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# **The Hydrothermal Reactions of Monosodium Titanate (MST), Crystalline Silicotitanate (CST) and Sludge in the Modular Salt Process (MSP): A Literature Survey**

F. F. Fondeur  
F. M. Pennebaker  
S. D. Fink

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Savannah River National Laboratory  
Savannah River Nuclear Solutions  
Aiken, SC 29808

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## REVIEWS AND APPROVALS

Authors:

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F. F. Fondeur Separations and Actinide Science Programs	Date
--	------

Technical Reviewer:

---

W. R. Wilmarth Environmental Management	Date
--	------

Approva;:

---

S. D. Fink, Manager Separation and Actinide Science Programs	Date
---	------

---

F. M. Pennebaker, Manager E&CPT Research Programs	Date
--	------

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S. L. Marra, Manager, Environmental & Chemical Process Technology Research Programs	Date
--	------

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T. H. Huff, Manager, SCIX Engineering	Date
--	------

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### *Executive Summary*

The use of crystalline silicotitanate (CST) is proposed for an at-tank process to treat High Level Waste at the Savannah River Site. The proposed configuration includes deployment of ion exchange columns suspended in the risers of existing tanks to process salt waste without building a new facility. The CST is available in an engineered form, designated as IE-911-CW, from UOP. Prior data indicates CST has a proclivity to agglomerate from deposits of silica rich compounds present in the alkaline waste solutions. This report documents the prior literature and provides guidance for the design and operations that include CST to mitigate that risk.

The proposed operation will also add monosodium titanate (MST) to the supernate of the tank prior to the ion exchange operation to remove strontium and select alpha-emitting actinides. The cesium loaded CST is ground and then passed forward to the sludge washing tank as feed to the Defense Waste Processing Facility (DWPF). Similarly, the MST will be transferred to the sludge washing tank. Sludge processing includes the potential to leach aluminum from the solids at elevated temperature (e.g., 65 °C) using concentrated (3M) sodium hydroxide solutions. Prior literature indicates that both CST and MST will agglomerate and form higher yield stress slurries with exposure to elevated temperatures. This report assessed that data and provides guidance on minimizing the impact of CST and MST on sludge transfer and aluminum leaching sludge.

Evaluation of pertinent literature to the Small Column Ion Exchange (SCIX) process leads to the following recommendations.

- Removal of all excess material from IE-911 before utilization in a packed bed column is required to minimize aluminosilicate formation during supernate processing. This includes removal of excess silica, niobium, lead, iron, chloride, fines and ungelled zirconia. This may be accomplished by washing with caustic solution in a non-radioactive facility.
- Any untreated supernate must have an aluminum and silicon concentration at or below the saturation concentration for forming aluminosilicate gels. An empirical observation has been to keep the product of the aluminum and silicon concentration below  $1 \text{ E-4 M}^2$  (for example,  $[\text{Al}] * [\text{Si}] < 1 \text{ E-4 M}^2$ ). The combination of IE-911 particles completely devoid of excess materials and an under-saturated supernate relative to aluminosilicate formation minimize the formation of gel or crystalline aluminosilicates at any temperature.
- In the unlikely event of loss of cooling resulting in the temperature in the ion exchange column exceeding 55 °C, minimize the length of time the column remains at this temperature. Data indicate remaining isothermal longer than a week may generate aluminosilicates. Aluminosilicates will deposit on walls and bed particles creating caking and interfere with the cesium-sodium exchange in the IE-911 particles.
- Similarly if cesium loaded IE-911 is dumped into a waste tank, avoid mound configurations and conditions that can lead to high temperatures (i.e., temperatures larger than 55 °C) since this can accelerate the formation of

aluminosilicates, chemically bridge the sludge and IE-911 particles, or release some cesium.

- Further studies are needed to evaluate the effect of having cesium loaded IE-911 particles present during aluminum leaching of sludge. Under aluminum leaching conditions, soluble aluminum from the sludge and leached silicon from IE-911 may form aluminosilicate. Similarly, the cesium loaded IE-911 particles can release cesium at 65 °C (approximately 5% of the loaded cesium is released at 65 °C). A series of tests are being currently conducted to determine the silicon leaching and cesium release of IE-911 under aluminum leaching conditions.
- For monosodium titanates no conditions were found in the SCIX process that can lead to the decomposition (leaching) of MST or the release of strontium and actinides from MST. However, titanium leaching and aggregation are risk factors.

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## LIST OF ABBREVIATIONS

CST	Crystalline Silicotitanate
HFIR	High Flux Isotope Reactor
MST	Monosodium Titanate
NAS	Sodium Aluminosilicate
ORNL	Oak Ridge National Laboratory
RMF	Rotary Microfilter
SCIX	Small Column Ion Exchange
SRNL	Savannah River National Laboratory
SRS	Savannah River Site



## 1. *Introduction*

The Small Column Ion Exchange (SCIX) Process seeks to deploy equipment to remove the Cs, Sr, and select actinides from the high level waste salt solutions using existing waste tanks for the shielding. The process will add monosodium titanate (MST) to the waste tank (i.e., Tank 41H) to sorb strontium and selected actinides (reducing Sr concentration to less than 40 nCi per gram and total alpha concentration to less than 20 nCi per gram or achieve about the same decontamination as the Salt Waste Processing Facility or SWPF),<sup>1,2</sup> remove the MST and entrained sludge with an in-riser rotary microfilter (RMF), and subsequently use an ion-exchange column containing crystalline silicotitanate (CST) to remove the Cs (to approximately 45 nCi per gram of supernate or about the same decontamination as SWPF).<sup>2</sup> After loaded with Cs, the CST will be ground to reduce its size ( $< 177\text{ }\mu\text{m}$  or 80 mesh) and dumped into a waste tank (e.g., Tank 40H, 41H or 51H) after processing salt supernate.<sup>3</sup> The MST, sludge, and CST (if dumped to Tank 41H) in the waste tank will be periodically transported to a sludge tank, and ultimately be transported to the Defense Waste Processing Facility (DWPF).

