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## **General Stability Models for Potential IE-911 Column Plugging Materials**

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Plugging Materials**

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**Abstract**

Column plugging is a potentially serious problem in implementing the UOP IONSIV® IE-911 ion exchanger for Cs recovery operations at Savannah River. Three materials have been identified that could lead to column plugging: aluminum hydroxide, sodium niobium hydrous oxide and sodium aluminosilicate (cancrinite). The chemical mechanisms responsible for the precipitation of each compound were investigated. Pretreatment with Al-free NaOH solutions eliminates problems associated with aluminum hydroxide precipitation. However, this is likely to precipitate a sodium niobium hydrous oxide that can also plug columns. This phenomenon can be explained based on the competing behavior of different aqueous niobium ions and slow changes in pH that arise when the IE-911 comes in contact with caustic preconditioning fluids. A combination of manufacturing changes and pretreatment process control should be effective at eliminating this problem. Sodium aluminosilicate zeolites will only precipitate during in-service exposure to actual wastes (or waste simulants). A thermodynamic analysis is being developed to define a performance envelope where waste solutions can safely be brought in contact with the IE-911. It is likely that this study will indicate a need for greater dilutions of the waste than are reflected in the chemistries of the fluids being used in IE-911 performance testing.

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## 1.0 INTRODUCTION:

The UOP IONSIV® IE-911 crystalline silicotitanate ion exchanger (CST), which consists of pure silicotitanate (IE-910) and binder (zirconium hydroxide), is one of three technologies being considered for the recovery of  $^{137}\text{Cs}$  from Savannah River waste fluids. Because these fluids are ultimately slated to be disposed of as saltstone, very high decontamination factors are needed. In the baseline technology the IE-911 would be deployed in large ion-exchange columns five feet in diameter and 16 feet high. With an anticipated flow rate of about 20 gallons per minute, the residence time for a fluid would be slightly less than an hour. This flow rate would not suspend IE-911 particles so plugging of the pore spaces is a concern. During the past few years a large number of different types of column tests have been performed in conjunction with various development activities. These tests have identified three materials with the potential for plugging a column: aluminum hydroxide, sodium niobium hydrous oxide, and sodium aluminosilicates belonging to the cancrinite-sodalite family of zeolitic materials. The following report addresses the precipitation and stability of each of these materials, and in doing so, meets Activity ID WACST2358 of the Salt Processing Project Workplan.

## 2.0 ALUMINUM HYDROXIDE PRECIPITATION:

Early in the development of the IE-911 it was found that when columns were exposed to simulated waste solutions, the columns plugged with aluminum hydroxide after just a few hours of testing. Analysis of the problem clearly revealed that the cause lay in three factors: the waste simulants are highly caustic; they contain significant concentrations of aluminum; and until recently, the manufactured form of the IE-911 was delivered in the acid form. The material used for early testing (IE-911, material 89990-999, Lot 20810-00009) had a hydrogen-ion exchange capacity of 3.3 meq/g and when initially added to water would lower the pH to about 3.4. [The most recent pre-production batch (9098-9) initially sets the pH of an IE-911 - water slurry to about 11.2 and has a base consumption capacity of only about 0.25 meq/g.] In addition, this "solid acid" had the rather unusual property of releasing its hydrogen ions very slowly. Figure 1 shows that a single addition of base to a well-stirred water-IE-911 slurry could take many hours, even days, to equilibrate.

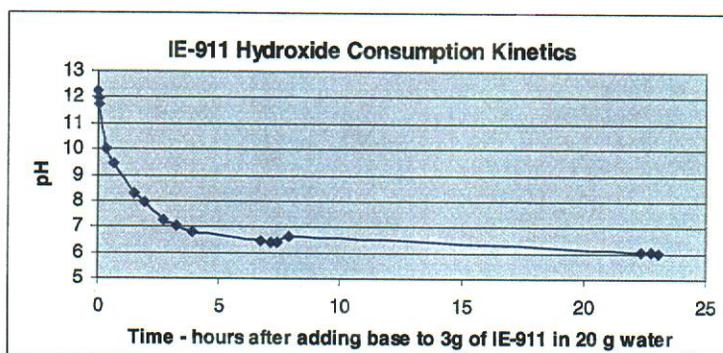


Fig. 1 Typical hydroxide consumption curve for an IE-911 - water slurry.

The other aspect of the aluminum hydroxide plugging problem is the chemistry of the waste (simulant) solutions themselves. They contain both high concentrations of aluminum and hydroxide. When these solutions encounter an acid, the pH drops and precipitation occurs according to the reaction:



In fact, after the start of aluminum hydroxide precipitation, an incremental decrease of only 1 pH unit will remove about 90% of the remaining aluminum from the solution (Fig. 2).

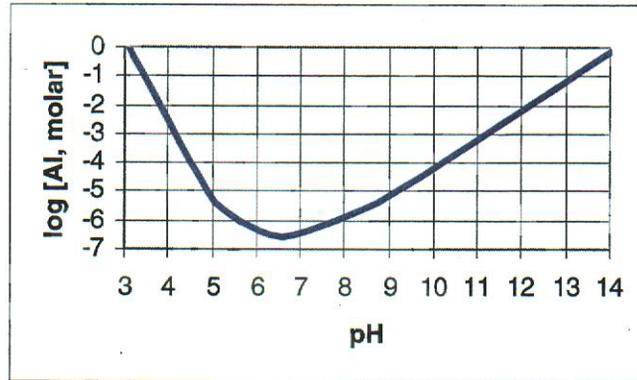


Fig. 2 Solubility of aluminum hydroxide as a function of pH (from Bayes and Mesmer, 1976)

The solution to this problem seemed fairly obvious: pretreat the "as-received" IE-911 with *aluminum-free* sodium hydroxide solutions prior to exposing the material to waste or waste simulants. In this manner, the hydrogen ions on the IE-911 would be replaced by sodium ions and the pH of the waste solutions would not fall when exposed to the IE-911. This was the basic rationale dictating that the IE-911 be pretreated before being placed in service. Although recent manufacturing successes suggest a much less acidic material may soon be available commercially, there will still be a need to wash the fines from the "as-received" materials before loading columns. This provides an opportunity to further optimize material performance, even though the material received from the manufacturer may be serviceable in the as-received condition.

