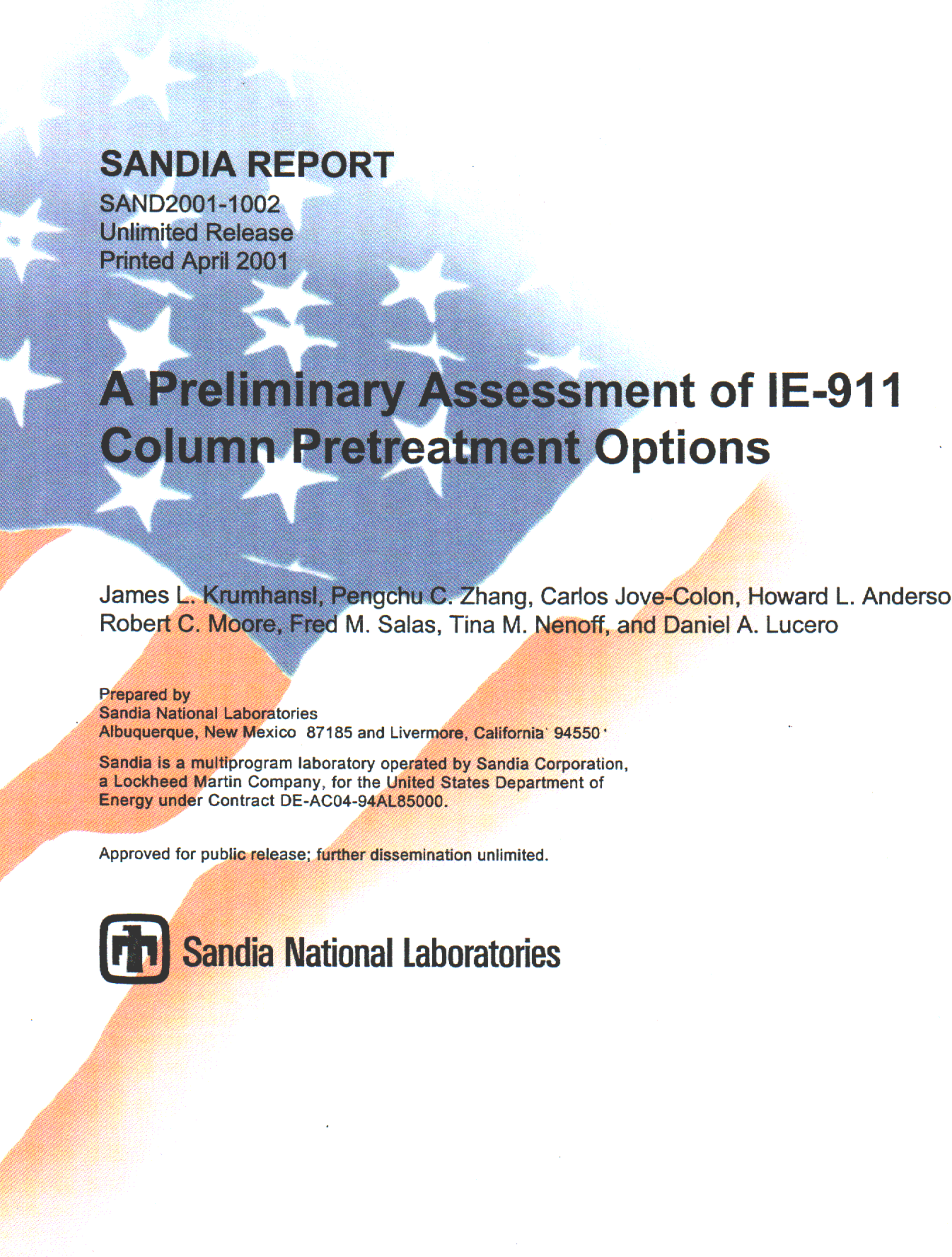

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A Preliminary Assessment of IE-911 Column Pretreatment Options

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A Preliminary Assessment of IE-911 Column Pretreatment Options

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Abstract

The use of a novel molecular sieve, IE-911 is one technology that may be used to recover cesium from liquid radioactive wastes at Savannah River and other DOE sites. Preliminary column tests performed at Savannah River and Oak Ridge National Laboratories indicated that ion exchange columns packed with this material had a potential for plugging. A Two-pronged approach was taken to assess this issue.

The key to using this material is that it must be pretreated to neutralize the acid content imparted by the manufacturing process. In addition to duplicating the processes that had historically led to column plugging, we also investigated a variety of other pretreatment options. In general, it was found that when problems arose, they could be traced to the accumulation of particulate matter at the inlet end of a column. Mass-fouling of the pore spaces in the column was not observed. Both the Ie-911 and a hydrous Nb oxided were implicated. However, several column tests were also performed in which plugging was not observed. Based on these results it was concluded that a

batch pretreatment, prior to loading the IE-911 into the column, was the preferable approach. However, if it is necessary to pretreat the material in a column then several techniques were developed which should minimize the chances of plugging.

The other approach taken was to develop an understanding of the chemical processes underlying the plugging problem. The parts of this problem are (1) Nb solubility, (2) Zr solubility, (3) titration characteristics of the IE-911 and (4) aluminosilicate precipitation. Niobium solubility was found to increase with both temperature and pH. Anions in the waste such as oxalate and carbonate were not found to have a large impact on solubility. Dissolution of the Zr oxide used to bind the IE-911 pellets together was an initial concern but should not present a problem as long as the pretreatment fluids do not exceed 3N hydroxide. The response of the as-received IE-911 during base titrations was rather unusual. Even after prolonged exposure to moderately basic fluids the IE-911 retains a substantial capacity to neutralize additional hydroxide when the pH is raised still further. In addition many hours must elapse after changing the pH before the IE-911 equilibrates with the fluid. It also appears that the base exchange capacity has been underestimated and that a better value is about 3.3 meq/g. Finally, an approach to predicting aluminosilicate precipitation has been initiated. A thermodynamic model has been developed using published data and tested against the chemistry of Hanford tank fluids. Although the model correctly predicts equilibration with zeolite-group minerals it does not select cancrinite, the zeolite that is commonly found in these tanks (and described as an alteration product of the IE-911).

At this stage our data supports the following conclusions:

a. We have been successful at pretreating the existing IE-911 formulation in a column without the occurrence of plugging.
b. On an industrial scale it should be possible to pretreat the existing IE-911 formulations in either a column or batch mode, though the latter appears to be preferable.
c. A detailed understanding of the chemistry of this material is the key to successfully scaling up the pretreatment process and assuring that IE-911 loaded columns will continue to function over the long term when exposed to real waste solutions.

CONTENTS

1.0 INTRODUCTION

A key element in the treatment of radioactive liquids at Savannah River (and potentially other DOE sites) is the ability to scavenge radioactive Cs so the bulk of the fluid can be disposed of in a cost-effective manner. The use of a novel molecular sieve is one of several technologies being considered to accomplish this objective. This material is available commercially from UOP LLP under the product name of IE-911 (see appendix 1 for full product designation and contacts). The IE-911 consists of an active crystalline silicotitanate (CST) molecular sieve component and an inert binder. The CST is comprised primarily of: Na, Si, Ti, and Nb (formerly referred to as proprietary material one, or PM-1) plus an exchangeable monovalent cation. The binder is based on a technology that employs zirconium (formerly PM-2).

If the CST becomes the Cs recovery technology of choice, the treatment process will involve sizeable ion exchange columns filled with palletized IE-911. A number of scaled-down column tests were therefore, carried out to evaluate performance parameters for the material. A key aspect of using currently available IE-911 formulations is that before exposure to actual wastes (or waste simulants), it must be pretreated with NaOH to neutralize the acid content of the as-received material. While pretreating in a recalculating mode it was noted that small columns loaded with IE-911 sporadically plugged, or the pressure needed to maintain flow climbed during the test (Walker, 2000). In one case, a mass of cloudy whitish precipitate was found at the top of a plugged column. When this was analyzed, it was found to contain, principally, Nb. The mass disappeared when the column was back-flushed with fresh 3 M NaOH (Walker et al., 1999).

Column plugging on an industrial scale would be problematic. Thus, it is important to develop guidelines for avoiding situations where this is likely to occur. This report presents results of a two pronged approach to develop such criteria. First, column tests employing a variety of pretreatment approaches were investigated. *These tests demonstrate that it is, in fact, possible to pretreat the material without plugging a column.* A number of mechanistic chemical studies were also started to support interpreting the results from the column tests. These studies provide a less empirical approach to understanding the phenomena that underlie column plugging. They are also a prerequisite to successfully scaling up the process or assuring its long-term operation.

From a programmatic perspective this report is submitted to address milestone A.1.1-1 for TTP Al21WT21: "issue report on causes of plugging and potential pretreatment modifications". Task elements from this TTP include:

a. Perform scaled down column pretreatment tests to duplicate the plugging processes and obtain a more complete analysis of the solids involved.
b. Develop better pretreatment strategies.
c. Develop an understanding of the impact of pH on Nb solubility and how pH controls the rate at which the hydrous oxide precipitates.
d. Develop a general chemical model for column plugging during pretreatment.
e. Develop an understanding of how in-service clogging by aluminosilicate precipitation progresses and assess whether this can by mitigated or eliminated by a pretreatment process.

This particular TTP applies to FY01 but references work conducted during FY00. Emphasis during FY00 was on the first two task elements. Since FY00 has just ended, this report primarily provides documentation on results related to these tests.

