performed using several modified MST samples. The general procedure for the titrations involved first performing the reaction between sodium iodide and peroxide to form iodine, which was then titrated with sodium thiosulfate using starch as an indicator (see reactions 1 and 2). An aliquot of a known weight percent suspension of mMST was placed in a 25-mL volumetric flask. The amount of suspension added corresponded to between 0.3 and 0.4 g of mMST. The suspension was then diluted to an approximate volume of 15-20 mL with distilled water. Then 0.42 mL of 18 M sulfuric acid was added to the suspension, and the sample was diluted to the 25-mL mark with additional distilled water. This suspension was then transferred to a glass vessel containing a stir bar, and 25 mL of a 0.27 M solution of sodium iodide was added. This reaction was then stirred at room temperature for a minimum of 17 hours. Aliquots of the reaction mixture were then removed and titrated with a 0.1 M solution of sodium thiosulfate, using starch as an indicator. All titrations were performed in triplicate.

$$H_2O_2 + 2\ I^- + 2H^+ \rightarrow I_2 + 2\ H_2O \qquad (1)$$

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI \qquad (2)$$

Control experiments were also performed without any material, i.e. just sulfuric acid and sodium iodide, and also with baseline MST, which contains no peroxide. No measurable amount of I_2 was formed in the blank control experiment; however, the baseline MST did cause the formation of iodine from NaI under the reaction conditions. Experiments were also performed using the supernatant from mMST and MST slurries, and also dried samples of MST. The results from the supernatant titrations indicated no formation of I_2 from the mMST supernatant. Reaction of the MST supernatant did lead to the formation of I_2, while the dried sample of MST did not. The formation of I_2 in the MST supernatant experiment is due to the presence of $NaNO_2$ added to the commercially prepared MST as a corrosion inhibitor (see reaction 3).

$$2\ HNO_2 + 2\ H^+ + 2\ I^- \rightarrow I_2 + 2NO + 2\ H_2O \quad (3)$$

Affect of Alkaline Solution on Peroxide Content

A series of experiments were also performed to determine how much of the peroxide was lost upon exposure to alkaline salt solutions, such as the simulated waste solutions used for performance testing. For these experiments, aliquots of mMST suspension (Optima Batch 06-QAB-0139), corresponding to 0.10 g of mMST solid, were added to 500 mL volumes of several salt solutions. The mixtures were then stirred at room temperature for 24 hours. The mMST solids were isolated by filtration through a 0.2-μm membrane, and were washed three times with distilled water. The washed solids were then transferred to a 10-mL volumetric flask. The solids were dispersed in water, 0.42 mL of 18 M sulfuric acid was added, and the mixture was diluted to a final volume of 10 mL. This suspension was then transferred to a glass vessel containing a stir bar, and 10 mL of a 0.27 M solution of sodium iodide was added. This reaction was then stirred at room temperature for a minimum of 17 hours. 6-mL aliquots of the reaction mixture were then removed and titrated with a 0.1 M solution of sodium thiosulfate, using starch as an indicator. All titrations were performed in triplicate. The three solutions tested included SWS-1-2010, a non-radioactive salt solution containing only sodium, SWS-1-2008, a non-radioactive salt solution containing Sr, and a control experiment using distilled water. The compositions of the salt solutions are presented in Table 1.

Affect of Age on mMST Performance

Iodometric titration analyses indicated that the peroxide content of modified MST samples decreases linearly with age. Sr and actinide sorption tests were performed with several lab prepared batches of mMST of varying age (see Table 2). Performance tests were carried out with a simulated waste solution (SWS-9-2009) having the composition shown in Table 3. 60-mL aliquots of this simulant were placed in 125-mL HDPE bottles. After equilibrating at 25 °C, overnight, aliquots of mMST were added, giving final mMST concentrations of 0.2 g/L. The experiments were carried out in a waterbath/shaker at 25 °C, with an agitation speed of 175 rpm. Samples were taken after 6, 12, and 24 hours of contact, and were filtered through a 0.1-μm PVDF filter. The samples were then acidified before being submitted for analysis of Sr, U, Np, and Pu content using ICP-MS, gamma scan, and PuTTA analyses.

Previous testing indicated that the mMST does not adsorb appreciable uranium, as opposed to MST, which does.[8] A performance test was designed using a uranium only simulant to examine if the loss of peroxide with age causes the mMST to begin sorbing uranium. Performance tests were carried out with simulated waste solution (SWS-8-2007) having the composition shown in Table 3. 60-mL aliquots of this simulant were placed in 125-mL HDPE bottles. After equilibrating at 25 °C, overnight, aliquots of MST (Optima Batch 00-QAB-417) and mMST (Optima Batch 06-QAB-0139) were added, giving final sorbent concentrations of 3.0 g/L. The experiments were carried out in a waterbath/shaker at 25 °C, with an agitation speed of 175 rpm. Samples were taken after 4 and 12 hours of contact, and were filtered through a 0.1 μm PVDF filter. The samples were then acidified before being submitted for analysis of U content using ICP-MS.

RESULTS AND DISCUSSION

Gas Release from mMST

During the synthesis of mMST, gas bubbles are readily formed during and after the addition of the hydrogen peroxide. To identify the composition of the gas formed during synthesis two gas samples were collected during the addition of the hydrogen peroxide. Gas Sample #1 was collected from the beginning of the hydrogen peroxide addition and up until one-half of the hydrogen peroxide had been added to the reaction flask. Gas Sample #2 was collected during the second half of the hydrogen peroxide addition. Both gas samples were analyzed in duplicate using gas chromatography.

Analysis indicated that both samples were principally oxygen (95 – 98 vol %) with small amounts of nitrogen (5 – 8 vol %). The small amount of nitrogen likely results from residual air that had not been displaced by the evolved oxygen. No hydrogen (<0.1 vol %) was detected in either sample. The high concentration of oxygen and absence of hydrogen is consistent with the decomposition of hydrogen peroxide to produce oxygen and water.

In addition to gas evolution during the synthesis of mMST, continued gas release was observed during storage of the mMST samples as aqueous suspensions. The amount of gas released decreased with time, but was observed to continue for many months. Thus, storage of mMST would likely require vented containers to prevent over-pressurization during transport and storage of the material as an aqueous suspension. Possible sources of the gas release include trapped oxygen from the synthesis of the mMST, decomposition of residual hydrogen peroxide, and decomposition of the titanium-peroxide species.