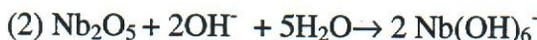
### 3.0 SODIUM NIOBIUM HYDROUS OXIDE PRECIPITATION:

Although a NaOH pretreatment seemed to be an obvious solution to the problem, it soon became apparent that additional complexities were involved. Bench-scale testing of this process typically involved small IE-911 loaded columns and a reservoir of NaOH, which was recirculated until the IE-911 was neutralized. However, in some tests the input ends of the columns became plugged by a loose mass of niobate-rich white precipitate. Further investigations revealed additional instances of plugging or unanticipated rises in pressure in columns employing this material (Walker, et al., 1999, Walker, 2000).

#### 3.1 Review of Previous Findings:

Because the underlying process responsible for this plugging was unknown, several studies into the factors governing Nb solubility were initiated. Although these studies were reported elsewhere (Krumhansl, et al., 2000), it is pertinent to briefly reiterate the results here:

1. Nb<sub>2</sub>O<sub>5</sub> solubility was found to increase in highly basic solutions, particularly above a pH of 11.5. In 2M KOH solutions, concentrations as high as 500 ppm Nb were observed. Below a pH of 11.5 (where the solubility is in the range of 0-50 ppm Nb), the slope of a log [Nb] vs pH plot is about 1.1. This suggests that dissolution involves formation of a monomeric species and consumption of 1 hydroxide per each Nb dissolved:



At higher pH values, the slope drops to about 0.53, which cannot be modeled by a simple dissolution mechanism.

2. Elevating the temperature increases the solubility of all pH values (with significant increases above pH 11.5).

3. Carbonate has no impact on Nb solubility up to the maximum concentration tested, 0.1 M.

4. At pH below 11.5, oxalate seems to slightly suppress Nb<sub>2</sub>O<sub>5</sub> solubility. Above pH = 11.5, the response is ambiguous with the possibility of a slight enhancement when oxalate concentrations are in excess of 0.1 molar (waste simulants contain 0.008 M oxalate).

5. Rather surprisingly, different archived samples of IE-911 and the unbound IE-910 exhibited a significant variability in the amount of Nb liberated in basic solutions. Though all dissolved Nb levels were less than the concentrations achieved using Nb<sub>2</sub>O<sub>5</sub> (at the same pH), the amounts in solution all increased with increasing hydroxide concentration in a manner similar to Nb<sub>2</sub>O<sub>5</sub>. This suggests that the amounts in solution were affected by the type of Nb-containing material in the sample as well as the total amount of readily liberated Nb in the material.

### 3.2 Sodium Hexaniobate Solubility Studies:

The nature of the Nb-rich precipitate plugging the column remains somewhat enigmatic, and on one occasion it was reported that sodium hexaniobate had been identified (D. Walker, personal communication). Certainly this is a reasonable possibility, given the complex chemistry of Nb and the fact that the material can be readily synthesized at mildly elevated temperatures (Goiffon, et al., 1980). To precipitate the disordered niobate phase, the following procedure was used: 2 g of  $\text{Nb}_2\text{O}_5$  was dissolved in 1 liter of hot 0.2 M NaOH. Then the solution was cooled. The identity of the precipitate was confirmed by X-ray diffraction (Fig. 4). The resulting precipitate was well crystallized (Fig. 5) sodium hexaniobate; it did not resemble the amorphous masses of material implicated in plugging a number of column tests.

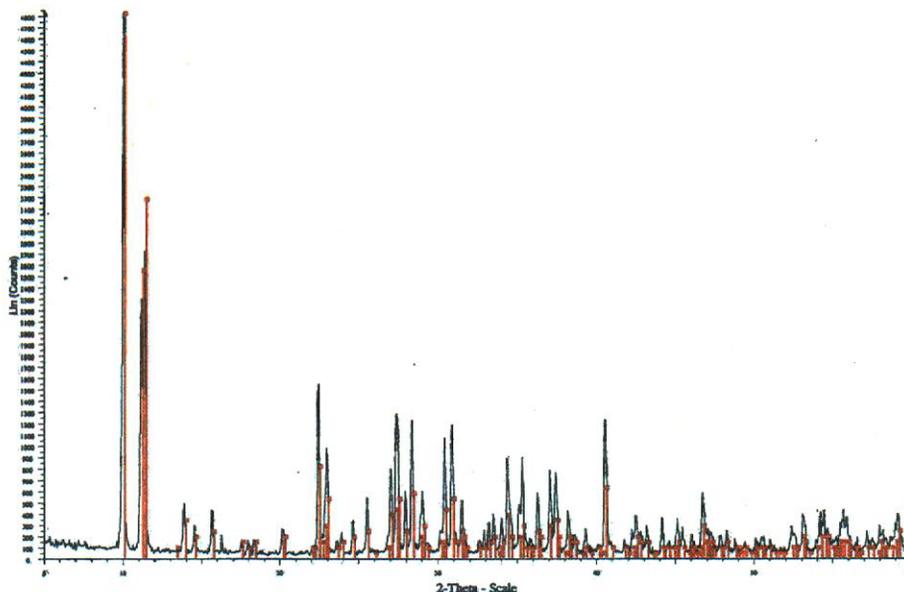
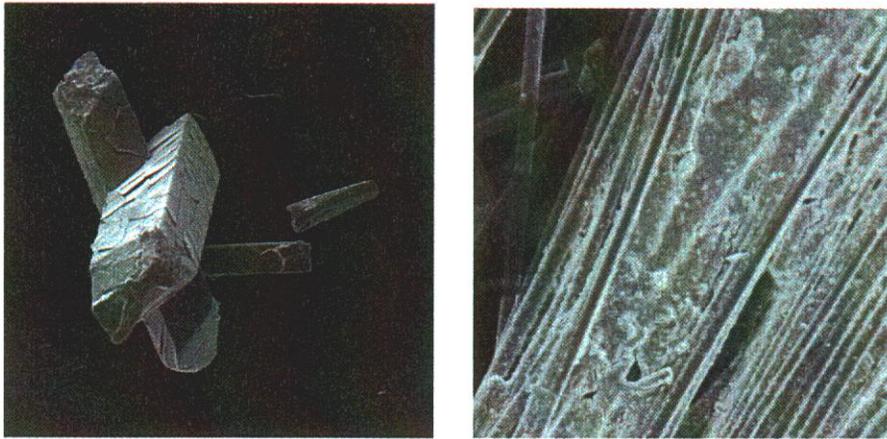
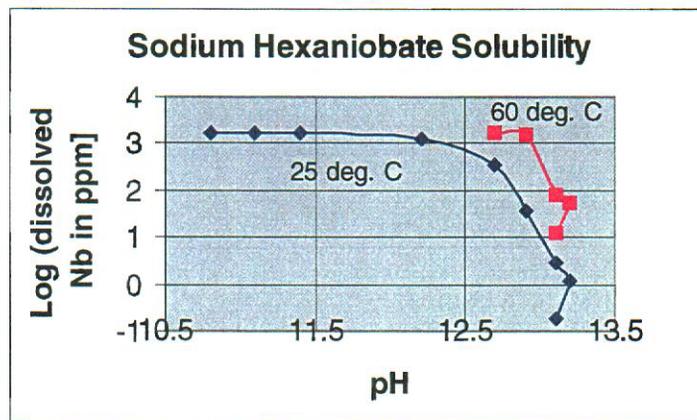


Fig. 4. X-ray diffraction pattern of synthetic sodium hexaniobate (black) compared with a reference pattern from the JCPDF files (red).