2.0 COLUMN TEST RESULTS

2.1 Experimental description

All of the column tests described in this report were performed with a granular or palletized material consisting of CST plus binder and described as IE-911, material 89990-999, Lot 20810-00009. This is the same material employed by Li et al. (2000) in their study. A recently provided material, Lot 9090-76 will be used in future tests but is not evaluated in this report. The experimental design used for our tests (Fig. 2.1.1) generally followed that of Walker (Walker et al., 1999), though limitations on the amount of CST that could be found for testing on short notice precluded an exact duplication of their design. For our tests, between 50 and 80 grams of IE-911 were loaded into a four-foot long fused silica tube. A roughly one inch long plug of fused silica glass wool supported and confined the IE-911 at either end of the charge. Both ends of the tube were closed with Teflon fittings equipped with O-rings to preclude leakage along the tube walls. Each end plug also has a threaded feed-through so that tubing connected to the end plugs would remain in place in spite of relatively high fluid pressures that occasionally developed during a test.

Fig. 2.2.1 Experimental apparatus used in column testing

The peristaltic pump is to the left and the fluid reservoir for recirculating the fluid is shown at the center. The bottom part of the four- foot column packed with IE-911 is shown to the right.

Fluid was circulated into the bottom of the column in a pulsed manner by a peristaltic pump that delivered 0.5 ml every six seconds. A shunt off the line feeding the bottom of the column went to a pressure transducer so that the driving pressure on the column could be monitored. Tubing from the top of the apparatus returned fluid to a plastic bottle so that it could be recirculated through the column multiple times. Both the exit and return tubes were plumbed through the bottle cap so that, except for a pinhole needed to preclude a pressure buildup in the bottle, the recirculating fluid was effectively isolated from the atmosphere. Often the recalculating fluid was highly basic and the possible dissolution of either the glass wool plug or the tube was initially a concern. However, after a considerable amount of post-test characterization, we were unable to find any evidence of mass wasting of either component.

Although the TTP only called for duplicating the column-plugging problem, a total of four column tests have been carried out to date. Each test had a slightly different objective and built on the experience gained from preceding tests (Table 2.1). The overall objective of the multiple tests was to demonstrate that under some circumstances (but not necessarily those employed earlier at Savannah River or Oak Ridge), it was possible to pretreat the material with NaOH and not plug the column.

Table 2.1 Summary of column test conditions and results

Experiment	Sample Preparation	Reservoir Fluid	Outcome
#1	None, dry loaded without washing	Deionized water Followed by 3N NaOH	Plugged within 12 hours
#2	Three batch washes with 10N NaOH, one deionized water rinse, then dried before loading	3N NaOH	Plugged after 1.5 days. Changing the glass wool plug allowed flow to resume.
#3	None, dry loaded without washing	Stopped pH increases: Deionized water; a pH 10 borax buffer, ~1 N NaOH, and finally ~3 N NaOH	Never plugged but driving pressure climbed with pH
#4	Fines removed by repeated deionized water washes and then dried prior to loading the column.	3N NaOH from the start	Never plugged but had high initial driving pressure that dropped slowly over a week.

2.2 Experimental narratives

Each column experiment had a different objective and responded in a unique manner. The overall intent of the experimental plan was to isolate potential causes of plugging and develop strategies that would eliminate or mitigate this problem. Observations made during these tests also provided the motivation for some of the mechanistic chemical studies described in Section 3 of this report.

2.2.1 Experiment #1

The first experiment in the column test matrix was intended to duplicate the plugging experiences at Savannah River and Oak Ridge (Walker et al, 1999; Walker 2000). Once the column was loaded with IE-911, the lines were leak-tested by circulating deionized water through the system over night. The next morning no increase in driving pressure was evident. The reservoir remained colorless and the pH had fallen to nearly 3. The acid condition is expected since the IE-911 currently arrives from UOP in a hydrogen-exchanged form. It is this acidity that is the motivation for pretreating the IE-911 since lowering the pH of wastes (or simulants) will precipitate abundant aluminum hydroxide and immediately plug a column.

Soon after the reservoir fluid was changed from the acidified water to 3N NaOH, the effluent from the top of the column became light yellow and then a fine precipitate started forming in the reservoir. At one point the fluid became sufficiently turbid that it was difficult to see through the bottle. By the next morning the 30 psi limit switch on the peristaltic pump had tripped and the flow had stopped. The reservoir continued to have a milky appearance. Removal of the glass wool plug at the base (input end) of the column revealed that an abundance of very fine white powder had collected there. No evidence of mass deterioration of the pellets in the column was observed.

2.2.2 Experiment #2

In the second experiment, the objective was to eliminate the possibility that the CST could continue to function as an acid prior to loading it into the column. Since the standard for pretreatment was nominally 3N NaOH the decision was made to rinse the IE-911 with 10N NaOH in a batch mode prior to loading the column. In the first attempt, the IE-911 was put in a polyethylene bottle with the 10N NaOH, which was then put on a shaker over the weekend. Rinsing this material removed a large portion of the charge as fines and when a column was loaded with this material, it would not permit the passage of any fluid.

A second batch of material was then prepared using 10N NaOH, but this time the mix was only given an occasional shake. Over two days the IE-911 was exposed to three changes in the rinse fluid in an attempt to get rid of the fines. After the third rinse it became apparent that rinsing would never produce a clear fluid so the charge was placed in a filter, rinsed off one last time with deionized water and allowed to dry at room temperature over a weekend. Our earlier experience had already shown that with our small diameter columns, it was futile to try and do the columns using a wet slurry of the material. Hence, all of the later tests were dry-loaded, either with or without the benefit of a previous washing step.

Once the column was loaded, the fluid reservoir was filled with about 400 ml of 3N NaOH and the peristaltic pump started at the same flow rate of 0.5 ml every 6 seconds. The reservoir fluid slowly became turbid but did not assume the same yellowish color that had been observed in the first test. The test ran for one and a half days before the driving pressure climbed to an unacceptably high level and the experiment was stopped. This time rather than ending the experiment, the glass wool support at the base (inlet end) of the column was replaced and pumping resumed. The driving pressure returned to an acceptable value and fluid flow was maintained without further incident for an additional two days before the experiment was ended.

2.2.3 Experiment #3

The third experiment was motivated by the consideration that immediately exposing the IE-911 to a strong base might increase the probability of plugging. This test, then, was intended to assess the impact of first exposing the IE-911 to a mild base for several days before going to a final 3N NaOH treatment. The sample was first dry loaded into the column without prior washing, and again, the plumbing was tested by circulating deionized water through the system overnight. In the morning the pH of the reservoir fluid was 3.4. In this experiment, a water-soluble pH indicator was added to the fluid with the objective of viewing pH changes as the fluid passed through the column (which initially imparted a red color to the reservoir water, Fig. 2.1.1). However, the IE-911 also proved effective at sorbing the dye so that the intense coloration remained confined to the base of the column and merely reflected the pH of the fluid in the reservoir that was feeding the column.

The next morning 27 grams of borax ($Na_2B_4O_7 \cdot 10H_2O$) were added to the deionized water in the reservoir. This immediately raised the pH to about 9.3. The amount of borax was selected based on an estimated exchange capacity of 2.2 meq/g of hydrogen ion for the IE-911 (Walker et al, 2000) but, this estimate is apparently low by a significant amount. This amount of borax was close to the saturation limit for the reservoir. Thus, rather than adding additional borax to compensate for the shortfall, the buffer was regenerated by repeatedly adding small amounts of sodium hydroxide to the reservoir. Other buffers exist with greater capacity and more versatility in maintaining intermediate pH values. However, borax was selected so there would be no possibility that residual contamination on the CST could impact, ultimately incorporating the loaded CST into a borosilicate waste form. By late afternoon both the column effluent and reservoir fluid had stabilized at a pH of about 7. Over the next twenty-four hours more NaOH was added incrementally until the column effluent and reservoir stabilized at a pH of 9.5. The fluid remained clear throughout this treatment, but because of the pH indicator, it was not possible to observe when (or if) a yellow coloring agent was leached from the IE-911.

Next, a larger addition of NaOH was made to over-ride the buffer and start approaching the 3N hydroxide level that is the standard for pretreating the IE-911 (Walker et al., 1999). Initially the reservoir pH was around 14.3, but after the fluid circulated overnight, the pH fell to a value that was almost identical to the reading obtained when the electrode was immersed in a 1N NaOH stock solution. Thus, although the IE-911 had been equilibrated with a moderately basic fluid for many hours, it still had a significant capacity to titrate base when the pH was raised still further. The fluid also remained clear through this stage of the process.

The final step involved replacing the effectively 1N NaOH - sodium borate fluid with a new solution of 3M NaOH. The impact of this transition was immediate and rather dramatic. After circulating for less than half an hour, the reservoir had become slightly cloudy and there was significant nucleation of gas bubbles on the bottle walls. The bubbles were transient phenomena and after shaking the bottle once they did not reappear. After circulating for about five hours, the reservoir cleared and what precipitate remained had settled to the bottom of the vessel. A small amount of pH indicator had carried over from the preceding stage of the test so, again, it was not possible to assess whether the reservoir fluid contained the light yellow coloring agent noted in earlier experiments.

Throughout this experiment it was possible to monitor the driving pressure at the inlet end of the column. During the deionized water phase, pressures were between 4 to 7 psi and when the borate buffer was added there may have been just a slight increase to a peak of 8 psi. Adjusting the hydroxide concentration to the 1N level did not immediately impact the driving pressure but after the fluid had circulated overnight it had risen to between 8 and 12 psi. However, no evidence of particulate matter in the fluid was observed at this stage of the test. Further increasing the hydroxide content to a 3N level had a large effect and within an hour the pressure had climbed to the 38 - 42 psi range. It remained at this level until the next day when the test was concluded.