The gas release rate (mL min^{-1}) of a freshly prepared batch of mMST (LS-5) stored as 15 wt % suspension at a pH of 4.0 was measured over time (see Figure S1 in

Supporting Information). The preparation of this batch of mMST featured washing of the mMST solids with pH 7.0 ultrapure water followed by briefly air drying on the filter. The solids were then suspended in water and the pH of the suspension adjusted to pH 4.0 with dilute nitric acid.

Initially the release rate measured approximately 0.15 mL min^{-1} (per 125 g of 15 wt % slurry) and rapidly decreased by an order of magnitude within 2 days and two orders of magnitude after about 20 days. Four weeks after the preparation of the mMST, the gas release rate was 1.1E-03 mL min^{-1}. Thus, after four weeks the gas release rate per gram of mMST slurry measured 8.8E-06 mL min^{-1}g^{-1}. Using a value of 1.10 g mL^{-1} for the density of the 15 wt % slurry of mMST, the release rate on a slurry volume basis is approximately 14 mL day^{-1}L^{-1}.

Two additional syntheses of mMST were performed with different washing conditions to determine if the washing conditions affected post-synthesis gas release. The standard preparation of the mMST isolates the solids by filtration followed by a pH 7.0 water wash (LS-5). After washing and final filtration, the solids are suspended in water to a solids concentration of 15 wt % and the pH of the suspension adjusted to 4.0 with nitric acid. This washing step of the procedure was modified to incorporate either an acidic wash (pH 4, sample LS-6) or alkaline wash (pH 10, sample LS-7). In the case of the alkaline wash, the final suspension was also adjusted to a pH of 10, rather than a pH of 4.

It was observed that after the acidic and basic washes the mMST suspensions exhibited similar gas release to the batch of material washed with pH 7.0 water (see Figure S1). Closer inspection of the initial gas release rates revealed that the mMST solids washed with the alkaline wash were initially lower than those with the neutral or acidic wash waters. In fact, the gas release rate of the alkaline washed mMST solids initially measured about an order of magnitude lower than that of the mMST solids washed with neutral or acidic wash water. During the first four hours of measurements, the rate of gas release increased to about 0.025 mL min^{-1} and then began to decrease similarly to that observed with the neutral and acidic washed mMST materials. After 2 days the gas release measurements are not statistically different among the different batches of mMST.

Hydrogen peroxide is well known to be less stable in alkaline solutions compared to neutral or acidic solutions.[12] Thus, the observed behavior suggests that the alkaline wash may have reduced the residual hydrogen peroxide that decomposes to release oxygen. Regardless of the pH of the wash water, the quantity of post-synthesis gas released from the mMST material is sufficient to require vented containers for the shipment and storage of large quantities of material.

Figure 1 provides a plot of the measured gas release rate (mL min^{-1}) versus elapsed time (days) for a freshly prepared batch of mMST at a temperature of 49 °C (LS-8) compared to the results from a room temperature experiment performed using the same round bottom flask apparatus (LS-9). The gas release rate at elevated temperature is consistently higher than the measured rates at room temperature. Initially the release rate at 49 °C measured approximately 0.525 mL min^{-1} and decreased by an order of magnitude in less than one day. After one month the release rate still measured approximately 2.7 times the rate at room temperature.

Solids Settling Characteristics

MST and mMST are fine particulate solids having particle sizes in the range of about 1 – 20 microns. Settling characteristics of the MST and mMST particles are important in assessing nuclear criticality safety upon settling in batch contact reactors within operating and planned pretreatment facilities at the Savannah River Site.[4,5] Resuspension of densely-packed solids can be an engineering concern in large batch reactors. Thus, we performed a limited number of settling tests to compare the settling characteristics of mMST and MST materials.

Figure 2 provides plots of the height of the settled solids (mm) versus settling time (hours) for the extreme pH conditions tested with each sorbent material. Initially, the height of each of the suspensions measured 17.5 mm. After 2 hours of settling, the height of the settled MST solids measured about 50% of the initial suspension height compared to about 58% for the mMST solids. The slower settling of the mMST suspensions is consistent with particle size measurements that showed a larger fraction of fines in mMST compared to MST.[8]

After 2 hours, the rate of settling decreases appreciably for both materials due to hindered settling. After 20 hours, both MST suspensions settled to about 40% of the initial height. The mMST suspensions exhibited slower settling rates in the hindered settling region reaching settled solids heights of 54% and 48% for the pH 4.84 and pH 10 suspensions, respectively. The overall reduced extent of settling for the mMST solids in this region is attributed to higher surface area and intraparticle porosity of the mMST solids compared to MST.[6] The higher porosity makes it more difficult to remove water restricting further settling of the solids.

Table 4 contains the results of the settled density measurements for mMST in both 0.5 M and 5.6 M Na solutions, and at centrifuge speeds of 6.3 x g and 1400 x g. As expected, the density of the settled solids increases with increased centrifuge speed. The density also increases slightly with increasing suspended solids concentrations, with the exception of 0.15 g/L at 6.3 x g. The effect of sodium concentration is minor, and in general does not produce a measurable difference in the density, for the sodium concentrations tested here.

Results from the gravity settling tests for MST and mMST in salt solutions with varying sodium concentrations (4.6, 5.6, and 6.6 M) are shown in Figure 3. The rates were determined by measuring the height of the clear supernate at the top of the graduated cylinder over time. As can be seen from the graph, the mMST settling rate is much slower than the MST settling rate, indicating the mMST contains a larger fraction of smaller diameter particles.[8] For MST, there did not appear to be a measurable effect of the sodium concentration on the settling rate. For mMST the settling rate was slightly lower in the highest sodium concentration solution. This is the expected trend, as the viscosity of the solution increases with increasing ionic strength.

High Temperature X-Ray Diffraction Analyses (HTXRD)

Previously, we reported that the mMST exhibited good thermal stability based on thermal gravimetric and differential scanning calorimetry measurements.[6] After use, MST and mMST will be incorporated into a borosilicate glass wasteform for disposal. To provide an indication of solid phase transformations that may occur during the early stages of heating in a glass melter, we obtained X-ray powder diffraction data upon heating MST and mMST at temperatures ranging from 25 to 800 °C.