Since retrieval of sludge containing CST and MST is not routinely performed at SRS and previous studies revealed the hydrothermal instability of unwashed CST in SRS waste,<sup>1</sup> the project team foresees possible risks in dispersing sludge with CST and MST. Therefore, SRS personnel issued a Task Technical Request to summarize pertinent publications related to this risk.<sup>4</sup> A Task Technical Quality Assurance Plan was issued to address this risk.<sup>5</sup> This report will summarize previous research on the compatibility between CST and SRS wastes under different conditions and assess possible reactions that may result from untested and likely conditions that may occur during SCIX. In particular, the summary will assess any unintended reactions that may lead to process upsets and recommend additional experimental studies that can reduce these risks

The chemical formula of CST is  $\text{Na}_2(\text{H}_2\text{O})_2[(\text{Ti}_2\text{O}_3(\text{OH})(\text{SiO}_4)_2]$  (sodium form).<sup>6</sup> CST contains two different size pores.<sup>7</sup> In one pore system only sodium and hydrogen can move freely. These pores are connected to a larger pore where cesium, hydrogen and sodium can move freely. In these larger pores is where cesium sorbs to the CST. IE-911 is an aggregate of CST glued together by zirconium oxide or zirconium hydroxide.

CST was shown to integrate well with High Level Waste system (HLW) in Savannah River Site (SRS).<sup>8</sup> The application of CST in the SCIX process presents new challenges and risks beyond those identified previously.<sup>9</sup> Table 1 gives a summary of potential scenarios that are considered in this report. As can be seen from Table 1, a change in supernate chemistry or high temperatures can lead to hydrodynamics and ion exchange difficulties as well as unexpected reactions downstream from the SCIX process

Table 1. Possible “upset” scenarios in the SCIX process

Supernate	Filter	Ion Exchange	Grinder	Aluminum Leaching
Unstable solution (saturated or supersaturated). Supernate may contain $\text{AlO}_2^-$ , $\text{SiO}_3^{2-}$ , $\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{F}^-$ , oxalate and other organic salts	-Plugging (flux reduction) -Fines bleeding -Corrosion & wear	-Changes in ion exchange (sodium molarity larger than 6 or large potassium concentration) or desorption of Cs due to high temperatures ( $> 55^\circ\text{C}$ ) -Problems sluicing IE-911 from the column -Large pressure drop due to temperatures larger than $55^\circ\text{C}$ (aluminosilicate formation)	-Fails to reduce particle size -Over reduce particle size -Grinder chemistry (that may be mixed with the grounded particles) may be incompatible with downstream processes	- Conditions at $65^\circ\text{C}$ can lead to: Aluminosilicate formation (between silicon leached from IE-911 and soluble aluminum) and cesium desorption from IE-911

## 2. Discussion and Results

### 2.1 Particle Precipitation: Dissolved Salt Cake Blending

Preparation of the waste for the SCIX process includes blending of dissolved salt cake supernate with inhibited water. Saltcake is a wet agglomeration of four different types of materials: water-soluble salt crystals (nominally 60 vol %), interstitial liquid (nominally 30 vol %), insoluble solids ( $<1$  vol %), and gaseous voids (nominally 10 vol %).<sup>10</sup> The sodium molarity of dissolved saltcake is approximately 8 molar.<sup>10</sup> High sodium molarity can interfere with ion exchange processes of IE-911. The optimal sodium molarity of dissolved saltcake supernate for cesium ion exchange with IE-911 (a key process in SCIX) is approximately 6 molar. To achieve a lower (6 M) sodium molarity, high ionic strength supernate are blended with low sodium solutions (or supernate).

Blending different streams changes the ionic strength and the concentration of species that may lead to precipitation. A survey of the literature on salt and hydroxide that typically precipitates from high level waste supernate in Hanford revealed several compounds that include double anions and cations precipitates may form in SRS supernate.<sup>11</sup>

Table 2 shows a list of the possible compounds that may form in SRS supernate. In the same table, data regarding their solubility (that of the anions to form the salt compound) and likelihood of forming in SRS supernate is also shown. The solubilities in Table 2

were computationally determined<sup>12</sup> where the concentration of the suspecting anions was incremented while maintaining the sodium molarity constant at 6 molar (by proportionally reducing the nitrate concentration). As can be seen from Table 2, any salt containing fluoride is unlikely to form in SRS supernate due to their low starting concentration although these compounds are seen in Hanford supernate.<sup>13</sup> On the other hand, oxalate and aluminum hydroxide are expected to form at 25 °C since the starting concentrations of these species are close to the calculated solubilities (i.e. sludge typically has high concentrations of aluminum, hydroxides and oxalate).

Table 2. Possible salt compounds that may precipitate at 6 M sodium ion concentration.

Precipitate	~ Solubility (M) in average, high hydroxide and high nitrate simulant	Expected	Reason
$\text{Na}_7\text{F}(\text{PO}_4)_2$ , $\text{Na}_2\text{F}(\text{SO}_4)$	0.16, 0.13, 0.23	No	Low initial [F]
$\text{Na}_2\text{C}_2\text{O}_4^*$	0.005, 0.011, 0.004	Yes	Tank 7
$\text{NaAl}(\text{OH})_4$	0.34, 0.31, 0.11	Yes	HM sludge
$\text{Na}_6\text{CO}_3(\text{SO}_4)_2$	0.16, 0.09, 0.02	Possible	Both $\text{CO}_3$ and $\text{SO}_4$ present
$\text{Na}_3\text{NO}_3(\text{SO}_4)_2$	0.28, 0.12, 0.3	Possible	Both $\text{NO}_3$ and $\text{SO}_4$ present

\*D. T. Hobbs, "Impacts of Sodium Oxalate on High-Level Waste Processing at the Savannah River Site," WSRC-TR-2003-00120, May 6, 2003

The particles expected to precipitate from the blending process (Table 2) may affect the filtration process in the SCIX process. Although it is difficult to predict the particle size distribution of any precipitate since the details relevant to precipitation such as mixing, temperature, concentrations, initial seeds, and ionic strength are not known before hand, the precipitate's shape can affect filtration rate. As shown in Figure 1, the fiber shape of sodium oxalate (Figure 1) affects settling and filtration rate.