2.2.4 Experiment #4

Although this test is still in progress, some early findings provide some perspective on the results of other tests. This test resembles Experiment #1 in that 3N NaOH was used as the first pretreatment fluid. However, it differs in three respects. During the first test the material was not washed prior to loading of the column due to difficulties that had previously been encountered in loading our small diameter columns with an IE-911 - water slurry (as suggested in the standardized pretreatment protocol, Walker et al., 2000). In this test, however, the material was well washed both by screening it under a stream of deionized water and then by placing it in a plastic bottle and allowing it to stand in contact with deionized water for several hours prior to rinsing off the fines. A second important difference was that a glass wool prefilter was placed in the line between the base of the column and the peristaltic pump. This was done so that if large increases in driving pressure were observed, it would be possible to change out the first filter without disturbing the column. Finally, the material was not exposed to deionized water in the column before the 3N NaOH was fed to the column.

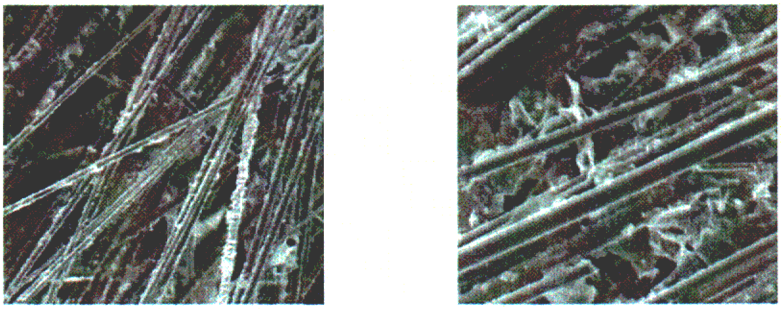
The pH of the first effluent to be sampled was about 7. This fluid was clear but had a distinct yellow coloration. The initial driving pressure in this test was 17-18 psi. It held steady until about four hours had elapsed, after which it slowly climbed to the 19-21 psi range for two days. Over the remainder of the week it then slowly declined to between 14 and 16 psi. Thus, the column had an elevated driving pressure from the very start even though this test contained only about two-thirds the IE-911 that was used in earlier tests. Further, this high driving pressure existed before any evidence of particulate matter was observed in the reservoir fluid.

After about 40 minutes the reservoir became turbid and the pH of the effluent returning from the column had risen to 13.8. Then, as before, after the fluid had circulated for several hours, the fluid in the reservoir was significantly clearer and the remaining precipitate had settled to the bottom of the reservoir. As soon as the precipitate was noticed, a 50ml sample of the suspension was withdrawn into a syringe and then passed through a 0.2 micron filter to catch the solids. The filtered fluid did not have the distinct yellow coloration of the initial column effluent so the coloring agent is apparently sorbed onto the precipitate. The precipitate was then rinsed by forcing an additional 50ml of deionized water through the filter.

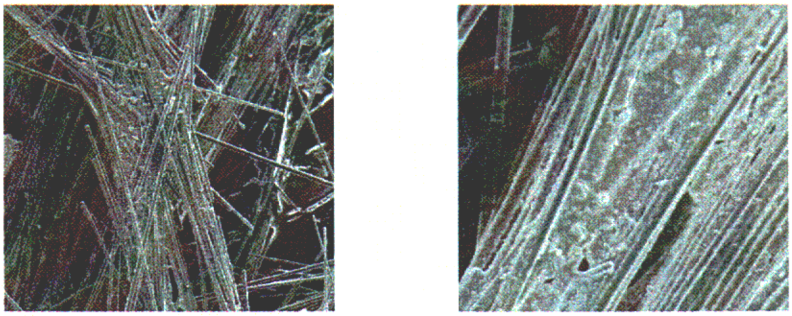
2.3 Filter analyses

After Experiments #1 - #3 were completed the apparatus was disassembled and the glass wool plugs were washed free of the highly caustic solutions they were exposed to during tests. They were then analyzed using a JEOL T-300 scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis capability (EDS). The SEM provides detailed imaging capability while the EDS provides complementary chemical data. Experiment #4 is still underway but an analysis is available of the fines recovered by filtering the turbid fluid produced early in the experiment. In the case of Experiment #1 enough material collected on the filter that an X-ray diffraction pattern could also be obtained to complement the results of the SEM/EDS study.

The materials trapped on the glass wool from Experiments 1-3 are shown in Fig. 2.3.1. In all cases, the trapped materials are too fine to be resolved into individual phases. This is not surprising given that suspensions of these materials usually took several hours to settle out. Sampling of these filters is somewhat subjective but it is evident that the Experiment #3 filter contained significantly less material than the other filters.



Experiment #1, 500x Experiment #2, 500x



Experiment #3, 250x Experiment #3 500x

Fig. 2.3.1 SEM photographs of the particulate matter trapped on the glass wool filters. At 500x a frame is 200 microns on a side and at 250x a frame is 400 microns on a side

The composition of the trapped material is documented in Fig. 2.3.2 and 2.3.3. X-ray diffraction of the voluminous precipitate from the Experiment #1 filter demonstrated that the only crystalline component present was the CST itself. There was relatively little material present so the pattern obtained from the filter sample (lower trace, Fig. 3) was not as well expressed as the reference

CST pattern (upper trace, Fig. 3). However, all of the peaks are in similar locations confirming the identity of the material.

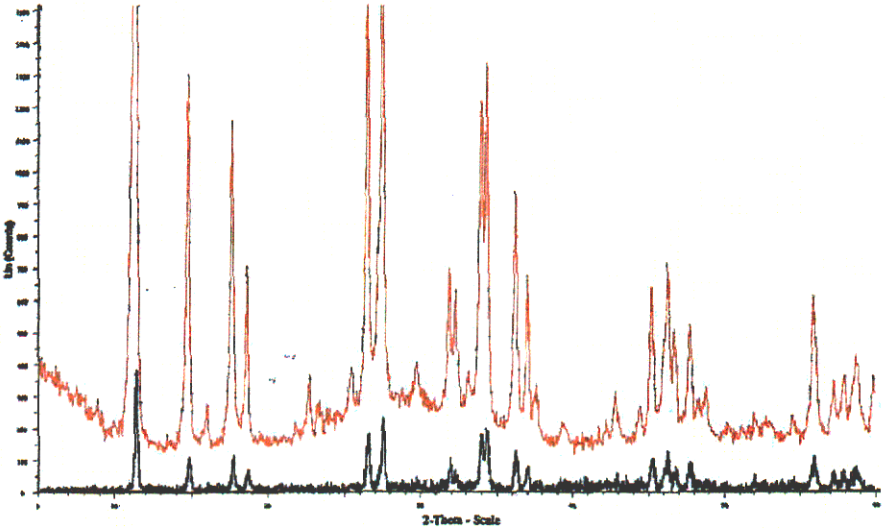
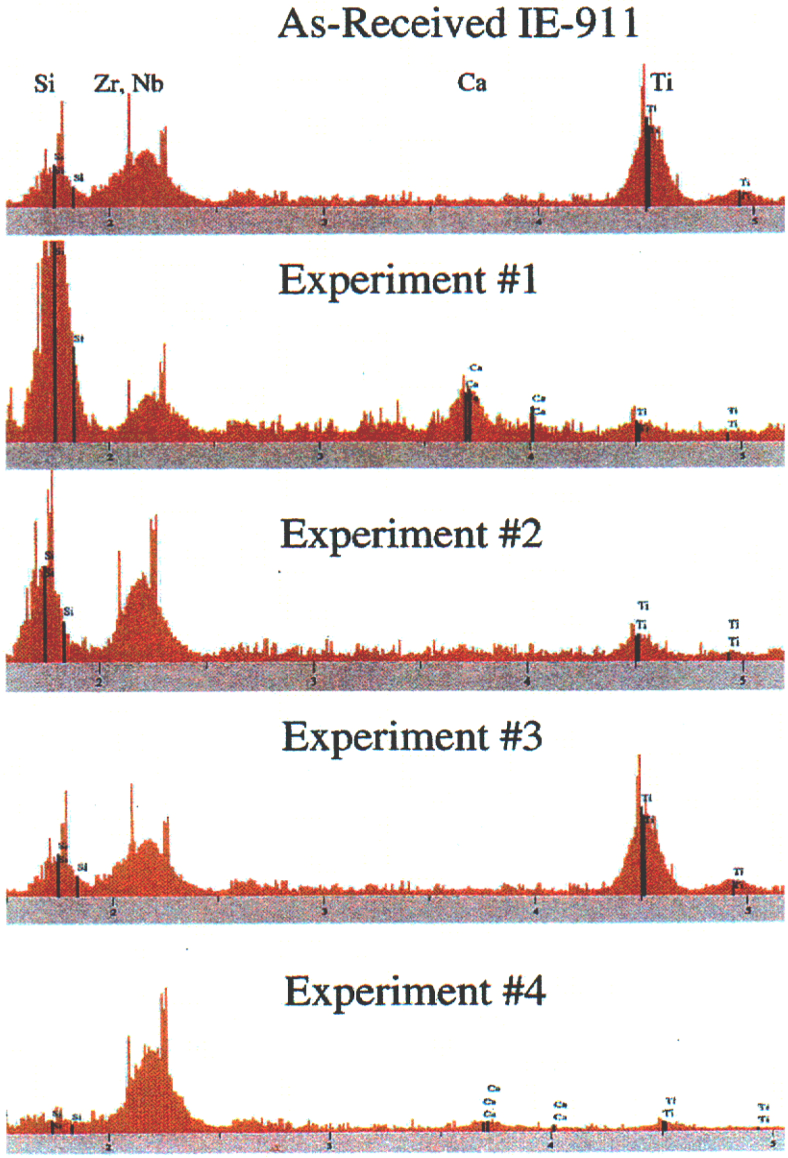


Fig 2.3.2 X-ray diffraction pattern of material recovered from the glass wool plug in Experiment #1 (lower trace) compared to a reference pattern for pure CST (upper trace).