A summary of the phases identified in these high temperature XRD experiments can be found in Table 5. Both MST and mMST samples are amorphous materials, but several crystalline phases were observed as the materials were heated from 25 to 800 °C. For MST, poorly crystalline sodium titanium oxide hydrate ($Na_2Ti_2O_4(OH)_2$) was the only phase detected in both the as-received and pH-adjusted samples from 25 to 300 °C. As the powders were heated, the unit cell for this titanate phase contracted along the a-axis in the direction of the (200) plane. The contraction continued until the phase disappeared above 300 °C. In the 600 °C scan, differences between the as-received and pH-adjusted samples began to emerge. Metastable phases, $Na_{0.8}Ti_4O_8$, (only found at 600 °C) and $Na_2Ti_6O_{13}$ or $Na_2O^{\cdot}6TiO_2$ (stable to 800 °C) appear in both samples. However, in the pH-adjusted sample the two titanium dioxide polymorphs, anatase and rutile, were also identified at 600 °C. The anatase completely transformed to rutile somewhere between 600 - 800 °C. At 800 °C, an additional sodium titanate, $Na_2Ti_3O_7$ or $Na_2O^{\cdot}3TiO_2$, appears in the as-received sample. The room temperature XRD analysis of the HTXRD residues found the same phases that were present at 800 °C in the high temperature scans.

The HTXRD results for the mMST decomposition were similar to those for the baseline MST with a few notable differences. Although sodium titanium oxide hydrate ($Na_2Ti_2O_4(OH)_2$) or a similar compound, such as sodium peroxotitanate, may also be present in both samples from 25 °C to 300 °C, the main phase identified was nano-crystalline anatase. Both the as-received and pH-adjusted samples exhibit the same unit cell contraction along the a-axis in the direction of the (200) plane as mentioned above. The main difference in the decomposition for the mMST samples occurs at 600 °C, with the metastable phase, $Na_{0.8}Ti_4O_8$, only observed in the pH-adjusted sample. As in the monosodium titanate HTXRD runs, at 800 °C and in the HTXRD residues, rutile and $Na_2Ti_6O_{13}$ were identified.

Iodometric Titration Analysis

Several batches of mMST of different ages, both lab prepared and vendor prepared, were analyzed using the iodometric titration method. The amount of peroxide in the samples was found to decrease linearly with the age of the sample (Figure 4). There was one exception to this trend, sample LS-8. This lab prepared sample had been held at 49 °C for one month (for gas release measurements), whereas the other samples had not been exposed to elevated temperatures. Sample LS-8 contained approximately one-half the amount of peroxide of a slightly older sample, LS-7.

Results from the titration of mMST samples synthesized using different H_2O_2:Ti ratios showed a logarithmic trend between the amount of peroxide added during the synthesis and the amount of peroxide present in the product.

Affect of Alkaline Solution on Peroxide Content

Results from the effect of salt solution experiments showed a significant decrease in peroxide content after exposure to the two salt solutions. The experiment using only distilled water showed a peroxide content within error of the previous results for this sample (Optima Batch 06-QAB-0139). This control experiment was designed to account for any loss of material during the soaking and recovery process, since the initial weight added to the salt solutions was used to determine the peroxide:Ti ratio. The peroxide:Ti ratios for these samples are presented in Table 6. The salt solution containing only sodium (SWS-1-2010) resulted in the largest reduction of peroxide content, to only about 42% of the control value. The Sr-containing salt solution (SWS-1-2008) resulted in a slightly higher peroxide content, 58% of the control value.

Affect of Age on mMST Performance

Figures 5-6 show the Pu and Np decontamination factors (DFs) obtained for each of the samples listed in Table 3. As can be seen from Figure 5, the Pu DFs for the oldest sample (LS-2) were significantly lower than the Pu DFs obtained with the other samples. Sample LS-8, which iodometric titration indicated had a reduced amount of peroxide, also showed lower Pu DFs. The Pu DFs for samples LS-7 and LS-9 were not statistically different at the 6 and 24 hour sampling times. Plutonium content in the samples from the 12 hour sampling time fell below the method detection limit, resulting in greater than values calculated for the DFs. Figure 6 shows the DF values for ^{237}Np. In this case LS-8 shows the highest ^{237}Np DFs, whereas the DFs for the other samples are not statistically different from each other. It is difficult to draw any conclusions regarding the ^{85}Sr removal, since ^{85}Sr concentrations in many of the samples fell below the method detection limit, resulting in greater than values being obtained for the DFs. However, it does appear that LS-2, the oldest sample, resulted in the least Sr removal, as the results for all time points for this sample were above the method detection limit. At the 6 hour time point, the Sr DF for LS-2 is clearly lower than that obtained for LS-8 and LS-9; however, at the later time points this conclusion cannot be drawn as the value falls within error of the minimum DF values for LS-8 and LS-9. There appears to be no effect of age on the uranium sorption of these materials. None of the samples appear to adsorb a measurable amount of uranium.

The performance of sample LS-2 has been measured a total of six times over a time period of approximately 56 months, including the results shown above.[9] Testing up to an age of 30 months showed no measurable decrease in Pu DF. However, the final testing at an age of 56.4 months showed a significant decrease in Pu DF to a value only 18% of the Pu DF averaged over the earlier test dates (Figure 7).

Testing was also performed using a U only simulant with high sorbent loadings (3.0 g/L) to determine if mMST begins to absorb uranium as the peroxide is lost with age. Similar testing with uranium only simulant was performed with these same batches of MST (Optima 00-QAB-417) and mMST (Optima 06-QAB-0139) 26 months earlier. These earlier results were used for comparison to determine if the loss of peroxide over time caused an increase in uranium uptake by the mMST. For the MST there is no measurable change in the uranium sorption between the two sets of data. For the mMST, there is an increase in the uranium sorption measured at the 12-hour time point (see Figure 8). The decontamination factor measured in 2009 was 1.21 ± 0.0109 compared to 1.10 ± 0.0178 in 2007.

CONCLUSIONS

The mMST material has been characterized to determine the gas release characteristics, thermal stability, settling characteristics, and peroxide content. Several characterizations also focused on how the material changes with age in order to establish a shelf-life of the material. The mMST material was found to release oxygen rapidly during the synthesis and continue to release gas at diminishing rates for an extended period of time. The short-term (<2 days) gas release rate was diminished by washing the mMST solids with alkaline water (pH 10). After several days the rate of post-synthesis gas release appeared similar regardless of the washing conditions. The quantity of post-synthesis gas released from the mMST material is sufficient to require vented containers for the shipment and storage of large quantities of material.

In the settling tests, mMST was found to settle at a slower rate than MST. The extent of mMST solids settling was also dependent on pH, unlike MST. Increased settling of mMST occurred with an increase in pH of the suspension. The ionic strength of solution did not appear to have a large effect on the settling rates of MST or mMST. For mMST there was a slight decrease in the settling rate in the highest sodium concentration tested, while there was no measurable change in settling rate for MST.