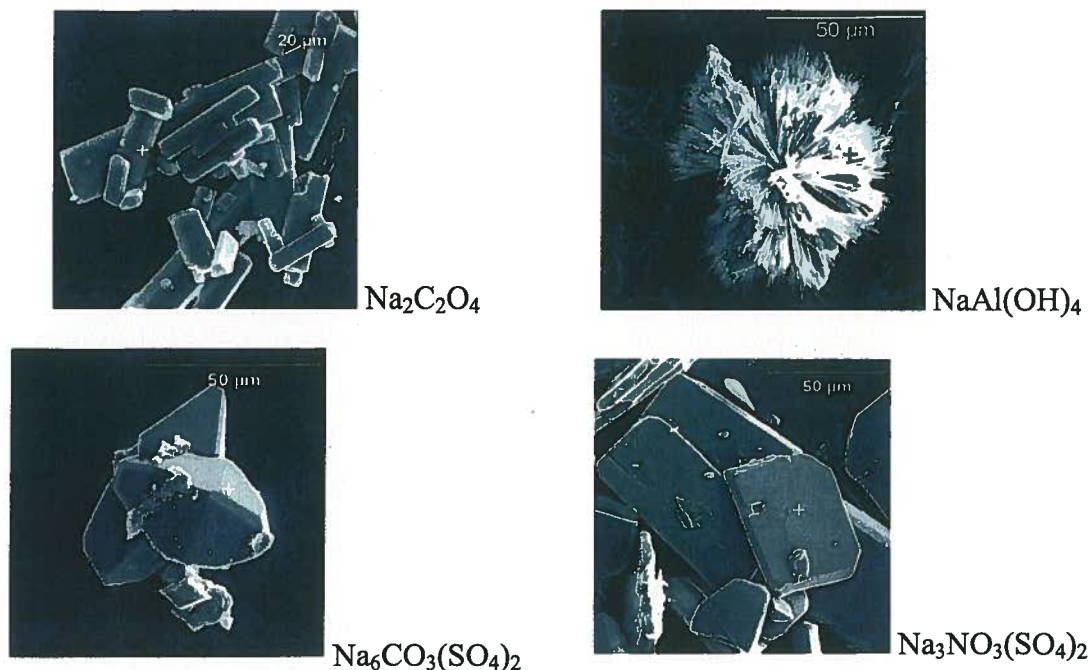
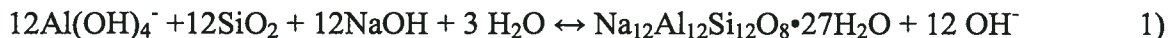


Figure 1. Morphologies of the possible precipitates in SRS supernate

D. L. Herting, R. W. Warrant, and G.H. Cooke, "Identification of Solid Phases in Salt Cake from Hanford Site Waste Tanks," HNF-11585, September 2002

Therefore, a detailed record of planned blending, mixing and evaporation must be evaluated in terms of precipitates and their impacts on the SCIX process. For example, some of the crystals are temperature sensitive (i.e., precipitation may occur at temperatures higher than 30 °C) and if the ion exchange column experiences a high temperature due to loss of cooling some of these particle may form and lead to column pressure increases. Therefore, it is desirable to operate the ion exchange column at 25 °C at all times.

Another particle that can form as a result of supersaturation or saturation is sodium aluminosilicate (NAS). Depending on the silicon, aluminum, and hydroxide concentration in solution as well as the temperature, a gel or a crystalline compound of NAS can form (by homogeneous nucleation). Several reports have detailed the formation of NAS.<sup>14a-14e</sup> It appears that amorphous NAS (NAS<sub>gel</sub>) is a precursor to the formation of crystalline NAS (Zeolite A, nitrated sodalite and nitrated cracrinite). NAS<sub>gel</sub> found in SRS evaporators have the stoichiometric composition listed in equation 1.



The free energy for the reaction listed in equation 1 is shown in equation 2 for homogeneous nucleation.

$$\log\left(\frac{Q}{K}\right)_{NAS_{gel}} = 9.8691 + 13.04 \log[Al(M)] + 11.09 \log[Si(M)] - 13.51 \log[OH(M)] \\ + 15.84 \text{Density}\left(\frac{g}{mL}\right) + 0.0163 \text{Temp}(\text{°C}) \quad 2)$$

Where Q equals  $[Al]^{12} \cdot [Si]^{12} / [OH]^{12}$  and K is Q at equilibrium values.<sup>14a-14c</sup> Equation 2 can be used to predict saturation and supersaturation of a solution relative to the formation of NAS<sub>gel</sub> for the homogeneous nucleation case. Equation 2 can be used to predict the supersaturation of three simulants used by SRNL<sup>15</sup> to be representative of SRS supernate as calculated in Table 3. The density term in Eq. 2 has been previously measured.<sup>16</sup>

Table 3. Estimation of the supersaturation of the three simulant representative of SRS supernate developed by SRNL.<sup>15</sup>

	NAS (moles)*	Al(OH) <sub>3</sub> (moles)*	Sodium Oxalate (moles)*
High Nitrate	9.73 E-4	0.298	0
Average	6.67 E-4	0.213	0
High Hydroxide	4.37 E-5	7 E-3	2.43 E-4
*Obtained by the OLI <sup>®</sup> version 3.1 which contains equation 2.			

Equation 2 can be used to help prevent NAS<sub>gel</sub> formation in dissolved salt cake. A solution with a Q/K value less than  $10^{-14}$  or a  $[Si] \cdot [Al]$  value less than  $3.5 \text{ E-}4 \text{ M}^2$  at a hydroxyl concentration of 1.91 M (or a sodium concentration of 6 M) will not form NAS<sub>gel</sub> at room temperature.<sup>14</sup>

To calculate an estimate of the amount of aluminosilicate that can precipitate from a supernate at equilibrium Eq. 2 (set Q/K = 1) and obtained the equilibrium constant as shown in Eq. 3.

$$[Al_{starting} - X]^{13.04} [Si_{starting} - X]^{11} = 10^{(9.9 + 15.84 \times \text{density} + 0.0163 \times \text{Temperature})} \times [OH]^{12} \quad 3)$$

In Eq. 3, the symbol “X” stands for the concentration (or moles used) of aluminum or silicon needed to make aluminosilicate gel. Recall from Eq. 1 that “X” represents that 12 moles of Al, 12 moles of Si and 12 moles of OH are needed to make one mole of stoichiometry NAS gel. If “Y” moles of NAS are needed to be made, then 12 times Y moles of Al and Si moles are needed. In this case “X” equals 12 times “Y.”

Since gels are difficult to filter and ion exchange columns are deep bed filters, conditions must be maintained to avoid NAS<sub>gel</sub> formation.

On the other hand, the SCIX process will employ a rotary filter unit (SpinTek<sup>®</sup>) that has proven to clarify up to 18 wt % sludge slurries. Given that sludge contains a wide variety of particles morphologies and aggregates of primary particles, the SpinTek filtration unit is expected to filter particles from dissolved saltcake and their aggregates (as described

earlier in this report). The filtrate is then sent to an ion exchange column packed with IONSIV® IE-911. We expect this filtration step to remove precipitates from the supernate and probably remove NAS gels.