Fig. 2.3.3 compares the EDS data for the particulate matter caught on the filters from various experiments with that obtained from a sample of as-received IE-911. When this information was being acquired, the identities of Nb and Zr were proprietary so these elements are not explicitly highlighted in black on the trace. However, the second peak from the left (centered at about 2.25 keV) reflects their presence. Evidence of Zr would be expressed as a bulge on the left (low energy) side of this peak. Due to the low concentration of Zr this is generally not observable. Hence, this peak essentially reflects the relative abundance of Nb. The height of the Si peak (far left) is erratic and can reflect a large contribution from the silica glass fiber beneath the precipitate.

In the reference spectra for "as-received" IE-911, the Ti peak is somewhat larger than that of the Nb peak, while in the precipitate from Experiment #1, the reverse is true. The presence of CST is known from the X-ray diffraction data so the difference in peak ratios suggests that an additional amorphous Nb compound be mixed into this sample. Ca may also play a role in the plugging process, although Fig. 2.3.2 contained no peaks characteristic of either calcium carbonate or hydroxide. Thus, the Ca is probably incorporated with the Nb into the amorphous fraction in this mix. The EDS trace from Experiment #2 also indicates that Nb is present in excess of that present in the as-received IE-911. The solubility of Ti is quite low relative to that of Nb so, although no X-ray evidence was obtainable, the presence of Ti implies that some CST materials have, again, been incorporated into the particulate matter trapped on the glass wool plug. Ca is, however, absent from this trace and this may reflect a difference in pretreatment processes. In Experiment #3 the filters were significantly cleaner (Fig. 2.3.1 lower left) and the Nb to Ti peak height ratio is closer to that of the CST materials. Again, no Ca was detected in this material. Finally, Nb is by far the dominant metal in the particulate matter filtered from the reservoir fluid in Experiment #4. Only a trivial CST component is probably present since the Ti peak is barely discernable. Ca is again present and recently UOP indicated that it came from the manufacturing process. At lower energies (not shown), the EDS analysis also indicated the presence of significant amounts of Na. This may represent incomplete washing of the sample but it is also possible that Na is an integral part of the Nb-rich material that precipitated early in the test.


As-Received IE-911

Experiment #1

Experiment #2

Experiment #3

Experiment #4

Fig 2.3.2 EDS spectra for filtered particulate matter compared to that for the as-received IE-911

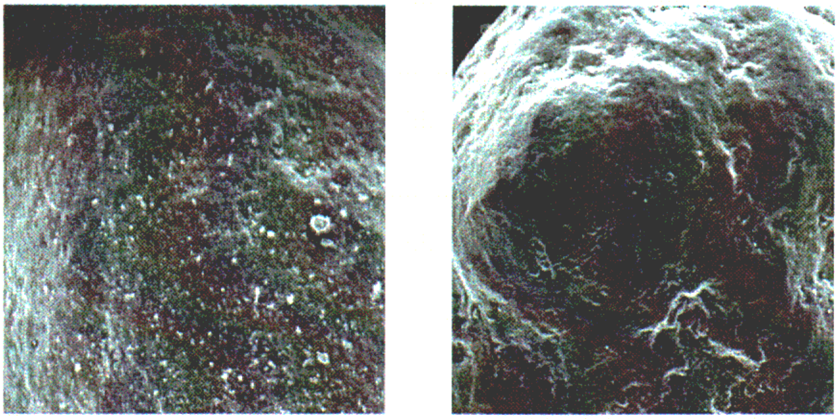
These results suggest a general pattern to the origin of particulate matter during pretreatment. Experiment #4 uniquely identifies the early formed compound as an amorphous oxide (or hydroxide?) of Nb, possibly with Na and Ca as additional constituents. Experiment #3 suggests that free hydroxide concentrations in excess of about 1N are needed before the IE-911 will free up enough Nb to produce this material. An unavoidable feature of recirculating the NaOH solution is that Nb concentrations in the reservoir will increase as the pH falls. Apparently, these opposing trends eventually cause the solution to become supersaturated and a precipitate forms. The partial disappearance of this precipitate later in the tests may either reflect its transport to the glass wool filters or re-dissolution, possibly in response to a further lowering of the pH in the reservoir. Detailed future studies will be needed to resolve this issue.

Given longer times CST particles may also accumulate in the glass wool. Washing prior to loading the column may, or may not, alleviate this issue. However, no fines were seen in the Experiment #3 reservoir even after several days of circulating at low pH. They also appeared almost immediately after introducing 3N NaOH. This suggests a correlation between the release of the Nb (which results in the short-term turbidity of the reservoir) and the production of CST-rich fines (which accounts for the Ti in the solids that had collected on the filters by the end of the experiments). Finally, and probably of greatest importance, is the observation that production of fines seems to vary greatly depending on the nature of the pretreatment process used. In fact, only in test one did the column plug to the extent that flow stopped.

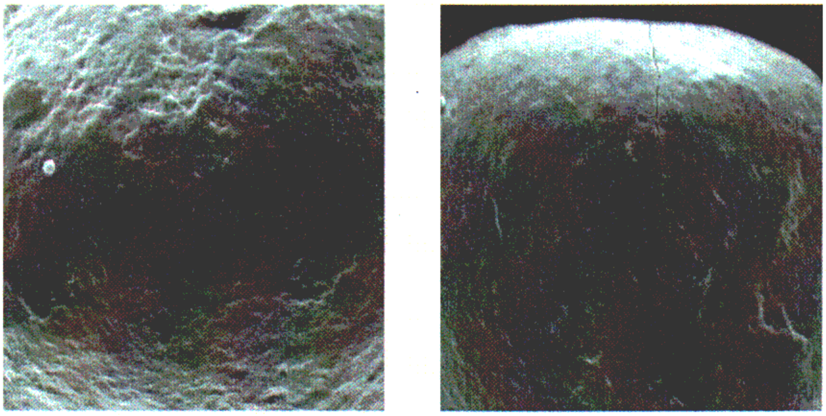
2.4 Pellet surface characteristics

The accumulation of CST particles on the glass wool plugs suggests that pellet integrity may be an issue. Hence, pellets from the first three experiments were examined in some detail using the SEM (Fig. 2.4.1). As-received materials (upper left) show fines adhering to a relatively smooth surface. The fines are missing from all the experimental materials and a slight roughening of the pellet surfaces seems to have taken place during Experiments #1 and #2. More significant is the cracking apparent in Experiment #3 pellets. About a quarter of the pellets had started to crack in materials from this experiment. At this point it is not known why the treatment in Experiment #3 led to cracking. However, the sample preparation was the same for all so it is unlikely that the cracking is an artifact of the post-test sample treatment.

The generally clean appearance of the post-test materials is also of considerable importance. Only Experiment #1 produced pellets with foreign materials adhering to their surface filter (Fig.2.4.2) and these were confined to the base of the column just above the filter. Not surprisingly, the material on the surface was the same as that caught on the glass wool support. Thus, the plugging process does not reflect a general mass fouling of the pore spaces in the columns. Rather, it is confined to the inlet region of the column and in most experiments only involved accumulation of materials on the glass wool.

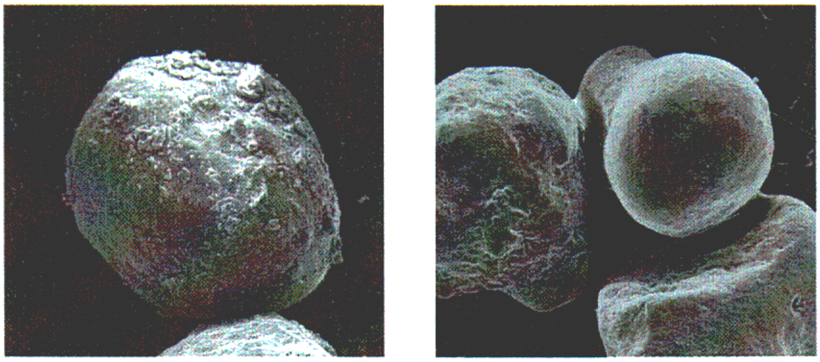


As Received, 500x Experiment #1, 500x



Experiment #2, 500x Experiment #3, 500x

Fig. 2.4.1 Comparison of surface textures (frames size is 200 microns)



Column base, 200x Mid-column, 200x

Fig 2.4.2 Comparison of IE-911 pellets from the base (left) and middle (right) of the column in Experiment #1. Note surface coating on the left particle and relatively clean surfaces of particles from the middle of the column. (Frame size is 500 microns).

2.5 Column test summary

A variety of pretreatment protocols were evaluated ranging from processes intended to plug the column to those designed to avert problems noted in earlier tests. In fact, it proved relatively difficult to completely plug a column. When circulation problems developed it could generally be traced to particulate matter that had accumulated on the glass wool plug at the inlet end of the column. Two types of particulate matter have been identified: fragments of the IE-911 itself and an amorphous hydrous Nb oxide that may also incorporate some Na and Ca depending on how the pretreatment was carried out.

A number of factors were also identified that appear to decrease production or mobility of the particulate matter:

a. Batch pretreatment to avoid strong pH gradients in the column and large pH differences between the fluid reservoir and what is likely to develop in the column as fluid circulates
b. Slowly stepping up the pH of the column feed stock rather than immediately applying a strong base
c. Strategic placement of line filters
d. A rigorous prewashing procedure, though some evidence suggests that this precaution may be defeated by later exposure to a strongly basic solution

3.0 MECHANISTIC STUDIES

The dominant picture derived from the column studies just described, as well as those documented in other project publications, is that column plugging is a capricious, though potentially serious, occurrence. Empirical testing has been unsuccessful in providing protocols that will preclude its occurrence in the future. To develop such procedures will require understanding the underlying chemical processes responsible for particulate matter production.