Although MST and mMST are amorphous materials, several crystalline phases were identified in the HTXRD analyses as these samples were heated from 25 to 800 °C. A major difference between the baseline and modified MST samples was that the major phase for mMST from 25 to 300 °C was nano-crystalline anatase, where as poorly crystalline sodium titanium oxide hydrate ($Na_2Ti_2O_4(OH)_2$) was the only phase detected in the same temperature range for baseline MST. Differences in the pH adjusted and as-received samples are only observed at temperatures of 600 °C and above for both the baseline and modified MST samples.

Iodometric titration was used to determine the peroxide content of the mMST samples. Results from these tests indicated a loss of peroxide content with age or extended exposure to elevated temperatures. A logarithmic trend between peroxide added during the synthesis and peroxide present in the resulting materials was also determined using this method. Further testing indicated a loss of peroxide content after exposure of the material to an alkaline salt solution, similar in composition to the simulated waste solutions used for performance testing. Performance testing also indicated some loss of actinide removal efficiency with age, especially for samples over four years of age.

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TABLES

Table 1. Composition of Salt Solutions.

Component	Units	SWS-1-2010	SWS-1-2008
$NaNO_3$	M	2.60	2.60
NaOH	M	1.33	1.33
Na_2SO_4	M	0.581	0.521
$NaAl(OH)_4$	M	0	0.429
$NaNO_2$	M	0.149	0.134
Na_2CO_3	M	0.029	0.026
Total Na	M	5.6	5.6
Total Sr	mg L^{-1}	0	5.5

Table 2. Age of mMST Samples.

Sample	Age at Time of Testing in years
LS-2	4.70
LS-7	0.30
LS-8*	0.19
LS-9	0.09

*Sample LS-8 was used in the gas release experiment at elevated temperature, therefore this sample was held at 49 °C for one month. Iodometric titration analysis indicates the peroxide content for this sample is lower than predicted based on age.

Table 3. Composition of Simulated Waste Solutions

Component	SWS-9-2009		SWS-8-2007	
	Target	Measured	Target	Measured
$NaNO_3$	2.60 M	2.35 ± 0.18 M	2.60 M	3.11 ± 0.31 M
NaOH	1.33 M	1.27 ± 0.13 M	1.33 M	1.38 ± 0.138 M
Na_2SO_4	0.521 M	0.531 ± 0.040 M	0.521 M	0.606 ± 0.0909 M
$NaAl(OH)_4$	0.429 M	0.389 ± 0.039 M	0.429 M	0.461 ± 0.0461 M
$NaNO_2$	0.134 M	0.127 ± 0.010 M	0.134 M	0.160 ± 0.032 M
Na_2CO_3	0.0260 M	0.0302 ± 0.0030	0.026 M	0.0314 ± 0.00471 M
Total Na^+	5.6 M	5.05 ± 0.01 M	5.60 M	5.10 ± 0.51 M
Total Sr	0.6 mg/L	0.676 ± 0.026 mg/L	0	-
^{85}Sr	≥10,000 dpm/mL	12,000 dmp/mL	0	-
Total Pu	0.2 mg/L	0.17 ± 0.033 mg/L	0	-
^{237}Np	0.5 mg/L	0.463 ± 0.026 mg/L	0	-
Total U	10 mg/L	10.1 ± 0.36 mg/L	10 mg/L	9.55 ± 0.29 mg/L
^{137}Cs	≥30,000 dpm/mL	123,000 ± 6130 dpm/mL	0	-

Table 4. Results of Settled Density Measurements for mMST.

	Sodium Concentration of Settling Fluid is 5.6 M		Sodium Concentration of Settling Fluid is 0.5 M	
Suspended Solids Conc. (g/mL)	**Ave. Settled Solids Conc. (g/mL) at 6.3 x g**	**St. Dev. of Settled Solids Conc. (g/mL) at 6.3 x g**	**Ave. Settled Solids Conc. (g/mL) at 6.3 x g**	**St. Dev. of Settled Solids Conc. (g/mL) at 6.3 x g**
0.03	0.188	0.0073	0.212	0.0150
0.09	0.201	0.0018	0.214	0.0051
0.15	0.197	0.0000	0.197	0.0000
	Sodium Concentration of Settling Fluid is 5.6 M		**Sodium Concentration of Settling Fluid is 0.5 M**	
Suspended Solids Conc. (g/mL)	**Ave. Settled Solids Conc. (g/mL) at 1400 x g**	**St. Dev. of Settled Solids Conc. (g/mL) at 1400 x g**	**Ave. Settled Solids Conc. (g/mL) at 1400 x g**	**St. Dev. of Settled Solids Conc. (g/mL) at 1400 x g**
0.03	0.300	0.0196	0.318	0.0039
0.09	0.338	0.0036	0.342	0.0020
0.15	0.365	0.0118	0.348	0.0052

Table 5. Summary of Phases Identified in HTXRD Experiments.

Baseline MST As Received		
Compound	**Formula**	**Temperature (°C) in He**
Sodium Titanium Oxide Hydrate	$Na_2Ti_2O_4(OH)_2$	25-300
Sodium Titanium Oxide	$Na_{0.8}Ti_4O_8$	600
Sodium Titanium Oxide	$Na_2Ti_6O_{13}$	600-800, residue
Sodium Titanium Oxide	$Na_2Ti_3O_7$	800, residue
Baseline MST pH Adjusted		
Compound	**Formula**	**Temperature (°C) in He**
Sodium Titanium Oxide Hydrate	$Na_2Ti_2O_4(OH)_2$	25-300
Sodium Titanium Oxide	$Na_{0.8}Ti_4O_8$	600
Anatase	TiO_2	600
Sodium Titanium Oxide	$Na_2Ti_6O_{13}$	600-800, residue
Rutile	TiO_2	600-800, residue
mMST As Received		
Compound	**Formula**	**Temperature (°C) in He**
Sodium Titanium Oxide Hydrate	$Na_2Ti_2O_4(OH)_2$	25-300 (?)
Anatase	TiO2	25-600
Rutile	TiO_2	800, residue
Sodium Titanium Oxide	$Na_2Ti_6O_{13}$	800, residue
mMST pH Adjusted		
Compound	**Formula**	**Temperature (°C) in He**
Sodium Titanium Oxide Hydrate	$Na_2Ti_2O_4(OH)_2$	25-300(?)
Anatase	TiO2	25-600
Sodium Titanium Oxide	$Na_{0.8}Ti_4O_8$	600
Rutile	TiO_2	800, residue
Sodium Titanium Oxide	$Na_2Ti_6O_{13}$	800, residue

Table 6. Peroxide:Ti Ratios for mMST Optima Batch 06-QAB-0139.

mMST Sample	Salt Solution	Peroxide/Ti ratio	% of Control Value
06-QAB-0139	None	0.202 ± 0.0018	n/a
06-QAB-0139	Control – Water	0.211 ± 0.0086	100
06-QAB-0139	SWS-1-2010	0.089 ± 0.0034	42.2
06-QAB-0139	SWS-1-2008	0.123 ± 0.0034	58.3

FIGURE CAPTIONS

Figure 1. Comparison of gas release rates from mMST at room temperature (diamonds, solid line) and at 49 °C (squares, dashed line).