**Fig. 5 Synthetic sodium hexaniobate synthesized at SNL (left) compared with fine grained precipitate (right) from a column test that was trapped on a silica glass filter (rods in right frame).**

The solubility of the sodium hexaniobate was then investigated as a function of hydroxide concentration. Unlike the previous studies on Nb compounds, the solubility of this material decreased with increasing pH (Fig. 6). It was also found that the solubility of this material increases significantly at higher temperatures. Additional studies are presently underway to assess whether the inverse relationship between solubility and pH reflects a common ion effect (involving the sodium added along with the hydroxide) or if the change is actually related to the increasing pH.



**Fig. 6 Sodium hexaniobate solubility in NaOH solutions at room temperature (blue, bottom) and 60° C (pink, top).**

### 3.3 Column Experiment #5 Results:

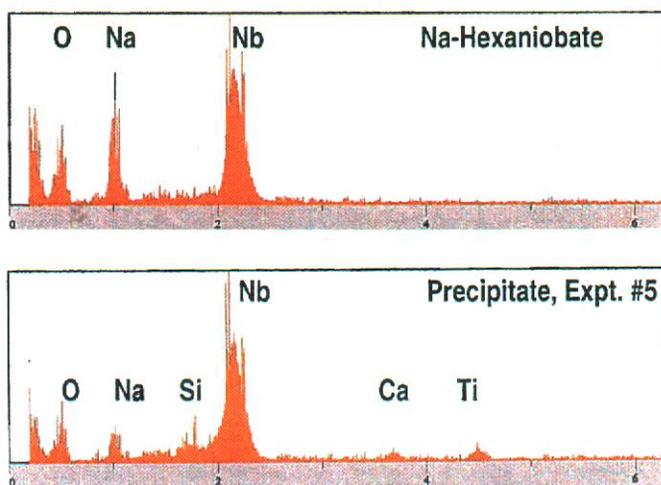
As an adjunct to the various solubility studies, Sandia also initiated a number of column studies. The most recent test in this series involved the acid form of the newest lot of IE-911(9090-76). Prior to loading the column, we exposed the material to repeated batch washes in NaOH solutions until the pH remained above 12. (This process took over a week.) Next, the IE-911 was rinsed with deionized water so that it dried as a loose powder that could be loaded into a column. 3M NaOH was then circulated through the column for three days without any problems or evidence of a precipitate forming. A

circulation line then broke which required refilling the reservoir with some fresh 3M NaOH. When completed, approximately two parts of fresh NaOH had been added for each portion of the original NaOH solution that had remained. In less than a hour, a white precipitate formed in the reservoir that persisted, unchanged, for 50 days until the experiment was disassembled. Although recirculation continued, this precipitate did not plug the column during this period. After the fluid had been circulating for 5 weeks, a sample of reservoir fluid was withdrawn for analysis (Table 1). When the experiment was disassembled the precipitate in the bottom of the reservoir was recovered, rinsed free of NaOH by dialysis in deionized water, and dried for analysis. A major concern in these analyses was to compare this material with the sodium hexaniobate that had been used in the tests described previously (section 3.2).

Constituent	Concentration
Nb	91 ppm
Si	83 ppm
Zr	10.4 ppm
Ti	4.5 ppm
pH	14 ppm

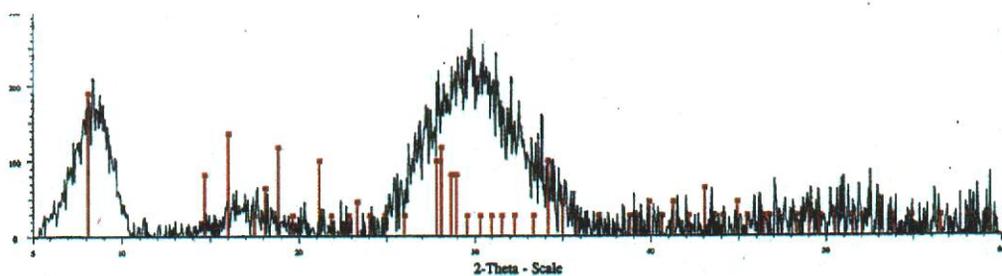
**Table 1. Leachate Analysis of column experiment #5**

SEM (Scanning Electron Microscopic) examination revealed that the precipitate was essentially amorphous (similar to the precipitate caught on the filter in Fig. 5, right) and did not resemble sodium hexaniobate. Figure 6 compares an EDS (energy dispersive x-ray spectra) of this precipitate with one obtained from the sodium hexaniobate grain illustrated in Fig. 5. Clearly, the sodium hexaniobate contains more sodium relative to niobium than the precipitate, though sodium is also clearly a significant constituent in the precipitate. As reported earlier for similar materials (Krumhansl, et al., 2000), the precipitate apparently also contains minor amounts of silicon, calcium and titanium. The titanium (and, hence silicon) may be coming from a trace of entrained CST powder since only a very low level of dissolved Ti was found in the fluid (Table 1).



**Fig. 6 Comparative EDS spectra from sodium hexaniobate (top) and precipitate from column experiment #5. Note that the lower pattern indicates the presence of significantly less Na than is found in the sodium hexaniobate.**

The next test performed on the precipitate was an examination by X-ray diffraction. Rather surprisingly, the precipitate did not prove to be completely amorphous. Broad peaks (indicative of a poorly ordered solid, or at least one comprised of crystallites that are at most a few hundred angstroms across), appeared indicating at least some degree of internal structure (Fig. 7). Although this pattern does not contain nearly enough information for a firm identification, it is much closer to the mineral franconite than to sodium hexaniobate. Franconite also has a lower Na to Nb ratio than sodium hexaniobate, which would be consistent with the SEM/EDS analysis results (Fig. 6).