Although the detailed chemistry is complex, it is relatively straightforward to enumerate the topics that need to be addressed if IE-911 loaded columns are to be successfully operated on an industrial scale:

a. Nb solubility, under basic conditions, Nb (presumably from an impurity phase and not the CST) is the most mobile constituent in the IE-911 and it has already been implicated as one potential cause of column plugging
b. Zr solubility, the appearance of CST particles in the glass wool plugs raises the question of binder integrity
c. Acid-base responses, successful treatment hinges on knowing both the kinetics and capacity of the IE-911 for H^+-OH^- exchange; pH is the master variable governing the precipitation and dissolution of many dissolved components found in both pretreatment and actual waste solutions
d. Aluminosilicate precipitation, this may become a serious problem during treatment of actual wastes and pretreatment may be called on to mitigate its occurrence

In the short time since the program started (about eight weeks ago) it was obviously not possible to completely address all these issues. However, the preliminary results already available shed considerable light on what may have occurred during the various column tests.

3.1 Nb solubility

The apparent tie between the appearance of Nb-rich precipitates and pH fluctuations provides the rationale for understanding the functional relationship between pH and Nb solubility. However, the impact of other system variables on Nb solubility also need to be addressed. Loss of circulation or cooling in the production mode may allow column temperatures to rise and perturb the equilibrium between dissolved Nb in the solid IE-911. Thus, in addition to pH effects, the impact of temperature changes needs to be evaluated. Treatment of actual wastes may also bring the IE-911 into contact with components that may complex Nb, increasing its solubility, or decrease its mobility by forming new, insoluble compounds.

3.1.1 Impact of pH on Nb solubility, a theoretical assessment

The literature contains only fragmentary data on the solubility of Nb though enough exists to predict the gross behavior of Nb as a function of pH. According to the Baes and Mesmer (1976) scheme for speciating aqueous Nb under basic conditions, the dissolution reaction is given by:

$1/2Nb_2O_5(act) + 7/2H_2O \leftrightarrow H^+ + Nb(OH)_6^+$ $\log K = -12.2$, and

$[H+][Nb(OH)_6^-] = 10^{-12.2}$ or $Nb(OH)_6^- = 10^{-12.2} / [H^+]$.

These equations predict a sharp increase in Nb solubility starting at about a pH of 7 and quite high solubilities in strongly basic solutions (Fig. 3.1.1.1). The solubility-controlling solid in these experiments was "activated" niobium pentoxide, which may resemble the precipitate formed early in the column tests.

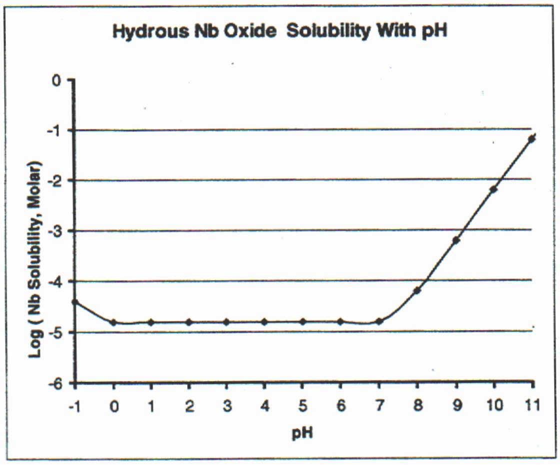


Fig. 3.1.1.1 Solubility of "activated" niobium pentoxide calculated from Baes and Mesmer, 1976.

However, the aqueous solubility of Nb is not as simple as would be inferred from the simple Baes and Mesmer, 1976 scheme, since a variety of polynuclear complexes are known to exist in solution. Rozantsev et al., 2000 suggest that the first polymerization of Nb occurs when:

$OH^- / \Sigma\ Nb(aq) \approx 7.5$

On the basic side of this limit the dominant form of dissolved Nb is likely to be NbO_6^{-7}, which is probably comparable to the $Nb(OH)_6^-$ monomer in the Baes and Mesmer, 1976, speciation scheme. On the acidic side of this limit Nb polymerizes to form $Nb_4O_{16}^{-12}$. As the pH falls further the hexaniobate complex, $Nb_6O_{19}^{-8}$, will form from the $Nb_4O_{16}^{-12}$ ion. This takes place when:

$OH^- / \Sigma\ Nb(aq) \approx 2.0$

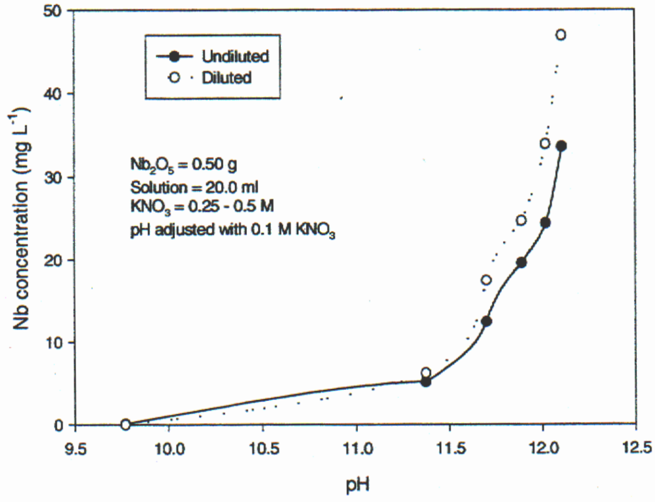
For reference, the impact of pH on Nb polymerization was assessed over a range of concentrations that might be encountered in pretreating the IE-911 with strongly caustic fluids: 50 and 250 ppm (Wilmarth and Walker, 1999). The first polymerization reaction, formation of $Nb_4O_{16}^{-12}$ from the monomer, occurs when the pH falls below a value of 12.3 in a 250 ppm Nb solution and below 11.6 in a 50 ppm solution. The second polymerization reaction (formation of hexaniobate ion, $Nb_6O_{19}^{-8}$, from $Nb_4O_{16}^{-12}$) occurs when the pH falls below 11.7 for a 250 ppm Nb solution and below 11.0 for the 50 ppm solution. Further, about half a pH unit lower, it is still projected that in both cases the hexaniobiate ion itself dimerizes to form $H_2Nb_{12}O_{36}^{-10}$. These pH values are encountered during pretreatment so it is likely that during the process a variety of polymeric species may form before the pH finally rises to the point where a monomeric species is stable. The kinetics of the appearance and disappearance of these phases may not be instantaneous. This may account for the seemingly transient appearance and disappearance of solids in some of the reservoirs holding recalculating fluids.

3.1.2 Solubility of Nb_2O_5 in KOH solutions

A variety of experiments were carried out to measure the solubility of Nb_2O_5 in solutions containing different KOH concentrations. The crystallinity of the Nb_2O_5 was verified by X-ray diffraction. By using a well-crystallized material, it was possible to establish minimum solubilities that might be observed at different pH values. The solubility of hydrous oxides could initially be several orders of magnitude higher, but such phase would be metastable with respect to the material tested in these experiments. KOH rather than NaOH was used because high Na concentrations are problematic when solution analyses are performed by direct current emission spectroscopy (DCP).

K-rich solutions present fewer problems. These experiments were only in contact with the Nb_2O_5 for about a day, and only a single analysis of the fluid was performed in each case; thus, it is not possible to demonstrate the degree to which equilibrium was approached. However, the results do give a quick experimental perspective on solubility levels that might be expected on a time frame commensurate with pretreatment processing. They also validated the general pH response predicted by the theoretical model described in 3.1.1.

In the first suite of experiments, Nb_2O_5 was exposed to relatively dilute KOH solutions. The fluids were analyzed by DCP at two degrees of dilution against a Nb standard prepared in deionized water without a potassium ionization. Although a matrix effect is clearly evident, both suites of analyses demonstrate a sharp jump in solubility when the pH exceeds 11.5. Because of the relatively dilute nature of these fluids, it was meaningful to plot the data against the measured pH values of the solutions (Fig. 3.1.1.1 - left). The next suite of experiments involved more concentrated KOH solutions, and as a result the outcome was initially plotted against the as-mixed hydroxide concentration of the fluids (Fig 3.1.1.1 - right).



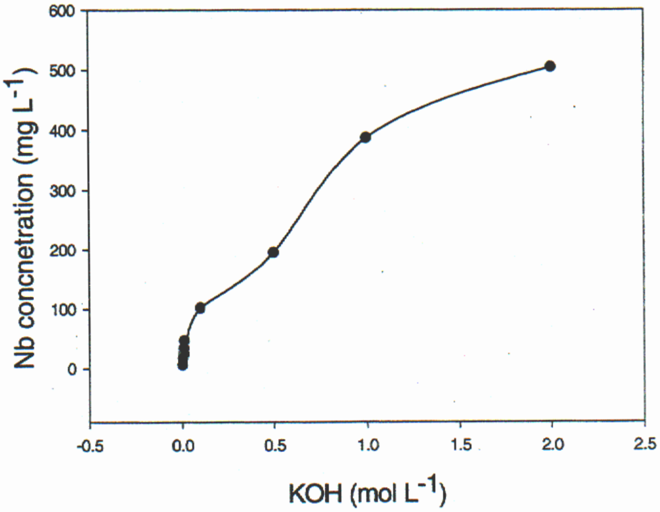


Fig. 3.1.1.1 Nb_2O_5 solubilities in dilute (left) and concentrated (right) KOH solutions

Assuming high OH concentrations can be translated directly into solution pH allows a comparison to be made between the two studies (Fig. 3.1.1.2). With a log – log plot of concentrations, a generally linear pattern results. However, closer examination reveals that the low pH data has a slope closer to 1.1 while the slope of the more basic fluids is closer to 0.6. A slope close to 1 is consistent with the formation of a $Nb(OH)_5^-$ complex, but it was not possible to find a simple model that would predict a slope of 0.6. This problem may ultimately be ascribed to aqueous complex formation, or to an error in assigning pH values to the concentrated solutions. In any case, the general result of importance is that over the entire pH range to be encountered during pretreatment, the Nb solubility should decrease with decreasing pH. These solubilities are also much lower than were predicted by Baes and Mesmer, 1976. This may reflect the great decrease in solubility that occurs when an oxide goes from a largely amorphous hydrous state being well crystallized.