Figure 2. Height of Settled Solids versus Settling Time for mMST (black) at a pH of 4.84 (filled circles) and a pH of 10 (open circles) and Baseline MST (gray) at a pH of 6 (open squares) and a pH of 10.47 (filled squares).

Figure 3. MST (filled symbols) and mMST (open symbols) fines settling rates vs. time in 4.6 M (circles), 5.6 M (diamonds), and 6.6 M (triangles) Na concentration salt solutions.

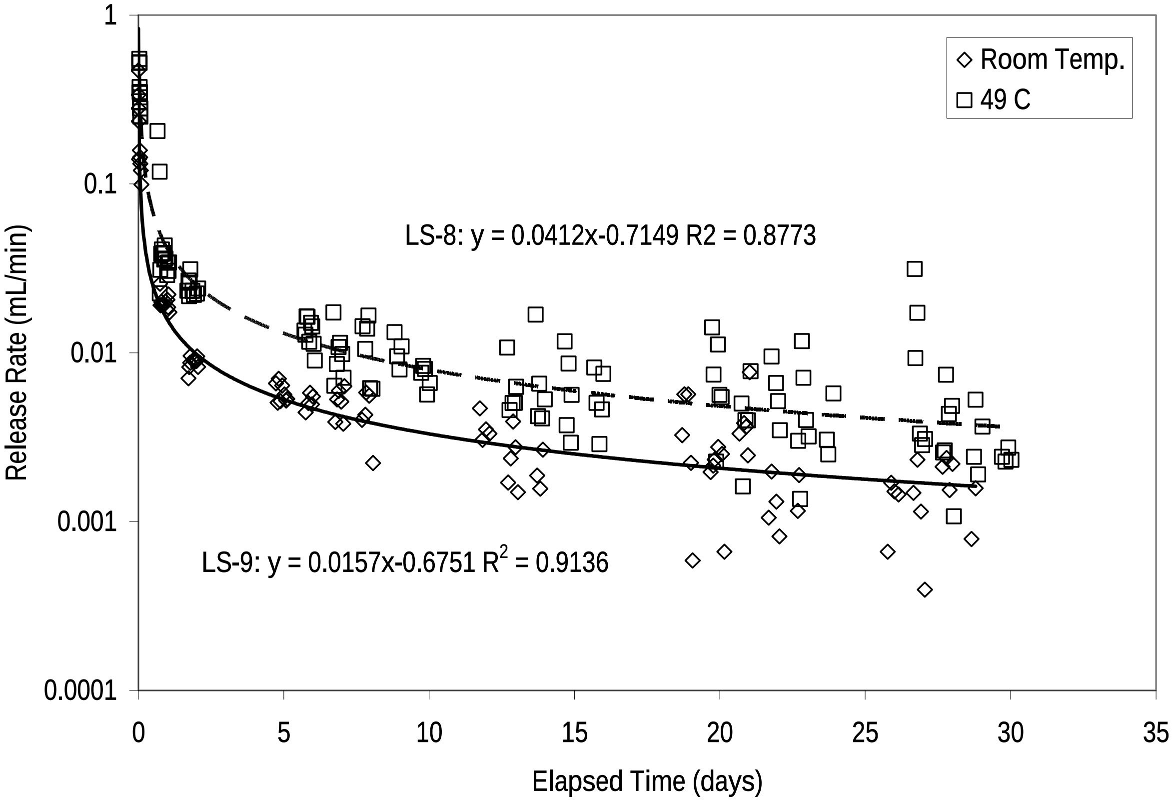
Figure 4. Peroxide content of mMST samples vs. age (LS-8 is excluded from the linear regression).

Figure 5. Pu DF versus contact time for LS-2, age 4.7 yr (diamonds), LS-7, age 0.3 yr (squares), LS-8, age 0.19 yr (accelerated aging) (triangles) and LS-9, age 0.09 yr (circles).

Figure 6. ^{237}Np DF versus contact time for LS-2, age 4.7 yr (diamonds), LS-7, age 0.3 yr (squares), LS-8, age 0.19 yr (accelerated aging) (triangles) and LS-9, age 0.09 yr (circles).

Figure 7. 6-h (diamonds) and 12-h (squares) Pu DFs for LS-2 as a function of elapsed time since preparation.

Figure 8. Uranium decontamination factors for mMST (Optima 06-QAB-0139) measured in October 2007 (gray) and in December 2009 (black).



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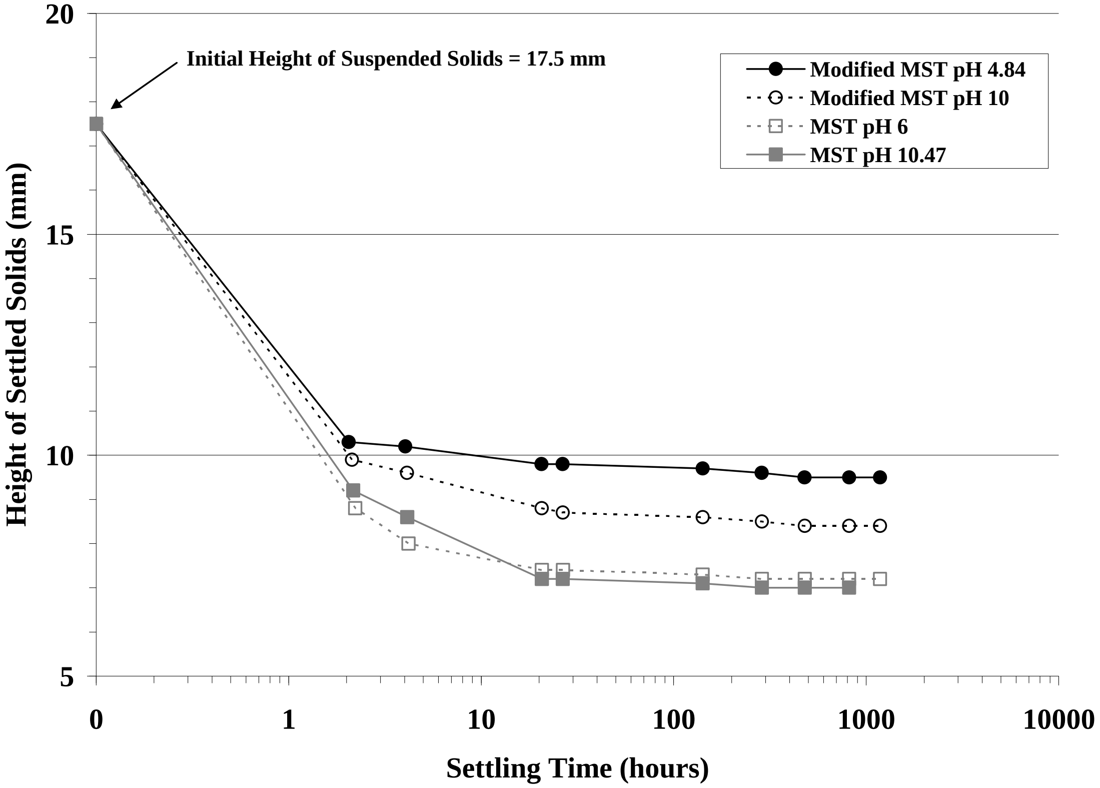