**Fig. 7 X-ray diffraction pattern of the material recovered from Column test #5. Red bars are a reference pattern for franconite –  $\text{Na}_2\text{Nb}_4\text{O}_{11} \cdot 9\text{H}_2\text{O}$ . Note that this has a main peak at close to 8 degrees while the main peak for sodium hexaniobate,  $(\text{Na}_7)(\text{H}_3\text{O})\text{Nb}_6\text{O}_{19} \cdot 14\text{H}_2\text{O}$ , (Fig. 4) has two large peaks at about 10 and 11.3 degrees two theta.**

Infrared (IR) and laser Raman spectroscopies are other tools that can be used to effectively "fingerprint" materials and judge whether structural similarities may, or may not, exist. Both were applied in a comparative manner to sodium hexaniobate and the precipitate from column test #5. The balance of the IR spectra (not shown) reflects incorporation of water into both structures. However, there is a limited range of wave numbers that does reflect metal-oxygen bonds (Fig. 9). Clearly, the spectra do not exactly match, again suggesting that the hexaniobate may not be an exact model for the precipitate formed in the column test.

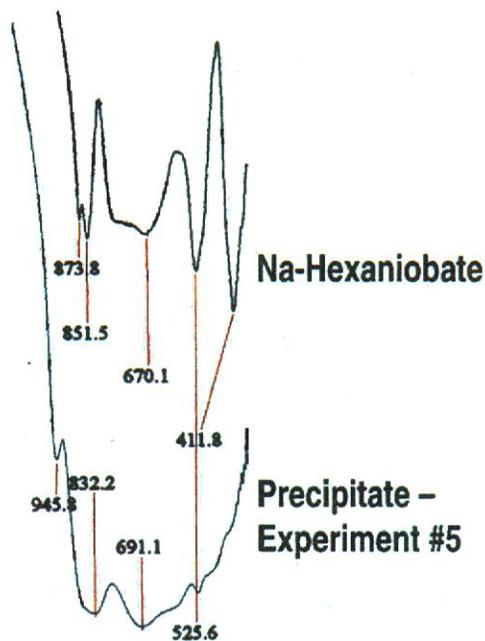


Fig. 9, Infrared absorption spectra obtained on sodium hexaniobate and column test #5.

In contrast, laser Raman spectra (Fig. 10) may indicate some similarity between the precipitate formed and the hexaniobate structure. Spectra were taken from the precipitate, solid sodium niobate, and a two parts per thousand solution that resulted from the dissolution of sodium hexaniobate in a NaOH – NaNO<sub>3</sub> solution

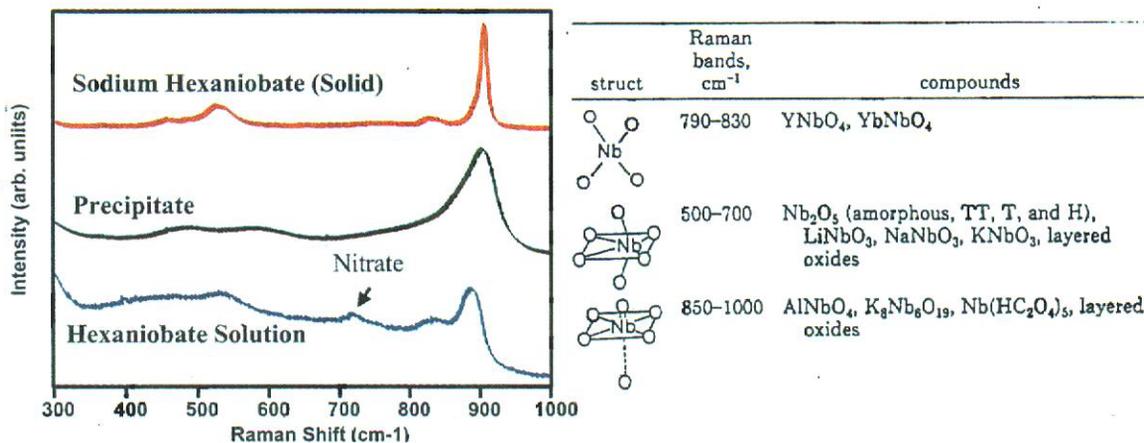


Fig. 10 Left - Comparison of Raman spectra from column test #5 precipitate (middle) with reference spectra for solid sodium hexaniobate (top) and a 2 parts per thousand sodium hexaniobate solution (bottom).

Right - Characteristic Nb coordination polyhedra, associated Raman bands, and representative compounds. (From: Jehng and Wachs, 1991).

Various niobium-oxygen coordination polyhedra have characteristic Raman bands (Jeng and Wachs, 1991, Fig.10 - Right). In addition to Fig. 10, Raman spectra were also collected from the solution that was in contact with the column test #5 precipitate for about 50 days. These spectra showed no characteristic adsorption bands. Apparently the technique is not sensitive to Nb at the 90 ppm level. However, it was possible to obtain a good spectra from the column test #5 precipitate. These data rule out the presence of four-fold coordinated Nb (in compounds such as  $\text{YNbO}_4$ ) and Nb a relatively regular octahedron such as hydrous  $\text{Nb}_2\text{O}_5$ ,  $\text{NaNbO}_3$  and layered oxide structures. The Raman bands detected most closely match Nb in a highly distorted octahedral coordination. In this environment, one oxygen bond is very weak, hence this oxygen is located much further from the Nb than the other oxygens. The opposite Nb-O bond, however, is quite short and almost strong enough to qualify as a double bond. Sodium hexaniobate is one compound with Nb in such a configuration, as is  $\text{AlNbO}_4$ .

It has not yet been possible to locate a crystal structure for franconite or to assess if Nb in this material lies in a distorted octahedral site. However, the fact that the franconite X-ray diffraction pattern has prominent peaks that index as (2,0,0), (4,0,0), (8,0,0), etc. are suggestive of a layered structure. The sodium nonatitanate currently being evaluated for removing actinides from waste fluids (David Hobbs, SRS, personal communication) has a similar formula (if allowance is made for adding an extra half oxygen atom to account for the difference between  $\text{Nb}^{+5}$  and  $\text{Ti}^{+4}$ ). This material is also thought to be comprised of edge-sharing titanium octahedra that have polymerized to produce a layered structure.

To summarize, various diagnostic techniques were applied to the precipitate formed in column test #5. The material proved to be neither  $\text{Nb}_2\text{O}_5$  or sodium hexaniobate, but instead a sodium salt with an intermediate level of polymerization. It is also apparent that the precipitate is very poorly crystalline, contains numerous waters of hydration, and may precipitate when conditions conducive to polymerization of dissolved Nb-containing monomers occur.