## *2.2 CST Stability and Hydraulics Performance in an Ion Exchange Column Pretreatment*

IE-911 is composed of a porous framework of silicon and titanium dioxide doped with niobium oxide to expand one of the two pores to allow more cesium atoms in the framework. The framework crystals (with average size less than one micron) are held together via a nitrate-based sol-gel synthesis with porous zirconium oxide.

The finished acidic form of IE-911 contains excess of silica, lead, iron, niobium, and un-gelled zirconia that needs to be removed during a pretreatment step.<sup>17</sup> Batch test with IE-911 in contact with solutions containing no silica leached detectable quantities of silicon, niobium and titanium.<sup>18</sup> That fact led to severe column plugging. A summary of previous column plugging at SRS, ORNL and Melton Valley<sup>19</sup> is given in Table 4.<sup>20</sup>

As can be seen from Table 4, the majority of the column plugging packed with IE-911 were due to failure to pH adjust the IE-911 (aluminum hydroxide precipitation) and failure to remove the excess chemicals from IE-911 (such as niobium and silica that lead to sodium hexaniobate and aluminosilicate formation respectively). Typically, the manufacturing process adds approximately 3 wt % excess silicon and niobium to the IE-911 particles. After 7 days in average salt simulant<sup>21</sup> and 5 days in a caustic solution containing no soluble aluminum,<sup>22</sup> the IE-911 particles leached 0.096 and 0.143 wt % silicon respectively (and 0.21 and 0.082 wt % niobium respectively). Therefore, incompletely leached IE-911 particles were used in column tests.

As a result of the numerous mechanisms for column plugging an IE-911 bed, a pretreatment protocol was developed to mitigate IE-911 leaching.<sup>23</sup> The pretreatment is a combination of pre-treating IE-911 at the same sodium molarity as the feed and with sufficient bed volumes to remove all excess materials which led to more inert IE-911 particles. Table 5 lists the pretreatments used for removing excess material and fines from IE-911. The currently accepted pretreatment is listed in the second row of Table 5 developed by D. D. Walker.<sup>24</sup> This pretreatment leaves the IE-911 particles with a smoother and more stable surface (as shown in Figure 2). In fact, reduced leaching and less impurities was obtained with this pretreatment in a column test.<sup>25</sup>

Table 4. Summary of Column Plugging Incidents Packed with IE-911

Number of Plugging Incidents	Failure Mode
3	<b><u>Solids in Feed</u></b>
	a. during pretreatment zirconia extracted from column precipitated in a different form and was fed back to the column
	b. aluminosilicate solids precipitated in feed tank and were pumped into column
1	c. calcium/aluminosilicate precipitated from feed solution; CST fines from incomplete backwash
	failed to pH adjust between waste solution and water rinse
3	<b><u>Unknown</u></b>
	a. during batch pretreatment
	b. Melton Valley Johnson screen
	c. ORNL long-term exposure

D. D. Walker, "Crystalline Silicotitanate Column Plugging Incidents" SRT-LWP-2000-00136, August, 2000.

Table 5. List of IE-911 Pretreatments and Subsequent Elemental Leaching from IE-911

Pretreatment	Reference	Results
Soak in mild caustic to pH 12 and backflow to remove fines	P. A. Taylor and C. H. Mattus, "Thermal and Chemical Stability of CST," ORNL/TM-99/233, October 1999	Niobium and Silicon continued to leach in further column tests.
Upflow with inhibited water and downflow caustic solution with 2 molar NaOH per gram of IE-911 (1- 10 bed volumens/hour) for at least 24 hours	D.D. Walker, "Pretreatment Guidelines," SRL-LWP-2000-0028, Rev. 0, March 2000	No silica, niobium or lead leached in post column tests.
None	W. R. Wilmarth, D. D. Walker, F. F. Fondeur, S. D. Fink, J. T. Mills, V. H. Dukes, and B. H. Croy, "Examination of Pre-Production Samples of UOP IONSIV® IE 910 and IE 911, WSRC-TR-2001-00221, June 2001	IE-911 in batch and column test leached niobium and silicon.



As Received



After Pretreatment with the optimal pretreatment recipe\*

Figure 2. The effect of a caustic wash\* on the surface appearance of IE-911.

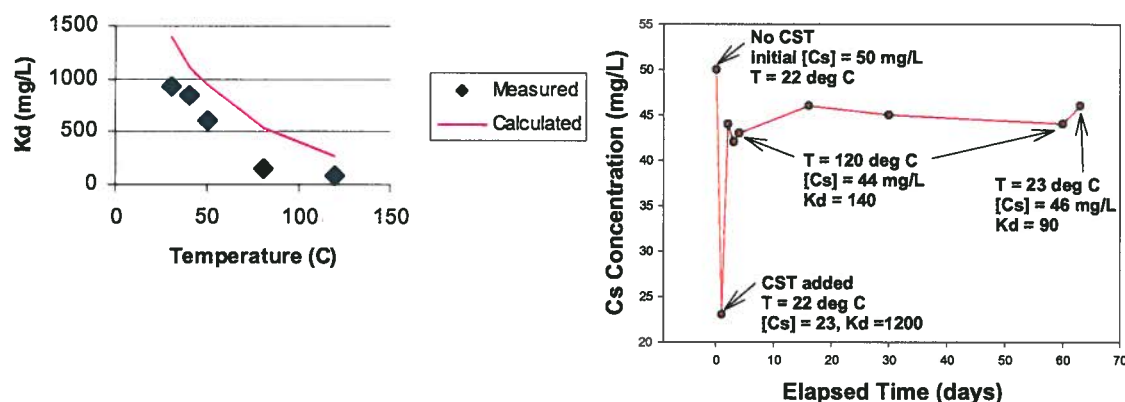
\*D.D. Walker, "Pretreatment Guidelines," SRL-LWP-2000-0028, Rev. 0, March 2000

Some of the column plugging also resulted from the salt solutions used that were unstable (i.e., saturated relative to aluminosilicates and aluminum hydroxide) to begin with.<sup>1</sup> For example, average salt simulant and high nitrate salt simulant will precipitate aluminum hydroxide and cancrinite while high hydroxyl salt simulant will precipitate aluminum hydroxide, cancrinite and oxalate as predicted by OLI<sup>®</sup> 3.1 software. If these solutions are not properly aged or seeded to equilibrium before use, they will precipitate particulates (aluminum hydroxide or aluminosilicates) in the columns.