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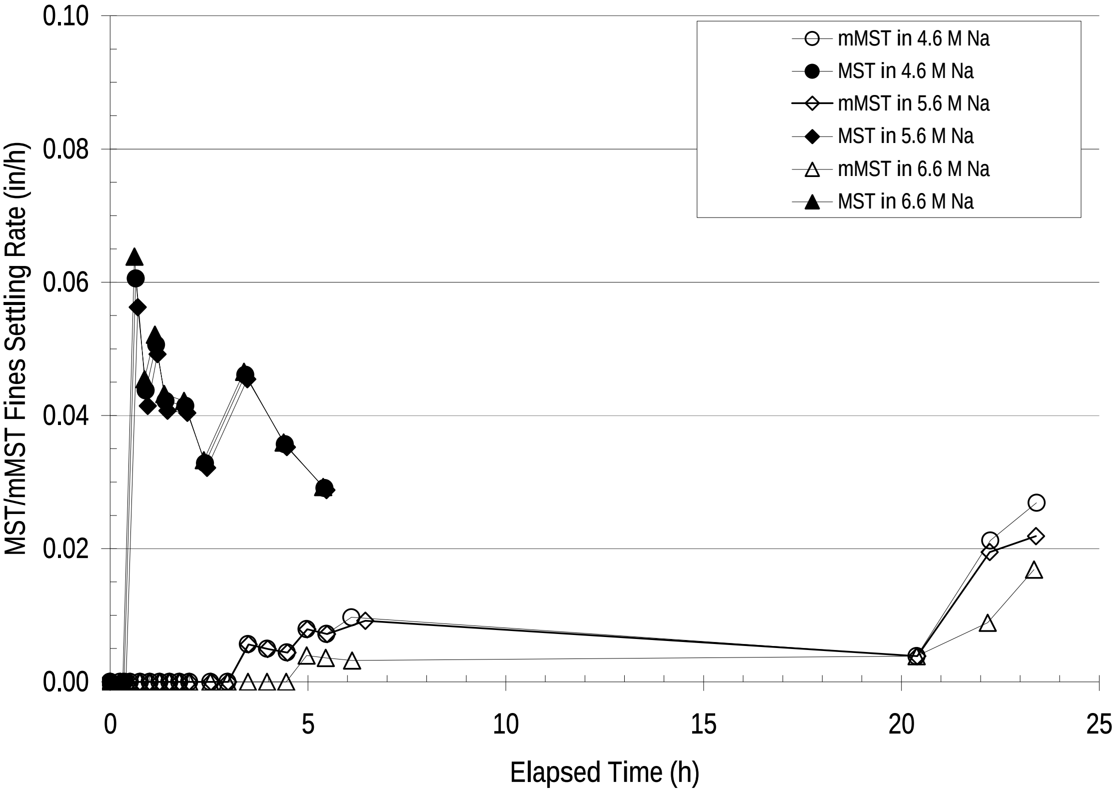

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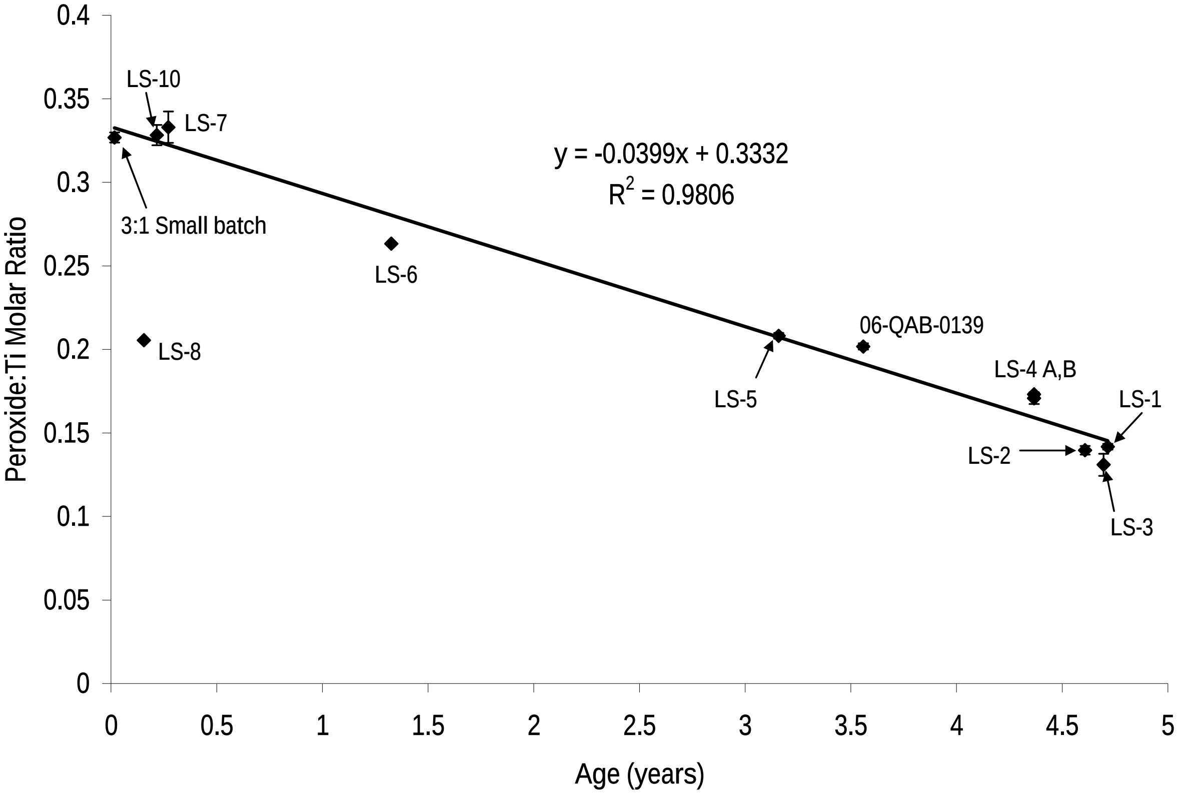