### **3.4 General models for formation of Nb-rich precipitates:**

Two end-member mechanisms leading to column plugging can be defined based on the competing trends illustrated in Fig.11. These scenarios are not mutually exclusive and, depending on local circumstances, either (or both) may produce detrimental effects. Further, without real-time monitoring of critical solution parameters it may be difficult to assess what caused a problem after the fact.

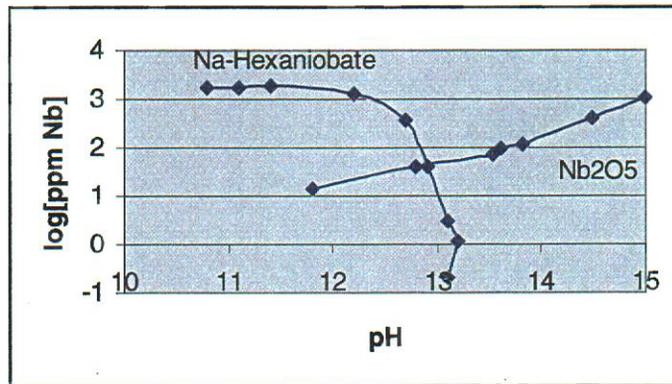
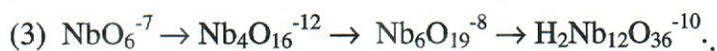


Fig. 11 Competing trends in Nb solubility

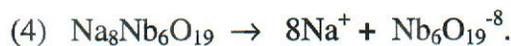
The simplest model explaining the origin of Nb-rich precipitates is based on the solubility of Nb<sub>2</sub>O<sub>5</sub> in conjunction with a slow drop pH as preconditioning progresses. As an increment of NaOH preconditioning fluid traverses the column it will both leach niobium and exchange sodium for hydrogen ions. Nb leached rapidly from early versions of the IE-911 (Wilmarth and Walker, 1999) but the exchange of Na for H was found to be quite slow (Fig. 1). Thus, initially the high pH fluid could circulate through the column and significant Nb levels could build up in the reservoir. Eventually, however, the pH of the reservoir would also start decreasing as more and more sodium was exchanged for hydrogen ions. The falling pH might eventually cause a previously unsaturated solution to become saturated with Nb. When this happened a precipitate could form that eventually would plug a column.

The end result ultimately depends on the masses of fluid and solid in the experiment. The acid loading on the early versions of the IE-911 was about 3 meq/g. Thus, a column containing just 100 g of IE-911 would consume *all* the NaOH in a 100 ml reservoir of 3M NaOH. (If the objective of this experiment were to actually have the pH be strongly caustic after equilibrium, then substantially higher liquid to solid ratios would have to be anticipated in planning the size of the reservoir.) With these constraints it is quite plausible that the precipitation of some material like hydrous niobium pentoxide could have led to plugging of some column experiments.

A second scenario leading to precipitation would involve the in-situ polymerization of dissolved Nb rather than a decreasing pH. As alluded to previously, the aqueous chemistry of Nb is far more complex than the simple dissolution reaction indicated by eq. 2. Recently, experimental studies by Rozantsev et al., 2000, suggested that a decreasing pH or increasing Nb concentration might lead to a series of polymerization reactions:



Using the hexaniobate ion as an analogue for various sodium salts of polymeric niobium species, it is possible to represent the dissolution reaction as:



This dissolution process does not depend on the pH, but is highly sensitive to the amount of Na present in the solution. The decreased solubility for hexaniobate in Fig. 10 may be a consequence of adding Na in the NaOH, and may not be at all related to the pH change. This conjecture is currently being assessed experimentally and data should be available before the date when the final data package is assembled prior to down selection.

In the second scenario, a column test, particularly one performed at elevated temperatures (where Nb solubilities are high and polymerization reactions relatively rapid), the Nb concentration might build up until hexaniobate formed. At this point sodium hexaniobate would govern Nb solubility and a precipitate would form even though the pH of the preconditioning fluid had not decreased appreciably.

The precipitate found in column test #5 suggests that an intermediate scenario may actually be the cause of low temperature column plugging. The fluid chemistry summarized in Table 1 indicates that the dissolved Nb concentration is much more compatible with a Nb<sub>2</sub>O<sub>5</sub> solubility model than with a hexaniobate model. The X-ray and Raman data both suggest a layered structure with a degree of polymerization that is less than that of sodium hexaniobate. Based on the analogous behavior of other layered materials (clays, for example), when such materials dissolve, the components released to solution are simple ions of the entities contained in the sheets. Entire sheets do not detach from the lattice and go into "solution". In this regard, the dissolution behavior of the layered lattice is much like that of the simple oxides rather than that of a sodium salt of a very large anion.

What probably happens in low temperature column tests is that the Nb concentration builds up until it is close to Nb<sub>2</sub>O<sub>5</sub> saturation. At that point it is at a level which greatly exceeds that of the sodium hexaniobate in these strongly caustic solutions. As condensation of the monomers starts, this implicitly high level of supersaturation dictates rapid precipitation. Thus, before a fully formed hexaniobate cage forms, poorly ordered sheets of partly polymerized niobium octahedra nucleate and grow. The result is that in low temperature experiments, we get an amorphous mass of material that can effectively plug pore spaces in IE-911-loaded columns. At higher temperatures well-formed hexaniobate crystals should form with less potential for column plugging, but which could make it difficult to disaggregate the IE-911 when the column is to be emptied.

The above scenario suggests a simple metric to avoid plugging low temperature column tests or in-column pre-equilibration activities. In these situations, the Nb concentration in a recirculating reservoir should be kept well below the solubility of Nb<sub>2</sub>O<sub>5</sub> at the same pH. In this setting the driving force for initial precipitation would be small and the Nb concentration would probably be low enough that hexaniobate should not form spontaneously in the few days needed to pre-equilibrate a column.

### 3.5 Pretreatment Protocols:

A previous report (Krumhansl et al., 2000) suggested a number of revisions to the pretreatment process based on the then available research results. Since then, the manufacturer (UOP) has acted on these findings. The newest version of IE-911 may, in fact, not even need to be pretreated. This new material is no longer delivered in the acid form. Steps have been taken to reduce the amount of Nb that can be leached from the IE-911. Nonetheless, there is value in reiterating these earlier suggestions because this material may not become commercially available in the immediate future, and because we have a slightly greater understanding of the processes responsible for column plugging. In reviewing these suggestions it should also be remembered that pretreatment can be done in a non-radioactive environment prior to exposing the IE-911 to wastes. Hence, there is far more latitude in handling these activities than would exist if the material were already radioactive.