### 2.3 Effect of Temperature on IE-911 Stability and Sorption Capacity

IE-911 irreversibly sorbs cesium but the steady state amount of cesium that IE-911 can absorb decreases the higher the sorption temperature is as shown in the left figure of Figure 3. This data was obtained for average salt simulant.<sup>1</sup> For example, 5% of the cesium is released from IE-911 when the temperature is raised from 29 °C to 50 °C (or equivalently the equilibrium cesium concentration increases by 46 %). Cooling IE-911 from a high temperature to room temperature also restores IE-911's capacity to sorb cesium at room temperature. In another study, heating IE-911 to 55 °C for two weeks and then cooling it back to 25 °C, the IE-911 irreversibly desorbed approximately 2.1% of the initially sorbed cesium.<sup>26</sup> However, in the presence of soluble aluminum, heating IE-911 that contains excess silica past 55 °C for two weeks or longer, the IE-911 particles can not re-sorb cesium at room temperature. As shown in the right figure of Figure 3, at room temperature IE-911 decontaminated a solution from a cesium concentration of 50 to 27 mg/L when the IE-911 slurry was heated to 120 °C for 5 weeks IE-911 as expected released the cesium. However, allowing the slurry to cool back to room temperature did not re-absorb cesium.<sup>27</sup> Examination of the IE-911 particles showed the particles were coated with a layer of nitrated cancrinite that rendered the IE-911 useless as a cesium sorbent.





Calculated values were obtained from the ZAM model developed by Texas A&M

This figure shows heating IE-911 beyond 80 °C and then cooling at room temperature in the presence of aluminum will not re-absorb cesium.<sup>28</sup>

Figure 3. The Effect of Temperature on the cesium uptake of IE-911

Further evidence of the cesium removal at 55 °C and 80 °C is shown in Figure 4 where 2.6% and 18.4% cesium desorbed. (Note that these values are less than those computed Figure 3 since different salt solutions were used.) This de-sorption is not due to any structural changes in IE-911 but simply the applied heat is sufficient to free cesium from binding sites in the IE-911 particles. IE-911 can also adsorb actinides (U, Pu, Am, etc.) and strontium from the supernate<sup>29,30</sup> but no data is available regarding thermal desorption of these elements from IE-911.

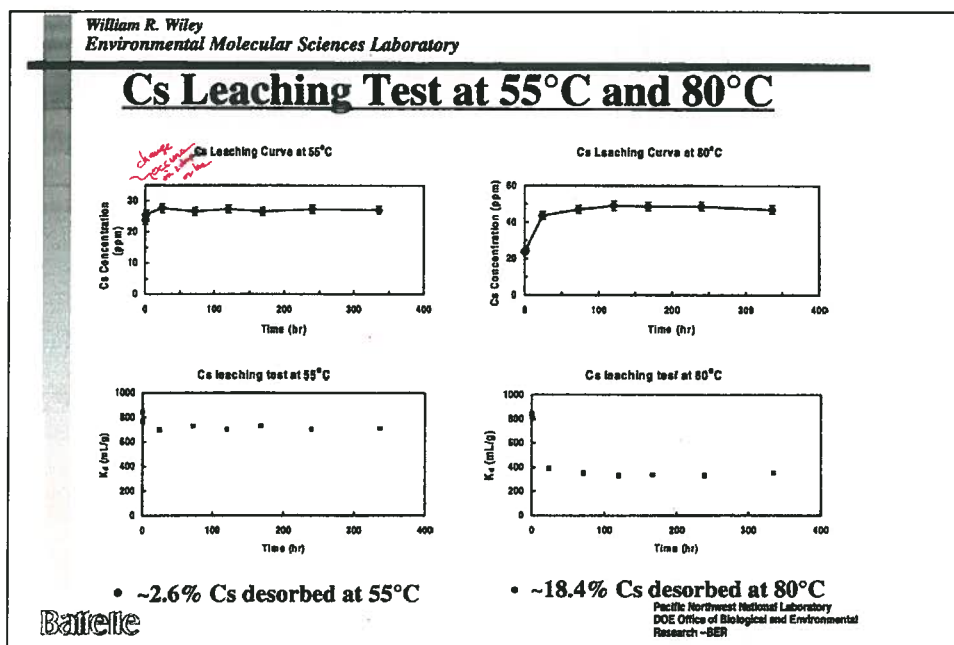


Figure 4. Cesium Desorption from IE-911 at 55 and 80 °C. From L. Li, Y. Su, J. S. Young and M. L. Balmer, "IE-911 Low-Temperature Thermal Stability (Interim Report)," PNNL-13352-A, September 2002

Rapid temperature increases in ion exchange bed packed with cesium-loaded IE-911 as a result of loss of cooling were determined in previous studies.<sup>31, 32, 33</sup>

Therefore, when operating an ion exchange column with cesium loaded IE-911 and loss of cooling occurs such that the column temperature reaches higher than 55 °C for at least 14 days or more, expect loss of cesium (approximately 3% from the IE-911 particles) and higher hydraulic pressure when column operations resumes. Please note that if the silicon concentration is low enough such that  $Q/K$  term in Eq. 1 is less than  $1\text{E-}14$  or the product " $[\text{Si}][\text{Al}]$ " is approximately  $1\text{E-}4 \text{ M}^2$ , then there are not enough reactants to generate sufficient product ( $\text{NAS}_{\text{gel}}$  or the crystalline NAS) that can interfere with cesium sorption (or resorption) or with the fluid flow down the column or with sluicing the IE-911 out of the column.

However, most of the saltcakes and supernate in SRS contain silicon. Therefore, it is expected that any dissolved salt cake will contain both soluble aluminum and silicon. If sufficient soluble silicon is present in the supernate,  $\text{NAS}_{\text{crystal}}$  (such as Zeolite A, hydroxy sodalite, nitrated sodalite, and/or nitrated crancrinite) may form on the surface of the IE-911 particles. The NAS containing IE-911 particles will have higher hydraulic radius (increased girth) leading to an increase in the column hydraulic pressure drop. As shown in equation 4 (Ergun's equation for a given porosity  $\epsilon$ ), any increases in the hydraulic radius of the IE-911 particles causes an increased pressure drop in the column. For example, a 10% increase in particle diameter may lead to 122% pressure increase (assuming the interstitial velocity does not change much by the change in porosity).

$$-\frac{\Delta P}{Length} = 150 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{viscosity \times velocity}{diameter^2} + 1.75 \frac{density \times velocity}{diameter} \frac{(1-\epsilon)}{\epsilon^3} \quad 4$$

In the case where information exists on the amount of aluminosilicate deposited per unit volume of the ion exchange bed, equation 5 provides the pressure drop in the bed.<sup>34</sup>

$$\frac{\Delta P}{\Delta P_{initial}} = \left[ 1 + \frac{\sigma(t)}{(1-\epsilon_{initial})(1-\epsilon_{post\ deposition})} \right] \left[ 1 - \frac{\sigma(t)}{\epsilon_{initial}(1-\epsilon_{post\ deposition})} \right]^{-3} \quad 5$$

The symbol “ $\sigma(t)$ ” stands for the amount of deposited material per unit volume of the ion exchange bed (in this case it represents the particle’s diameter increase as a result of NAS deposition) and “ $\Delta P$ ” stands for the pressure drop in the bed. For example, adding 0.01 grams of NAS per mL of the column leads to a 4% reduction in porosity (assuming uniform coating) which in turn leads to a 9% increase in the pressure drop (using Eq. 5).