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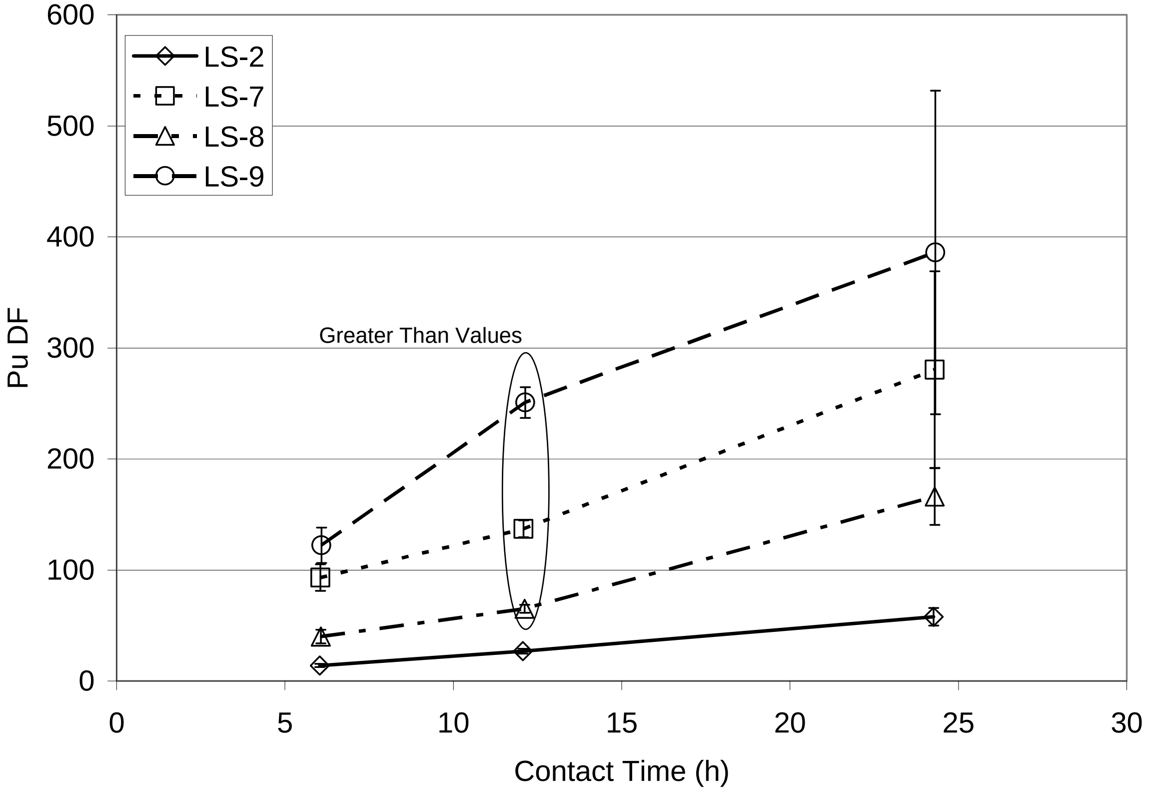

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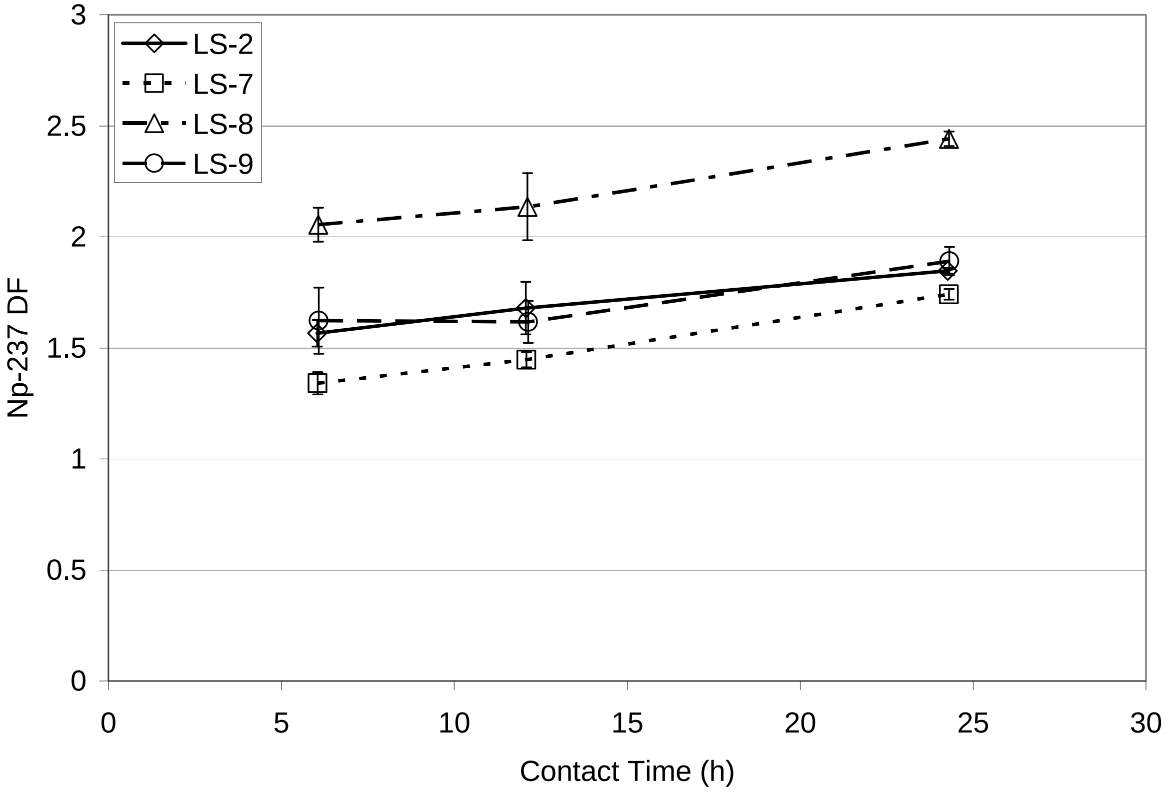