1. Perform pretreatment prior to loading the IE-911 into a column. With pretreatment being performed in a batch mode, it would be possible to monitor the progress of critical process parameters (pH, dissolved Na and Nb, etc.) and be reasonably sure that the measurements represented conditions throughout the entire mass of material. Plugging would not be an issue since no column would be involved and there would be no penalty to allowing the mix to sit long enough to satisfy the slow kinetics of the titration reaction. Also, small column tests cannot really model the full pH drop that would occur along a 16-foot long column. In bench scale tests we seem to develop problems in the reservoir. On a much larger scale the pH might fall enough that these problems could occur part way into the IE-911 bed and not be readily amenable to remediation activities.

2. If column pretreatment is necessary, there may be considerable benefit to using buffered solutions to accomplish much of the titration. In this manner much of the available hydrogen ion content of the IE-911 would be neutralized at pH values low enough that Nb solubility should not be an issue. This might also be coupled with a very slow flow rate, or possibly one that was pulsed to accommodate the slow kinetics of the Na-H ion exchange reactions. An additional modification would be to only flow the material through the column once (as opposed to a recirculating system) so that the transient issues relating to a reservoir of recirculating fluid could be avoided. Finally, monitoring the build-up of Nb in a recirculating NaOH fluid would be a prerequisite to avoiding problems.

3. A number of factors such as elevated temperature and possibly high oxalate concentrations appear to significantly enhance the solubility of both Nb-oxide and the polymeric sodium niobium salts. Manipulation of these factors in a recirculating pretreatment system might also help prevent a column from plugging, or cause a coarsely crystalline material to form instead of a gelatinous mass.

4. Finally, one may be faced with a situation where column-mode preconditioning is necessary and precipitation of Nb in a recirculating reservoir cannot be

prevented. Using readily replaceable in-line filters at the input end of the column can easily solve this problem.

#### 4.0 Sodium Aluminosilicate (Cancrinite) Plugging:

Sodium aluminosilicate plugging is not an issue during pretreatment. The IE-911 does not contain enough aluminum to precipitate significant amounts of zeolites and, unlike the wastes, pretreatment fluids do not introduce additional aluminum or silicon into the system. However, the in-service precipitation of this material is an issue both from the standpoint of its effect on column flow properties as well as its impact on Cs sorption. In keeping with our larger goal of investigating (and hopefully preventing) column plugging mechanisms, a considerable amount of effort has been directed at understanding this process. As discussed previously (Krumhansl et al., 2000), the tactic being taken is to identify thermodynamic limits on the formation of zeolitic sodium aluminosilicates. This, in turn, should allow development of waste dilution or blending strategies that preclude zeolite precipitation. The following discussion is an updated summary of progress in this area.

The material that is of the most immediate concern is a member of the cancrinite zeolite family. There are numerous natural derivatives of this basic structure (Table 2). This arises because the basic zeolitic cage ( $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ ) is neutrally charged but the cavities are large enough to enclathrate both an anion and a cation; this will happen with any salt found in the principal solution electrolyte. Most of the existing literature deals with the common natural derivatives of this structure; those that incorporate sodium carbonate or hydroxide into the cages. These may also be of some concern in waste management applications. However, nitrate (and to a lesser degree, nitrite) are major anions in most tank supernates. As a consequence, evaluating the solubility characteristics of these derivatives is of particular importance.

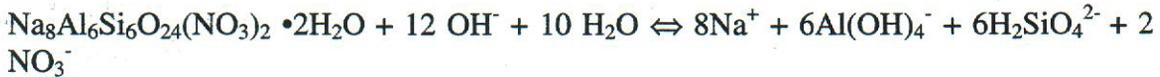
**Table 2 – Naturally Occurring Members of the Cancrinite – Zeolite Mineral Group**

Comment: Some of these formulas look suspect. From where did they come?

Afghanite $(\text{Na,Ca,K})_8(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4,\text{Cl}_2,\text{CO}_3)\cdot 3(\text{H}_2\text{O})$
Bystrite $(\text{Na,K})_7\text{Ca}(\text{Si}_6\text{Al}_6)\text{O}_{24}\text{S}_{17}\cdot 5(\text{H}_2\text{O})$
Cancrinite $\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2$
Cancrisilite $\text{Na}_7\text{Al}_5\text{Si}_7\text{O}_{24}(\text{CO}_3)\cdot 3(\text{H}_2\text{O})$
Davyne $\text{Na}_4\text{K}_2\text{Ca}_2\text{Si}_6\text{Al}_6\text{O}_{24}(\text{SO}_4)\text{C?}_{12}$
Franzinite $(\text{Na,Ca})_7(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4,\text{CO}_3,\text{OH,Cl})\cdot 3(\text{H}_2\text{O})$
Giuseppettite $(\text{Na,K,Ca})_{7-8}(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4,\text{Cl})_{1-2}$
Hydroxycancrinite $\text{Na}_4(\text{AlSiO}_4)_3(\text{OH})\cdot (\text{H}_2\text{O})$
Liottite $(\text{Ca,Na,K})_8(\text{Si,Al})_{12}\text{O}_{24}[(\text{SO}_4),(\text{CO}_3),\text{Cl,OH}]\cdot 4(\text{H}_2\text{O})$
Microsommitte $(\text{Na,Ca,K})_{7-8}(\text{Si,Al})_{12}\text{O}_{24}(\text{Cl,SO}_4,\text{CO}_3)_{2-3}$
Pitiglianoite $\text{Na}_6\text{K}_2\text{Si}_6\text{Al}_6\text{O}_{24}(\text{SO}_4)\cdot 2(\text{H}_2\text{O})$
Quadridavyne $(\text{Na,K})_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_4$
Sacrofanite $(\text{Na,Ca,K})(\text{Si,Al})_{12}\text{O}_{24}[(\text{OH})_2,(\text{SO}_4),(\text{CO}_3),\text{Cl}_2]\cdot 3n(\text{H}_2\text{O})$
Toungkite $(\text{Na,Ca,K})_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2\text{Cl}\cdot (\text{H}_2\text{O})$
Vishnevite $(\text{Na,Ca,K})_6(\text{Si,Al})_{12}\text{O}_{24}[(\text{SO}_4),(\text{CO}_3),\text{Cl}_2]\cdot n(\text{H}_2\text{O})$
Wenkite $\text{Ba}_4\text{Ca}_6(\text{Si,Al})_{20}\text{O}_{39}(\text{OH})_2(\text{SO}_4)\cdot 3n(\text{H}_2\text{O})$