In addition, the particles of NAS<sub>crystal</sub> may also reduce porosity of the bed by plugging some channels. In this case, the prediction for pressure increase is more complicated since fluid back flow (eddies) play a large role in the pressure increase but the expected pressure increase will be larger than predicted by equation 4. Plugging of interstitial channels in a bed reduces the amount of cesium that can be removed from solution.

The IE-911 particles sorbed with NAS<sub>crystal</sub> crystals may start bridging across other IE-911 particles creating an effective yield stress that resist re-suspension or fluidization of the bed for later disposal. If the particle to particle bridging force is large enough, then the whole bed may move as a unit with an applied force (or pressure). When this happens the applied pressure is larger than shear strength between the bed and the walls of the column ( $\Delta P > 4 \times (\text{shear strength}) \times \text{Length of bed} / \text{diameter of the bed}$ ).

Some of the IE-911 columns previously tested plugged to the point of using an external applied force to break the agglomeration. Therefore, we do not expect caking or other agglomeration mechanism of the IE-911 particles to be effective in the SCIX process as long as the conditions of low silica concentrations (< 0.001 M), low temperatures (< 55 °C), in the presence of soluble aluminum (~ 0.003 M) and short exposure times at temperatures higher than 55 °C (i.e. less than two weeks) are met simultaneously.

Since the concentration of aluminum and silicon in the supernate can not be varied continuously and temperature is difficult to control, changing the hydroxyl concentration of the supernate by the addition of caustic (or diluting with inhibited water) can lower the supersaturation of the supernate. For example, if the silicon concentration in the supernate (average salt simulant) is 0.02 M then by using Eq. 2, the hydroxyl concentration should be increased from 1.91 M to 2.23 M to eliminate the supersaturation relative to aluminosilicate formation. Also note that increasing the hydroxyl concentration also removes the supersaturation of the supernate relative to aluminum hydroxide formation (Table 4). Note adding low caustic (such as 3 M sodium hydroxide)

solution to increase the hydroxyl concentration of a dissolved saltcake solution as a method to reduce NAS precipitation leads larger solution volume. In this case, adding 3 M caustic can lead to a 41.5% increase in total volume which in terms dilute the species (in this example, the silicon concentration will be 70% of 0.02 M). Adding higher caustic solution is preferable but care must be exercised since other precipitations may occur (and the likelihood for caustic stress corrosion is higher at hydroxyl concentrations higher than 5 M).

There is also the possibility of aluminosilicate deposition on the wall of the ion exchange bed.<sup>35, 36, 37, 38, 39</sup> The deposited NAS can act as an anchor for adhering IE-911 particles that may remain after sluicing the column. The net effect is the accumulation of loaded IE-911 in the column possibly lowering the total volume of waste that can be processed as estimated by modeling as well as possible increase in the pressure drop. As illustrated in Figure 5, patches of loaded IE-911 islands or “plaques” may remain in the column after several sluicing cycles. A cleaning protocol must be developed that is compatible with the corrosion program and high level waste processes.

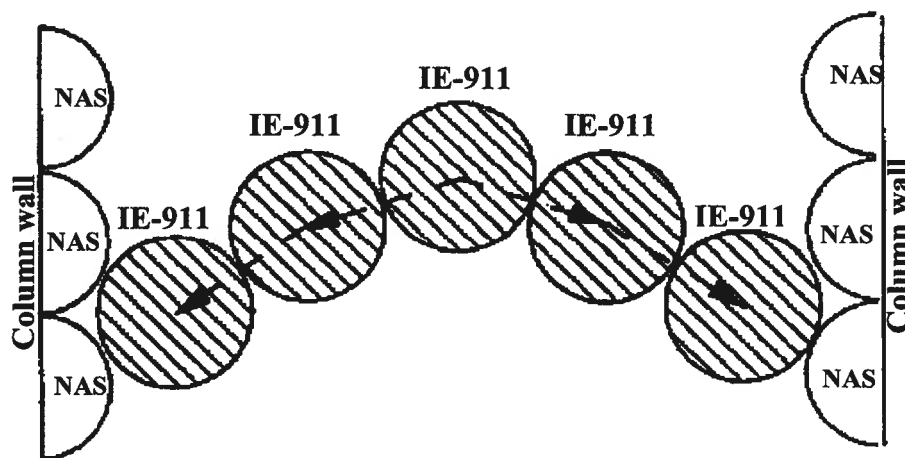


Figure 5. A cross section view of IE-911 anchored by NAS deposited on the inside wall of the column (after several cycles).

#### 2.4 Gas Generation in Columns packed with Cesium loaded IE-911

Testing has investigated two locations where gas (hydrogen and oxygen) may generate in IE-911 particles and in a packed bed aggregation (interparticle and intraparticle). Testing with hydrogen peroxide saturated salt simulant passing through an IE-911 column (3" x 16 ft long) revealed that up to 7% hold up of gas.<sup>40</sup> Most gas bubbles passed through the column and out with the feed solution. No large trapping of gas in the column have been observed where a portion of the IE-911 is excluded from the feed.

The ORNL HFIR test used 10 times more gas (hydrogen peroxide) per liter of simulant than will be expected in gamma radiolysis of SRS supernate for a fully loaded IE-911 column.<sup>41</sup> Results from that test showed no intraparticle gas formation, no effect on cesium breakthrough and no clumping or accelerated crystallization of IE-911.