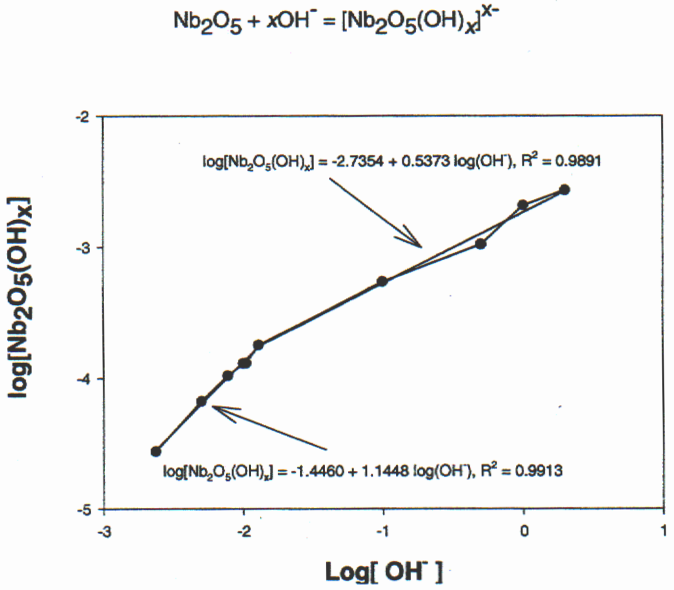


Fig. 3.1.1.2 Log-Log plot of Nb_2O_5 solubilities in KOH solutions

In a second set of solubility experiments (Fig. 3.1.1.3), the source for the Nb was the CST material itself (available commercially as IE-910), or its engineered form as IE-911 in various stages of development. The CST material was from an archive sample dating from the mid 1990s as were two of the palletized forms of the IE-911 (8671-08 and 07398-38B) that presumably used a CST base similar to the archived IE-910. The modern IE-911 samples are abbreviated 99-7 and 99-9. Unfortunately, on short notice it was not possible to obtain a sample of the IE-910 feedstock from which the modern IE-911 samples were prepared. The pH was adjusted with

KOH and the ionic strength was held relatively constant by using a matrix of 1 M of KNO_3. Results of this study generally support the other pH studies in that above a pH of roughly 12, the solubility increases sharply. These results also suggest that binding the pellets can have a moderate to large effect in suppressing the actual amount of Nb liberated to solution in short term testing.

Fig. 3.1.1.3 Nb solubilities derived from CST-based materials

To summarize, Nb solubility depends strongly on pH. Above a pH of about 11.5, a variety of aqueous complexes may form leading to a sharp increase in total dissolved niobium. This has strong implications for the pretreatment process. Strongly basic solutions may come in contact with the IE-911 and be partly neutralized. Preliminary results also suggest that the as-received Na form of the CST (IE-910) may be at least as effective an Nb source, as the acid-treated IE-911 that is subsequently exposed to an excess of strong base.

3.1.3 Effect of temperature on Nb solubility

To address this problem, the first bank of Nb_2O_5 solubility experiments was expanded to include samples held at 60° and 90° C. Samples were quenched quickly so that the solubilities reflect concentrations at temperature. The pH measurements were made after the fluids had returned to room temperature. It is evident that even modest temperature excursions greatly increase Nb solubility, particularly at pH values above 11.5. Thus, if there were a temperature excursion in a column, then on cooling, some particulate matter would be expected to precipitate.

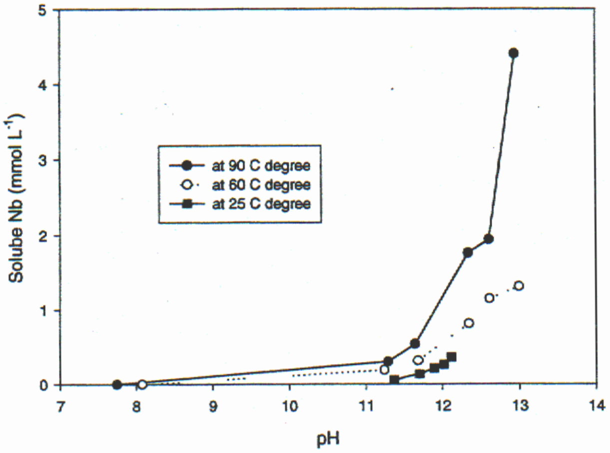


Fig. 3.1.3.1 Effect of temperature and pH on Nb_2O_5 solubility

3.1.4 Effect of Oxalate and Carbonate on Nb solubility

Actual waste fluids coming in contact with the IE-911 will contain a variety of components that may complex Nb and alter its solubility. Two obvious choices are carbonate, that at least in simulants, is present at the 0.16 M level, and oxalate, that is added to simulants at a concentration of 0.008 molar (Walker, 1999). In order to assess whether either anion had the potential for complexing Nb, the solubility of Nb_2O_5 was measured in both 0.01 M and 0.1 M solutions of these anions. In the case of carbonate, no evidence of complexing was observed (Fig. 3.1.4.1 – left). Oxalate (Fig. 3.4.1.1 – right) had a more complex effect. At pH values below 11.5 elevated oxalate levels suppressed solubility, while above this pH, the solubility was enhanced. It is only speculation but the explanation for this behavior may lie in the formation of a high pH complex that gives way to a relatively insoluble salt in less basic solutions.

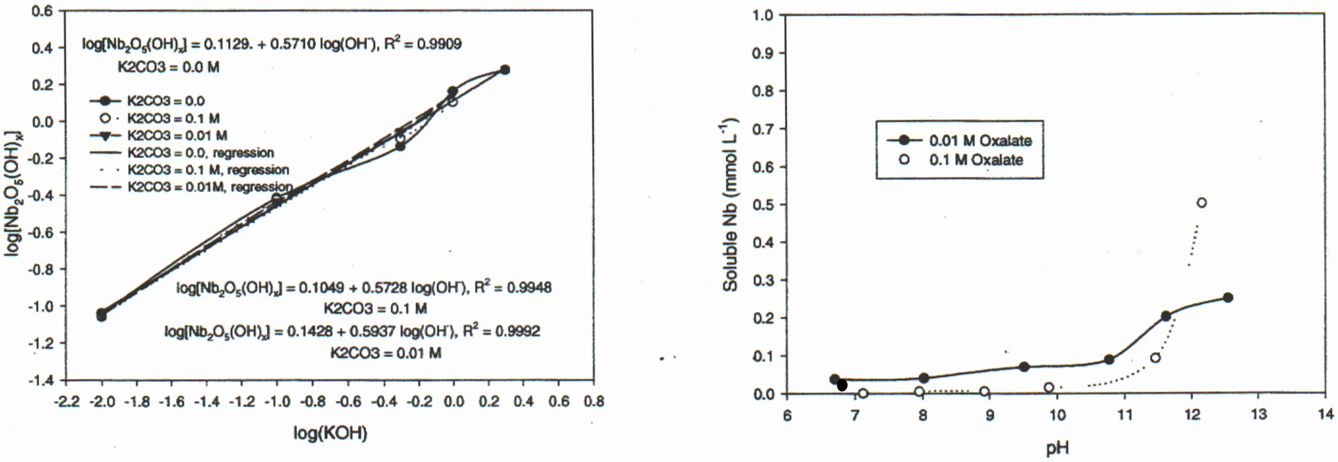


Fig. 3.1.4.1 Effect of carbonate (left) and oxalate (right) on Nb_2O_5 solubility.

3.2 Zr solubility

The solubility of zirconium is of concern since dissolution of the binder could be one mechanism whereby the CST particles found on the glass wool fibers could be liberated. Baes and Mesmer (1976) indicate that, like Nb, the solubility of Zr should increase dramatically in strongly basic fluids. To locate the inflection point where this occurs, the solubility of freshly precipitated hydrous zirconium oxide was prepared by neutralizing a solution of zirconium oxy-nitrate. This material was selected because of its relationship to what may be used in binding the IE-911. After the precipitate formed, it was placed in a dialysis bag and rinsed free of sodium salts. Samples of the dried material were then placed in 1N, 3N and 8N KOH and allowed to equilibrate for a day. Solutions were then filtered, diluted and DCP (Table 3.2.1).

Table 3.2.1 Zr concentrations in equilibrium with freshly precipitated hydrous zirconium oxide.

Solution	PPM Zr
1N KOH	0.96
3N KOH	4.9
8N KOH	106

To complement these analyses, a number of the archived pretreatment solutions from Experiment #2 were also analyzed for the principal IE-911 components. The very high sodium levels in these solutions presented considerable analytic difficulty, so results reported in Table 3.2.2 are only approximate. In addition, because of the large solid:fluid ratio in these tests, much of the initial hydroxide had been consumed. Thus, the initial hydroxide levels in the solutions were of little use in evaluating the post-treatment hydroxide concentration. Hydroxide levels shown in Table 3.2.2 are based on pH meter readings that were then calibrated against readings obtained in 1N, 3N and 10M NaOH stock solutions.