From: Athena Mineralogy: Systematic List of Minerals -  
<http://un2sg4.unige.ch/athena/mineral/minppcl.html>

The solubility of a nitrate-cancrinite (and nitrate-sodalite) in alkaline solutions can generally be expressed as:



The solubility product expression for the above reaction can be expressed as:

$$K = \frac{a_{\text{Na}^+}^8 a_{\text{H}_2\text{SiO}_4}^6 a_{\text{Al}(\text{OH})_4^-}^6 a_{\text{NO}_3^-}^2}{a_{\text{OH}^-}^{12} a_{\text{H}_2\text{O}}^{10}}$$

Precipitation can only occur when the entity on the right exceeds the solubility product. To perform this evaluation requires both a solubility product (derived from thermodynamic considerations) and activity coefficients relevant to the solutions being evaluated. The equilibrium constants can be derived in a number of ways. We are in the process of extracting what information is available from the published literature (section 4.1), as well as performing program-specific solubility studies (section 4.2). The current state of our modeling efforts is presented in section 4.3.

#### 4.1 Literature Review:

Although thermodynamic studies are unavailable for nitrate-cancrinite there is some data on related natural materials. The only thorough calorimetric study over a wide range of temperatures is on dehydrated sodalite ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Cl})_2$ ) as reported by Komada et al.(1995). Additional information has also been gleaned from less comprehensive treatments of the problem (Gasteiger et al., 1992; Park and Englezos, 1998b; Park and Englezos, 1999b). In particular, Park and Englezos (1998b; 1999b) have combined thermochemical data for the estimation of thermodynamic properties for sodalite dihydrate ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ ) and hydroxysodalite dihydrate ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ). The same authors utilized Pitzer parameters to estimate the activity coefficients of the aqueous species present in this type of alkaline solution and to finally develop a predictive solubility-product model (Park and Englezos, 1999b). Their thermodynamic constants proved useful for our immediate purposes; however, the solutions were not a close match to the waste fluids. Thus, their Pitzer coefficients are only a partial solution to the challenges presented by modeling high ionic strength waste fluids.

Reported solubility data for cancrinite are largely restricted to carbonate-cancrinite, which is the solid phase of interest in alkaline solutions associated with recovery cycles in Kraft pulp/paper mills and the resulting Bayer liquor (Barnes et al., 1999a; Park and

Englezos, 1999b; Ulmgren, 1982; Zheng et al., 1997). As an exploratory exercise, these data were used to estimate the solubility product of carbonate-cancrinite using “b-dot” activity coefficients, and assuming all the silica and alumina existed as  $\text{Al}(\text{OH})_4^-$  and  $\text{H}_2\text{SiO}_4^-$  respectively. For comparison with the other studies it was also necessary to assume that all salts make the same contribution to the free energy of dissolution of the cancrinite lattice.

The outcome of these efforts is illustrated in Fig. 11, relative to a common carbonate-cancrinite model that incorporates the solubility products of Park and Englezos (1999b) for the two sodalite phases. The polynomial regression is based on the data from Ulmgren (1982) and Barnes et al. (1999a) at temperatures from 90° to 220 °C. The chemical reactions defining the solubility products between the sodalite and cancrinite differ slightly in the silica species considered. Notice in the figure there is a tendency for the  $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$  experimental data to fall between the two theoretical sodalite solubility curves.

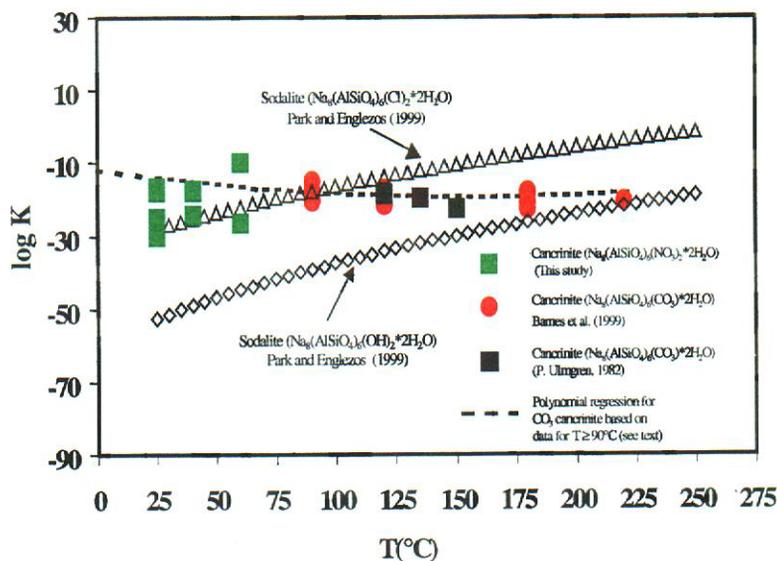
Although b-dot activity coefficients are useful for providing “first cut” assessments, they can also introduce considerable inaccuracies when high ionic strength fluids are modeled. To properly treat these fluids, a robust thermodynamic model is needed which accounts for a large number of aqueous species, and which properly quantifies their relative abundance at very high ionic strengths. The most common method utilized in the determination of activity coefficients for highly concentrated multi-component electrolyte solutions is the Pitzer model (Pitzer, 1991). In order to evaluate these activity coefficients, an extensive compilation of Pitzer binary (e.g.,  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^{(\phi)}$ ) and mixing ( $\theta$  and  $\psi$ ) parameters is being assembled from the literature (Felmy et al., 2001; Felmy et al., 2000; Park and Englezos, 1998a; Park and Englezos, 1999a; Park and Englezos, 1999b; Pitzer, 1991). When completed, this effort will provide a reasonably complete, though unverified, database that then can be coupled to the software in the Geochemist’s Workbench Software package (Bethke, 1998). These data can then be used in conjunction with solubility products gained from the literature or solubility experiments to predict whether zeolites will, or will not, form in wide variety of potential waste solutions.

#### 4.2 Experimental Studies:

To perform solubility-product experiments, it was first necessary to prepare the phase and assure its purity. The material synthesized has been examined in the following ways:

1. by X-ray diffraction, to assure that the correct basic lattice was synthesized;
2. by microprobe, to verify its composition;
3. by IR spectroscopy, to verify that nitrate (rather than hydroxide or carbonate) was the principal anion incorporated during synthesis and;
4. by TGA, to measure the amount of sorbed water; about 2 waters per formula unit were identified.