Additionally radiolysis of water indicates<sup>42</sup> the possible formation of hydrogen peroxide in the liquid between the particles and the liquid inside the IE-911 pores. The ORNL HFIR showed that hydrogen peroxide somewhat reacted with the IE-911 particles but it did not affect the loading performance; therefore, any hydrogen peroxide that may form as a result of water radiolysis from loaded IE-911 will not affect appreciably the cesium and sodium exchange or mass transfer nor will the hydrogen peroxide induce any clumping of the IE-911 particles.

With regard to interparticle gas bubble generation, gas generation and gas transport calculations have shown that no gas bubble is formed inside the pores of IE-911.<sup>43</sup> Therefore, there is no hindering of mass transport (cesium transport) inside the pores (pore wall diffusion remains active) and no loss of sorption capacity.

However, there is also the scenario of a partially drained cesium-loaded column (with residual interstitial water between the particles) that may lead to clumping. In a partially drained column, the remaining liquid bridging the particles will undergo radiolysis thereby generating peroxides (as illustrated in Figure 6). The peroxides may leach titanium from neighboring particles<sup>44</sup> and as the liquid evaporates, a mineral (titanium, silicon and dried salt solution) rich bridge may form joining the particles. This will reduce porosity and increase the yield stress necessary to break the bed.

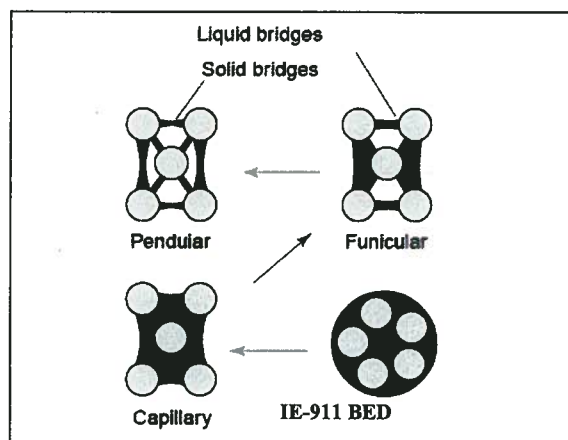


Figure 6. Possible Formations of Mineral Bridges Between IE-911 Particles during Draining and Under a Gamma Irradiation

In a packed bed of spheres (non-bridging), the downward force reaches a maximum at the bed's wall.<sup>45</sup> That force is proportional to the gravity constant "g" (32 ft/sec<sup>2</sup>). Also at the column's wall, the spherical particles configuration must have a large slope or "arch" configuration to support the spherical particles above the "bridge" or "Catenary" like

configuration that resin particles make at the wall. Any chemical bridging or particle coordination increase at the wall will lead to large yield stresses. Furthermore, if the wall of the column is wetted with aluminosilicate solids, these solids will act as anchor for the spherical (IE-911) particles and the bed, in turn, will resist any applied external force.

### *2.5 Monosodium Titanate (MST) Hydrothermal Reactions*

One potential scenario of the SCIX process is dumping cesium loaded IE-911 to the bottom of the tank where MST and sludge may reside. In the bottom of the tank under radiation, temperature may rise depending on the geometrical configuration of the segregated IE-911 relative to the sludge and MST mixture. If the temperature rises enough (for example greater than 55 °C) we may expect some aluminum to leach from the sludge and some silicon to leach from the IE-911. The soluble components may form NAS and the NAS may deposit on the sludge and MST grains acting as a binder to create a cake mound that may resist dispersion by the pressure and forces from a mixer. This behavior can be mitigated by avoiding conditions that can lead to NAS formation, namely high temperature and high hydroxide concentrations.

Aged mixtures of sludge and MST have shown a yield stress (inability to re-suspend) that depends on the ratio of MST to sludge (the higher the MST the higher the yield stress above that of pure sludge).<sup>46</sup> In fact, evidence of engineered MST sorbing iron was seen in a column test.<sup>47</sup> The surface of an iron covered MST particle will chemically behave as an iron oxide particle. Therefore, an affinity between MST and iron particles can lead to aggregation that can resist dispersion. In addition, iron particles can sorb silica<sup>48</sup> and, therefore, we expect adhesion between aluminosilicates, iron particles and MST that can lead to macro-aggregation when the three components are present. As temperature in the tank increase above 25 °C, adhesion between iron, IE-911 and MST grains mixtures increase with a corresponding increase in yield stress (or require higher re-suspension power).

Another area of concern is titanium leaching from MST. Titanium leaching from MST has been observed in the Tank 48H supernate.<sup>49</sup> Insoluble titanium was also detected in Tank 50H.<sup>50</sup> Titanium leaching of MST can occur at temperatures larger than 250 °C. Destruction of tetraphenylborate mixed with MST by the Wet-Air-Oxidation reaction showed that titanium leached from MST at temperatures higher than 250 °C.<sup>51, 52</sup> This high temperature is not expected to occur in the tank. However, a small and finite titanium leaching rate from MST may occur at lower temperatures (below boiling water).

The leached titanium may re-precipitate and react with other soluble components to form precipitates that can deposit on walls and in hard-to-reach geometries. For example, soluble titanium can form titanium-aluminates with soluble aluminum at slightly acidic solutions.<sup>53</sup> The titanium-aluminates deposited on the walls of the test reactors. Freshly precipitated titanium dioxide (from a saturated titanium solution) can sorb heavy metals<sup>54</sup> and possibly actinides.

## 2.6 Grinder

A previous literature survey evaluated three different grinders: Hammer Mill (from Pulva Corp.), Grinder/Dispersing/Rotor-Stators pair (from IKA Works), Vibrating Cylinder containing steel and/or ceramic balls (from Micro Grinding Systems), and Toothed Mill Grinder or Stationary/Rotating Disks grinder (from Glen Mills Inc.).<sup>55,56</sup> In that study, the Rotor-Stator grinder from IKA Works was recommended for grinding CST based on its ability to handle 10 wt % slurry of CST in water in a single pass and to provide a good control over maximum particle size (i.e., unimodal distribution with the maximum particle size  $< 37 \mu\text{m}$ ). In addition, this grinder can be operated remotely. A simulant test (zeolites) with the Rotor-Stator grinder showed satisfactory performance (low wear, good heat dissipation, and acceptable particle size distribution).<sup>57</sup> However, this technology must be evaluated for downstream impacts. For example an assessment is needed to determine if the chemistry of the ground mixture (CST and grinder) is compatible with the chemical requirements of DWPF processes (to avoid hydrogen generation in operations of Chemical Process Cell), proper rheology<sup>58, 59</sup> and glassmaking chemistry (liquidus temperature and molten glass viscosity).<sup>60, 61</sup> The grinder must reduce the average size of the IE-911 particles to maintain the efficiency of the Hydragard sampler to collect a representative sample of the insoluble materials for glassmaking.<sup>62</sup>