Table 3.2.2 Analyses of pretreatment fluids from Experiment #2

OH-Molar	Nb - PPM	Zr - PPM	Si - PPM	Ti - PPM
0.57	425	0.25	22	11
1.7	398	5.7	53	12
2.2	408	10.5	60	13
5.0	1,500	178	127	66

Several general conclusions may be drawn from this data. Bases and Mesmer, 1976, were clearly correct in ascribing an amphoteric behavior to Zr since in both sets of analysis the high-pH fluids show a distinct Zr enrichment. Further, with fluids normally used to pretreat the IE-911 binder solubility should not be a significant problem. These fluids are, however, near the upper limit of the hydroxide concentration that would be appropriate for this purpose. It is also apparent that Nb solubility always greatly exceeds that of any of the other components from the IE-911. Thus, if a loss of particle integrity is suspected, the underlying cause may be the removal of the Nb-containing phase, rather than binder dissolution.

3.3 H^+ - OH^- exchange properties

The reason for pretreating the IE-911 is that it is currently produced in an acid form that will precipitate aluminum hydroxide from alkaline waste fluids and clog ion exchange columns. Thus, the hydrogen ion – hydroxide exchange properties of this material are of great concern. There are two parts to the problem. The exchange capacity determines how much hydroxide must be supplied to overcome the acidic nature of the as-received IE-911. However, the kinetics of the exchange processes decide how long the pretreatment process must last.

To assess the exchanging capacity, three grams of the as-received IE-911 were placed in 20 ml of deionized water. The exchangeable hydrogen ion was then titrated by making successive small additions of KOH, and each time recording the pH once it stabilized (Fig. 3.3.1, bottom trace, triangles). For comparison, the theoretical pH was calculated in two ways: The top trace (squares) represents what the pH ought to be observed at each step if the total amount of hydroxide added to the fluid had all remained in solution. The middle trace (also near the top of the figure, diamonds) represents the pH that should result at each step if the current increment of hydroxide is added to a fluid with the pH that existed immediately before that increment of base was added. Though less conventional, this way of representing titration data provides a much more sensitive measure of when the buffer capacity of a material has been consumed (e.g. the "end point" of the titration).

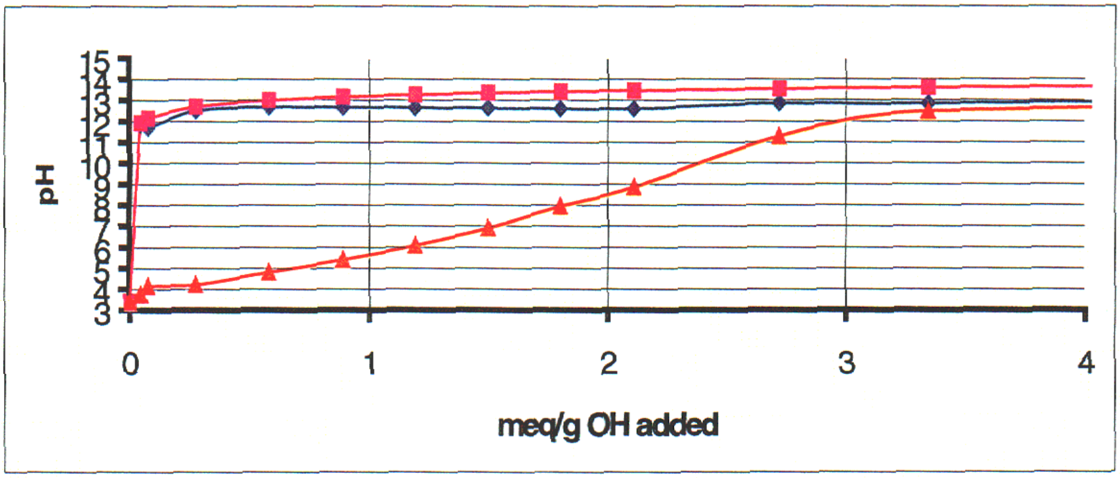


Fig. 3.3.1 Titration curves for IE-911. The vertical axis is measured or calculated pH and the horizontal axis are milliequivalents of hydroxide added per gram of IE-911.

The results of this test are highly significant and rather unexpected. The tabulated hydrogen exchange capacity in the as-received material is given as 2.2 meq/g (Walker, et al, 2000). However, to fully neutralize material from this lot took about 30% more base, roughly 3.3 meq/g of material. What is even stranger, however, is the shape of the titration curve. Normally, buffer titration curves are sigmoidal with most of the capacity consumed above a well-defined pH value. The IE-911, however, continues to consume hydroxide over an exceedingly broad pH range. This behavior is probably a reflection of the fact that the hydrogen ion is bonded to the CST structure with a continuum of bond energies ranging from relatively weak to quite strong. This result has great programmatic significance. Treating material at the factory to achieve mildly basic conditions will not alleviate problems when the IE-911 is exposed to actual wastes. It must be rendered highly caustic, with a stable pH of at least 13, before the material will no longer act as an acid that could lower the waste pH and precipitate aluminum hydroxide.

The other important aspect of the hydrogen ion–hydroxide exchange problem is the rate at which it occurs. This will ultimately impact how the material is pretreated in bulk, as well as possibly explain some of the rather odd behavior observed during some column tests. This process was repeatedly measured while waiting for the pH to stabilize in the titration experiment just described. Representative pH – time curves from these studies are shown in Fig 3.3.2. From this illustration, and many other data sets not presented, it is apparent that the time constant for this material to respond to even a single pH perturbation is several hours. In fact, although the balance of the change occurs in the first 3-4 hours, it was rather common to note a further decrease (typically about 0.1 pH unit) after an overnight equilibration.

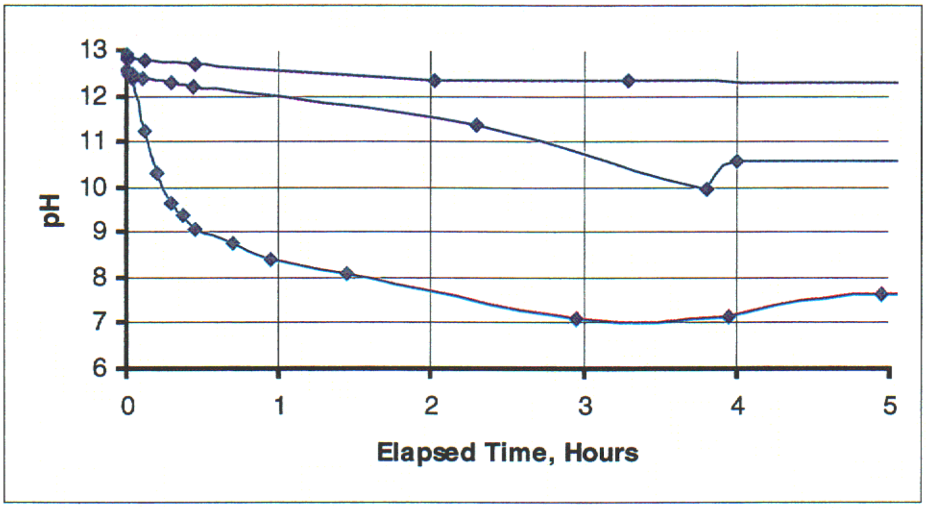


Fig. 3.3.2 Representative pH equilibration time curves. These curves represent the results of three successive additions of KOH to a slurry of IE-911 in what was initially deionized water.

3.4 Na-Aluminosilicate precipitation

The issue of sodium aluminosilicate precipitation is somewhat different since this material will not form during pretreatment because no source of aluminum is provided. However, it may be a major problem during waste processing, and developing ways to circumvent its occurrence could become a secondary objective of the overall pretreatment protocol.

Problems associated with sodium aluminum silicate precipitation are not restricted to environments where IE-911 materials may be employed. They are encountered in the processing of aluminum ores (Barnes et al. 1999) and in the paper pulp industry (Ulmgren, 1982). Closer to home, it has been implicated in plugging of pipelines transporting high level wastes (HLW), and as a component in the heels found in some HLW storage tanks at both Hanford and Savannah River. Although problems associated with the occurrence of sodium aluminum silicates occur widely, "off the shelf" remedies are seemingly lacking. The approach taken for the CST program involves first understanding the chemical processes leading to their formation, and then attempting to define what chemical environments must be avoided in order to avoid plugging a column.

The first step has been to initiate a thermodynamic analysis of the problem. Based on the similarity of results obtained by all of the groups working the issue for the CST program, we have focused on a zeolitic material named cancrinite. The cancrinite structure is unusual in that in addition to having an exchangeable cation, this structure contains an anion as an integral component. Natural cancrinite-group minerals have been described that contain most of the common groundwater anions. However, in HLW tank environments, nitrate is probably the dominant anion and, obviously, sodium would be the dominant cation. Parenthetically, we have been unsuccessful at finding published exchange constants for cancrinite that would allow us to predict if waste constituents such as Cs^+, UO_2^{++}, or TcO_4^- have a preference for displacing either sodium or nitrate.

The dissolution reaction for a carbonate-cancrinite can be written as:

$Na_8Al_6Si_6O_{24}(X)_a \bullet n\ H_2O + 12\ OH^- + (12 - n)\ H_2O \leftrightarrow 6\ Na^+ + 6\ H_2SiO_4^{--} + 6\ Al(OH)_4^- + Na_2CO_{3(aq)}$ where $X = Cl^-, OH^-, NO_3^-$ or CO_3^{--}; $a = 2$ for Cl^- and OH^- or 1 for CO_3^{--}; n = number of H_2O molecules

From this, it follows that if cancrinite equilibrates with a solution, the following mathematical identity must be satisfied:

$$K_{eq} = [Na^+]^6 [H_2SiO_4^{--}]^6 [Al(OH)_4^-]^6 [Na_2CO_{3(aq)}] [OH^-]^{-12}.$$

K_{eq} is an equilibrium constant derived from the thermodynamic properties of the solids and aqueous components in the system. The expression to the right is the activity product of the dissolved constituents. It is developed from the dissolution reaction for cancrinite and evaluated, based on the concentrations of dissolved components, in a particular solution. If the activity product exceeds the value of K then the solution is supersaturated and precipitation may occur. If the reverse is true, then any cancrinite in contact with the fluid should be dissolving. It is noteworthy that this expression says nothing about the rates of precipitation or dissolution, just which direction the process should go in different solutions.