Having documented the quality of the synthetic cancrinite, it was next necessary to measure the solubility of the material over a range of solution chemistries. Experiments were started to assess the approach to a steady-state solubility condition from both under- and oversaturated conditions and over a range of pH values. The results of these measurements are also summarized in Fig. 11 (green boxes between 25° and 60° C). In preparing this diagram it also was assumed that all the Si was present as  $\text{H}_2\text{SiO}_4^-$  and that all the Al was present as  $\text{Al}(\text{OH})_4^-$ . Again, the data were plotted using b-dot activity coefficients.



**Figure 12.** Log K vs T(°C) diagram showing the theoretically derived solubility curves for sodalite phases (Park and Englezos, 1999b) and the compiled experimental data for CO<sub>3</sub> cancrinite (Barnes et al., 1999b; Ulmgren, 1982). Notice also the preliminary experimental data for NO<sub>3</sub> cancrinite generated in this study (green squares). The polynomial regression curve is based only on the CO<sub>3</sub> cancrinite data at T ≥ 90°C and extrapolated to 25°C. For the CO<sub>3</sub> cancrinite data, the aqueous species activities were calculated using the extended Debye-Huckel (b-dot) equation for activity coefficients. In the solubility calculation of the NO<sub>3</sub> cancrinite data, it is assumed that  $a_i = m_i$  (i.e.,  $\gamma_i=1$ ).

### 4.3 Current Status of Modeling:

Figure 13 summarizes the current state of model development. Stability fields were predicted using the Geochemist's Workbench software package (b-dot activity coefficients, Al as  $\text{Al}(\text{OH})_4^-$ , Si as  $\text{H}_2\text{SiO}_4^-$ , etc.) using stability constants derived from the polynomial regression of the carbonate-cancrinite data presented in Fig. 12. The lower left of each diagram represents a field (e.g. a variety of fluid compositions) where cancrinite should not precipitate. Since the boundary moves little with temperature or pH, one would assume that these variables will not have a large influence on when cancrinite will (and will not) precipitate.

These diagrams also contain plots of the cancrinite experimental data (oval) and supernate compositions from the Hanford tanks obtained from the TWINS database (dark points). The two data sets plot in a similar location that is considerably to the right of the

stability-field boundary. This implies that these fluids are significantly supersaturated with respect to cancrinite. In assembling this diagram it was also necessary to suppress precipitation of other zeolites, notably analcime and clinoptilolite, or a cancrinite field would fail to appear on the diagram. To what degree these shortcomings represent kinetic aspects of zeolite precipitation or inaccuracies in the thermochemical data are unknown. However, a first step to resolving these issues is to complete the integration of the Pitzer activity coefficients into the REACT databases. If this does not resolve the discrepancies, then a reasonable conclusion might be that it was not a good choice to use the carbonate-cancrinite as an analogue for nitrate-cancrinite. However, at that point more data will be available from the experiments on the nitrate-cancrinite so the issue of which data to use would become moot.

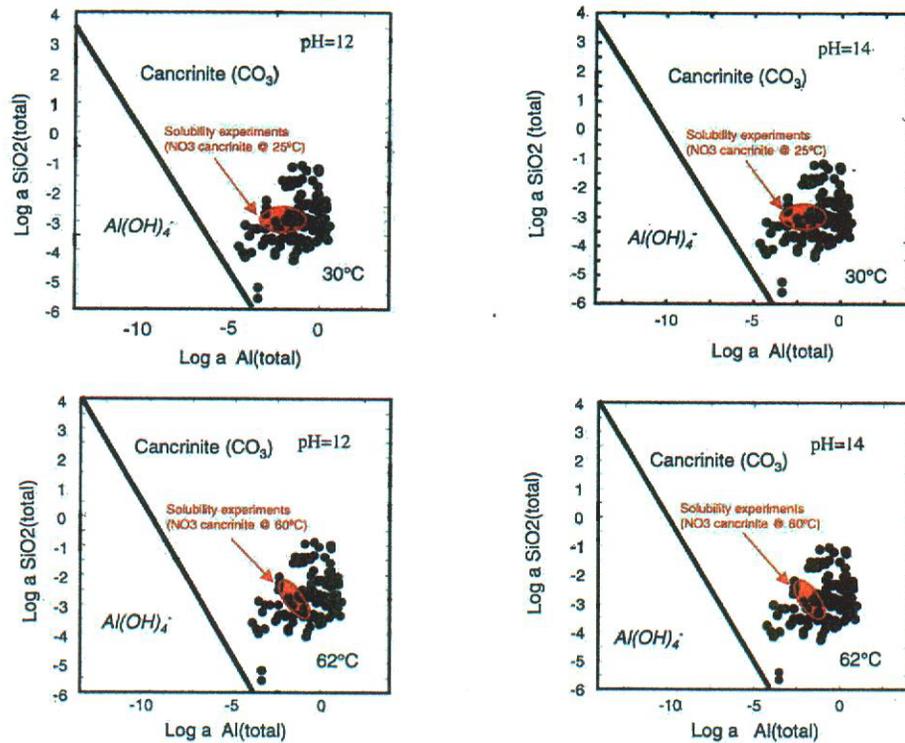


Fig. 13 Comparison of experimental solubility study fluids (red oval), Hanford tank fluid chemistry (black dots), and modeled stability fields for cancrinite.

In a more immediate sense, Hanford and Savannah River tank fluids have relatively similar chemistries. As a consequence, the juxtaposition of the two fluid chemistries in Fig.13 confirms the inference that tank fluids may “naturally” be at, or near, saturation with respect to cancrinite (Wilmarth et al., 1997). Thus, even small changes may initiate precipitation of zeolitic materials and no amount of preconditioning of the IE-911 could

be expected to eliminate this problem. Dilution may be a necessary step to prevent cancrinite precipitation as the fluids pass through a column loaded with IE-911. When the modeling effort is completed, it is likely that an estimate of the degree of dilution required will be possible. However, it should also be pointed out that cancrinite precipitation could occur in the other two technologies being evaluated for Cs recovery. A full analysis of the importance of this process would have to include an assessment of its potential impact on these other technologies as well.

## 5.0 General Conclusions

1. Causes of column plugging by Al and Nb-rich materials are understood.
2. Manufacturing and pretreatment techniques to avoid these problems have been developed.
3. In-service precipitation of sodium aluminosilicate is still a concern.
4. *However*, research to develop limits on allowable waste composition is progressing satisfactorily.

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