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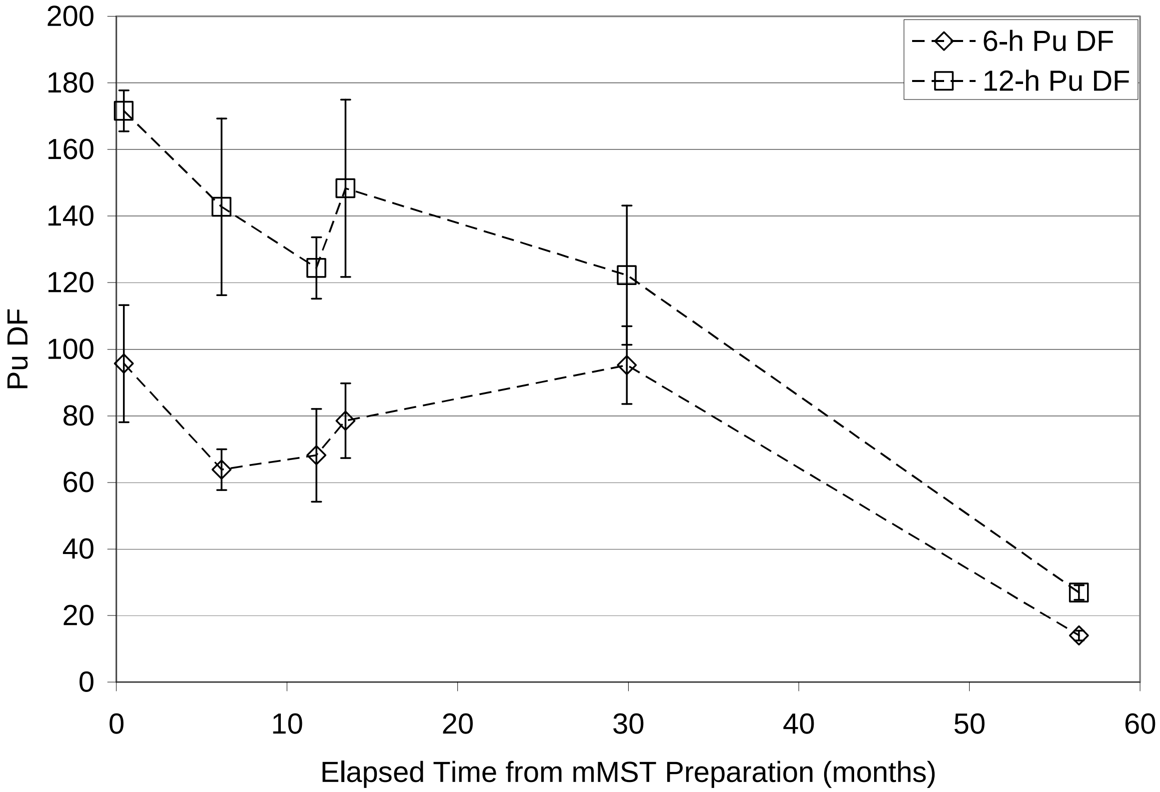

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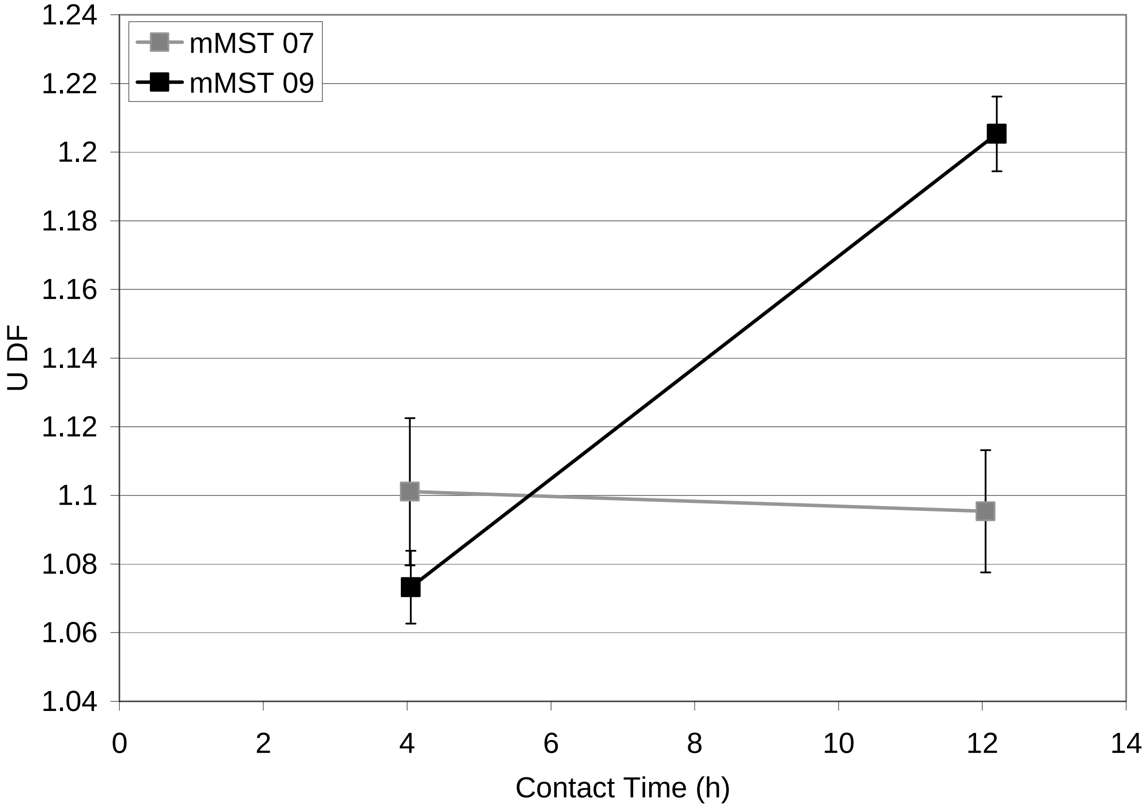

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