In practical applications a number of problems are encountered. The first is simply obtaining a value for the equilibrium constant. Various attempts have been made based either on experimental work or different theoretical formalisms or based on the proportions of the different oxides in the material. The outcome assembling this data is illustrated in Fig 3.4.1. Unfortunately, the published data only covers experiments down to about 100° C (Barnes et al.,1999; Gasteiger et al.,1992, Ulmgren, 1982) and even the theoretical formalisms (Park and Englezos, 1999) will not allow for evaluating the solubility of a nitrate-cancrinite. However, the information on the other cancrinites has been incorporated into the database for the REACT code. This will allow us to begin modeling and to get a preliminary assessment of whether cancrinite would be stable or unstable in different types of solutions.

Before making such calculations, however, it is also necessary to deal with the fact that the components in brackets are activities of the dissolved components. In very dilute fluids, activities and concentrations are very similar, but in concentrated solutions a sizeable correction must be applied to analytic concentrations to yield activities. Several approaches have been developed to address this problem depending on the solution concentration. For our preliminary studies we have adopted an extended Debye-Hückel approach because of its convenience. These activity coefficients are not strictly applicable to high ionic strengths. They are, however, close enough to give a general idea of expected system performance until time permits incorporating the more correct Pitzer coefficients into the database.

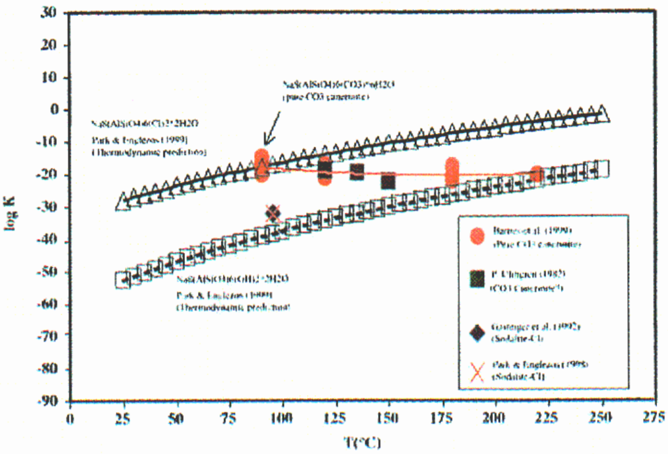


Fig 3.4.1 Theoretical and experimental solubility products for cancrinite at different temperatures.

Once activity coefficients and equilibrium constants were defined, it was possible to calculate whether a cancrinite would dissolve or precipitate from a particular solution. This model was then tested against the chemistry of Hanford tank fluids as tabulated in the TWINS database (Fig. 3.4.2). Many of these tanks probably contain cancrinite as part of the sludge so a successful outcome would be a grouping of points in the cancrinite stability field. In fact, the points do fall surprisingly close to the cancrinite field but, unfortunately, not in that field. The model, instead, picks other zeolites to coexist with the fluids though these materials have not been described as occurring in the tanks. It is unknown whether this difference reflects the activity coefficient problem or simply that a carbonate-cancrinite was modeled when the tanks actually contain a nitrate-cancrinite. Research in the upcoming months will be directed at remedying these problems and then applying the model to solutions of more immediate relevance to the CST studies.

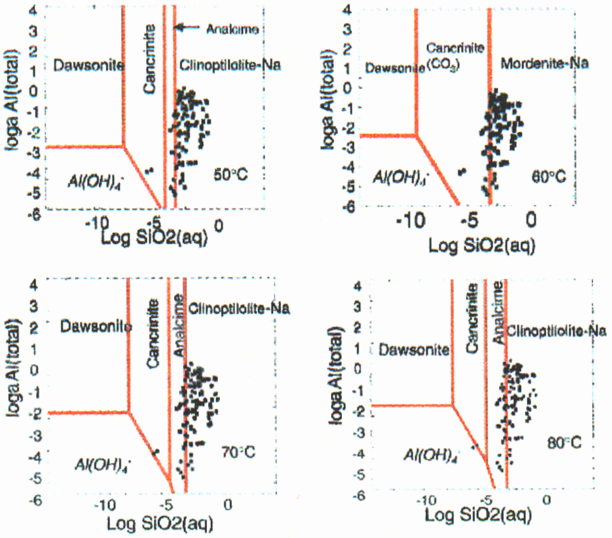


Fig 3.4.2 Stability of cancrinite and other minerals relative to Hanford tank fluid chemistry.

4.0 CHEMICAL PRECIPITATE MODEL

The column tests provided a wealth of empirical information about the collection of particulate matter that could eventually lead to column plugging. One constituent in the particulate matter was found to be the IE-911 material itself, which argues for some deterioration of the pellets. Fluid analyses suggest that freeing of the CST materials may be caused by the dissolution of niobium from the sample rather than the binder dissolving. Research is underway to identify the Nb source and preliminary findings suggest that an impurity phase, rather than the CST itself, is the source of this material. What is clear even now, however, is that the Nb liberated during this process can also lead to the accumulation of particulate matter on filters.

One important finding is that Nb solubility is clearly higher in more basic solutions. But, why should it build up in the reservoir and then precipitate, rather than precipitate as an increment of fluid moves down the column? The key to understanding this almost certainly lies in the very slow rate that hydrogen ions are liberated from the CST. It is likely that an increment of fluid could pass the length of the column, still retain a moderately elevated pH, and hence solubilize an elevated level of Nb. However, after multiple passes, the pH of all the fluid eventually falls to the point where the Nb accumulated in the reservoir precipitates.

5.0 PRETREATMENT STRATEGY DEVELOPMENT

At the conclusion of section 2 (column testing), a number of suggestions were advanced based on the relative lack of obstruction observed in different pretreatment options. It is now possible to elaborate on these suggestions based on the results of the chemical studies just presented. Problems seem most likely to arise when the pH of the pretreatment fluid is cycled and when the material is exposed immediately to a strong base. Minimizing Nb dissolution and mechanical stresses are also priorities.

If it is necessary to pretreat in a column with a recirculating fluid, then slowly stepping up the fluid pH with a buffer is advisable. This is done so that by the time the pH increases to the point where Nb solubility is high, most of the acid generating capacity of the IE-911 has already been exhausted, and the return fluid should not cause as much Nb to precipitate in the reservoir. It is also advisable to allow several days of equilibration time with the high pH buffer before going on to the final stage involving use of a strong base. This assures that the buffer has had time to titrate the maximum amount of hydrogen ion before the last step of the pretreatment starts.

A far preferable protocol would be using a batch pre-equilibration process prior to loading the column. The *slow* addition of base, combined with the *only occasional* mixing of the slurry, should create optimal conditions for pretreatment while avoiding all the problems that arise from circulating a fluid through a transient chemical environment. At the intermediate pH range, use of a buffer may allow adding significant amounts of base carrying capacity to the fluid without establishing transient pH values high enough to solubilize Nb significantly. It is also essential to know the total amount of base needed to actually get at all the acid-generating capacity for the particular lot of IE-911 being used. This will allow for adding enough base to effect complete neutralization without overshooting and dissolving unnecessary Nb. Equilibration times will have to be used that are commensurate with the rates of hydroxide-hydrogen ion exchange for that particular lot of IE-911. However, given reasonable care and a degree of insight, it should be possible to pretreat the IE-911 in a manner that creates a minimum of particulate matter.

6.0 SUMMARY AND CONCLUSIONS

Four column experiments were carried out to test a variety of pretreatment protocols. These studies showed that with the correct procedure it is possible to pretreat IE-911 in a column mode without plugging the column. They also demonstrated that when problems occurred, the cause was always just a small accumulation of material at the input end of the column. No instances of mass fouling of the column pore spaces were observed.

Preliminary results are also available from a number of chemical studies directed at understanding mechanisms that may lead to decreased performance. Niobium solubility was investigated and found to increase as the pH climbs. This explains why flushing a column with fresh NaOH solutions can occasionally re-dissolve a plug that has formed. Taken together with the slow liberation of acid that is an inherent property of the IE-911, the amphoteric nature of Nb solubility also explains why such plugs develop in the first place. We found no evidence that binder dissolution would be a problem during normal pretreatment operations. However, it is not advisable to use hydroxide levels above 3N in pretreating the material. The titration behavior of the as-received IE-911 was found to be rather unusual. From a programmatic standpoint it appears several days exposure to a basic solution will be needed during pretreatment. In addition, to be sure that no acid is left that might interact with waste solutions, the pretreatment must achieve a stable pH in excess of 13. Finally, progress has been made in developing a predictive tool to help avoid sodium aluminosilicate (cancrinite) precipitation, but much work remains to be done on this topic.

General conclusions from this study are:

a. The current lot of IE-911 material can be pretreated in a column mode if the correct precautions are taken
b. Batch pretreatment is preferable to pretreatment in a column
c. The key to successfully implementing IE-911 use on an industrial scale lies in understanding the basic chemistry of the material. Column tests are useful in highlighting problems, but give little insight into what must be done to resolve issues once they are identified
d. Progress has been made toward understanding the long-term issue of sodium aluminosilicate deposition

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Appendix A: Commercial Product Designation

The supplier is:
UOP LLC.

The product may be ordered as:
UOP IONSIV(tm) IE-911.

The UOP LLC contact regarding this material is:
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