Since  $\text{ZrO}_2$  has a different hardness than CST (recall that IE-911 is 10-30 wt %  $\text{ZrO}_2$  and 90-70 wt% CST)<sup>63</sup>, the grinder process may lead to a broad particle size distribution (or bimodal distribution) and to a physical separation (or de-aggregation) of  $\text{ZrO}_2$  from CST during handling and processing (due to a difference in density 5.68 versus 2 g/mL and the expected particle size differences between grounded  $\text{ZrO}_2$  and CST) of grounded IE-911. Grounded CST is not expected to sorb much noble metal from salt supernate to cause a hydrogen gas generation in the SRAT process.<sup>64</sup>

## 2.7 Aluminum Leaching

Some of the spent IE-911 particles mixed with MST and sludge may be sent to an aluminum leaching tank. The aluminum leaching conditions includes adding 3 M sodium hydroxide at a ratio of 3 moles of hydroxide to 1 mole of aluminum at 65 °C while maintaining the free hydroxide concentration at 3 molar.<sup>65</sup> Given the high hydroxide concentration and high temperature (65 °C),<sup>66</sup> silicon may leach from IE-911. The soluble silicon may then react with soluble aluminum (from the leaching process) and reform aluminosilicate (and possibly hydroxy-sodalite). The resulting NAS may form on the walls of the tanks and may bridge the remaining sludge into a hard cake.

The formation of NAS in a leaching tank may defeat the original purpose of the aluminum process in that the aluminum is returned to the solid phase into a more durable (more leaching resistance) form. In addition, the leached IE-911 may also release  $^{137}\text{Cs}$  (due to the high temperature and leached silicon) into the leaching solution and thereby defeat the objective of the ion exchange column in SCIX. The leached supernate may be sent to an evaporator and then the condensed aluminum hydroxide is to be sent to the

Saltstone (after filtration). Continued operation of aluminum leaching for sludge batch preparations will need to be evaluated if CST is released into Tank 41H.

### 3.0 Conclusions

The use of crystalline silicotitanate (CST) is proposed for an at-tank process to treat High Level Waste at the Savannah River Site. The proposed configuration includes deployment of ion exchange columns suspended in the risers of existing tanks to avoid building a new facility. The CST is available in an engineered form, designated as IE-911-CW, from UOP. It is recommended that the IE-911-CW form of CST is used for the Small Column Ion Exchange process. Prior data indicates CST has a tendency to agglomerate from deposits of silica rich compounds from the alkaline waste solutions. This report documents the prior literature and provides guidance for the design and operations that include CST to mitigate that risk.

The SCIX process will also add monosodium titanate (MST) to the supernate of the tank prior to the ion exchange operation to remove strontium and select alpha-emitting actinides. The cesium loaded CST is ground and then passed forward to the sludge washing tank as feed to the Defense Waste Processing Facility (DWPF). Similarly, the MST will be transferred to the sludge washing tank. Sludge washing includes the potential to leach the aluminum from the solids at elevated temperature (e.g., 65 °C) using concentrated (3M) sodium hydroxide solutions. Prior literature indicates that both CST and MST will agglomerate and form higher yield stress slurries with exposure to elevated temperatures. This report assessed that data and provides guidance transfers the sludge tank for aluminum leaching.

Evaluation of the literature revealed the following conclusions.

- Removal of all excess material from IE-911 before utilization in a packed bed column is required to minimize aluminosilicate formation during supernate processing. This includes removal of excess silica, niobium, lead, iron, chloride, fines and ungelled zirconia. This may be accomplished by washing with caustic solution in a non-radioactive facility.
- Any untreated supernate must have an aluminum and silicon concentration at or below the saturation concentration for forming aluminosilicate gels. An empirical observation has been to keep the product of the aluminum and silicon concentration below  $1 \text{ E-4 M}^2$  (for example,  $[\text{Al}] * [\text{Si}] < 1 \text{ E-4 M}^2$ ). The combination of IE-911 particles completely devoid of excess materials and an under-saturated supernate relative to aluminosilicate formation minimize the formation of gel or crystalline aluminosilicates at any temperature.
- In the unlikely event of loss of cooling resulting in the temperature in the ion exchange column exceeding 55 °C, minimize the length of time the column remains at this temperature. Data indicate remaining isothermal longer than a week may generate aluminosilicates. Aluminosilicates will deposit on walls and bed particles creating caking and interfere with the cesium-sodium exchange in the IE-911 particles.



- Similarly if cesium loaded IE-911 is dumped into a waste tank, avoid mound configurations and conditions that can lead to high temperatures (i.e., temperatures larger than 55 °C) since this can accelerate the formation of aluminosilicates, chemically bridge the sludge and IE-911 particles, or release some cesium.
- Further studies are needed to evaluate the effect of having cesium loaded IE-911 particles present during aluminum leaching of sludge. Under aluminum leaching conditions, soluble aluminum from the sludge and leached silicon from IE-911 may form aluminosilicate. Similarly, the cesium loaded IE-911 particles can release cesium at 65 °C (approximately 5% of the loaded cesium is released at 65 °C). A series of tests are being currently conducted to determine the silicon leaching and cesium release of IE-911 under aluminum leaching conditions.
- For monosodium titanates no conditions were found in the SCIX process that can lead to the decomposition (leaching) of MST or the release of strontium and actinides from MST. However, titanium leaching and aggregation are risk factors.

#### 4.0 *Recommended Future Testing*

Given that previous work on CST considered IE-911 in ion exchange columns outside of a tank, introducing an IE-911 packed ion exchange column inside of a tank (in a modular configuration) brings additional risks that further testing can answer.

To that end additional testing to investigate the following is recommended.

- Flowing average salt simulant with no soluble silicon through a bed packed with IE-911 to determine if the soluble aluminum in solution reacts with the silicon in IE-911 to form aluminosilicate. This test determines if silicon in the IE-911 particles can absorb aluminum and the resulting aluminosilicate is sufficient to bridge the IE-911 particles in the bed.
- Perform sludge aluminum leaching in the presence of IE-911 particles and MST to determine if silicon leaches from the IE-911 particles, forming aluminosilicate with soluble aluminum and consequently whether cesium leach from IE-911.
- Partially drain a column packed with IE-911 that was in contact with average salt simulant and expose the column to gamma irradiation to determine if drying from radiolysis leads to mineral bridging between the IE-911 particles in the column.

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