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An Investigation of Density Driven Salt Dissolution Techniques

by

B. J. Wiersma

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WSRC-TR-96-0160 (U)

***AN INVESTIGATION OF DENSITY DRIVEN SALT
DISSOLUTION TECHNIQUES (U)***

B. J. Wiersma

Savannah River Technology Center
Applied Science and Engineering Technology Department
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Publication Date: August, 1996

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APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Keywords: Waste Tanks, stress
corrosion cracking,
technical standards

Retention - Permanent

An Investigation of Density Driven Salt Dissolution Techniques (U)

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Prepared for the U. S. Department of Energy under Contract DE-AC09-89SR18035

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WSRC-TR-96-0160

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An Investigation of Density Driven Salt Dissolution Techniques (U)

1.0 Summary

Laboratory experiments were performed to support the salt dissolution demonstration in Tank 41H. This demonstration is sponsored by the Office of Science and Technology. The tests were designed to investigate three techniques of density gradient type dissolution: (1) Drain-Add-Sit-Remove, (2) Modified Density Gradient, and (3) Continuous Salt Mining. Removal of saltcake left attached to equipment after the solution was removed (i.e., perched saltcake) with a water jet was also simulated. The desire was to improve upon past salt dissolution operations and develop a safe, efficient and cost effective means for future operations. The experiments were performed on simulated Tank 41H saltcake that was formed in a three foot long rectangular trough.

The primary safety issue is whether or not the dissolved salt solutions that are produced will cause significant corrosion degradation of the tank walls or cooling coils. The parameter investigated during the tests to answer this question was the concentration of corrosion inhibitors in the dissolution water added to the simulated saltcake. It was observed that dissolution with 1 M sodium hydroxide solution resulted in salt solutions that were within the current corrosion technical standards for fresh waste storage. This result was independent of the density gradient technique. However, if inhibited water (0.01 M sodium hydroxide and 0.011 M sodium nitrite) was utilized, the salt solutions were frequently outside the technical standards. In the early stages of dissolution, the interstitial liquid which has high concentrations of corrosion inhibitors maintained the salt solution within corrosion standards. The Drain-Add-Sit-Remove technique was the most effective means for maintaining the interstitial liquid. Interstitial liquid entrapped by the surface tension between crystals, mixes with the salt solution as it flows through the saltcake matrix. The other two techniques, modified density gradient and continuous salt mining tend to displace the interstitial liquid. However, even with the Drain-Add-Sit-Remove technique as more salt was dissolved, the chemistry of the resulting salt solutions became outside the corrosion technical standards.

The corrosion technical standards are being evaluated for their application to waste removal. The current standards apply primarily to storage of fresh waste. The temperatures during waste removal are expected to be much lower than the maximum temperatures allowed during waste storage. The saturated salt solutions which form during waste removal have very high nitrate concentrations (> 4 M) and usually have a very high pH (12-13). Stress corrosion cracking may be a concern at these chemistries and at high temperatures (> 75 °C). Pitting is usually a concern in dilute solutions (nitrate concentrations < 1 M) and at lower pH (9.5-10).

The lower temperatures may require less corrosion inhibitors to prevent stress corrosion cracking. Corrosion tests are in progress to investigate the potential for stress corrosion cracking in salt solutions similar to those removed during tests with inhibited water as the dissolution water. Therefore these solutions will have lower levels of corrosion inhibitors than are specified in the corrosion technical standards. If these tests show that carbon steel is not susceptible to corrosion damage, recommendations for a corrosion technical standard applicable to waste removal will be made.

A comparison between the three dissolution techniques and several key observations of the dissolution process that impact the efficiency and cost of operations are summarized

in Table 1. The primary parameters investigated during the tests to address these issues were the dissolution water addition rates, the salt solution removal rates, and the depth at which the outlet line was located. Salt dissolution was observed to be a very rapid process as salt solutions with densities between 1.38-1.4 were frequently removed. Given the fast dissolution rate, the techniques needed to be performed in a manner that ensured good contact between the unsaturated salt solution and the saltcake (i.e., no channeling or short-circuiting). Slower addition and removal rates and locating the outlet line at deeper levels below the top of the saltcake provided better contact between the dissolution water and the saltcake. Near the bottom of the trough, salt solutions with lower densities were removed (1.15-1.25). It is likely that the removal rate was too fast, given the shallow depth of the outlet line, to provide adequate contact time between the dissolution water and the saltcake. Slower removal rates than those tested are recommended in order to achieve a higher salt solution strength for salt near the bottom of a tank.

2.0 Introduction

Radioactive waste is stored in 44 carbon steel tanks at the Savannah River Site. To economize on waste tank space, evaporators are utilized to reduce the volume of waste. After the hot waste is returned from the evaporator to the waste tank, soluble salts precipitate as the waste cools. The mixture of soluble salts, insoluble metal oxides, and soluble fission products and insoluble fissile material is commonly referred to as saltcake. Twenty of the waste tanks are currently utilized for salt storage.

The In-Tank Precipitation (ITP) process precipitates the soluble fission products in order to prepare feed for the Defense Waste Processing Facility. The feed for ITP is the saltcake and its interstitial liquid. The saltcake must be dissolved in order to provide the feed. SRS is currently evaluating safe, efficient and cost effective means for salt dissolution and waste removal. Given the schedule for waste processing, the rate at which the saltcake is removed is not a determining factor.

As part of this evaluation, the Office of Science and Technology (OST) is sponsoring a demonstration of salt removal from Tank 41H. The salt dissolution techniques which will be demonstrated are: (i) single slurry pump method, (ii) modified density gradient method, and (iii) a yet to be determined technique for removal of insoluble solids.

Removal of saltcake was performed in Type IV tanks and Tank 10H, a Type I tank, during the late 1970's and early 1980's. The techniques utilized then were steam jet circulation, density gradient and slurry pump agitation [1]. This demonstration is designed to test improvements to these processes. For example one of the concerns from the earlier salt removal operations was non-homogeneous vertical saltcake dissolution resulting in mounds of inaccessible salt at the edges of the tank [2]. It is desirable to develop a method in which the saltcake profile remained horizontal. Another problem that occurred was perched saltcake [3]. This phenomenon occurred when the liquid did not completely cover the salt. An upper crust of saltcake dries and remained clinging to the cooling coils, while the salt below continued to dissolve. To dissolve a crust similar to this in Tank 10H, the tank was refilled with additional dissolution water.

One of the primary concerns during salt removal is that the salt solutions produced are potentially corrosive [4]. The soluble salts which precipitated have a high concentration of nitrate anion (an aggressive corrosion species) and relatively low concentrations of hydroxide and nitrite anions (corrosion inhibitor species). Therefore, corrosion inhibitors must be added to the dissolution water to ensure that the salt solutions produced are not corrosive towards the tank walls or cooling coils. The options being considered are inhibiting the dissolution water so that the sodium hydroxide concentration is between

0.01 M and 1 M. Dissolution tests in the laboratory were performed with dissolution water inhibited at the extremes of this concentration range.

Laboratory tests were performed to investigate the dissolution phenomena that occur during density gradient type dissolution. Three techniques were tested: 1) Drain-Add-Sit-Remove, 2) Modified Density Gradient, and 3) Continuous Salt Mining. Removal of perched saltcake with a simulated water jet was also tested. In addition to observing the dissolution phenomena, the concentrations of the salt solution removed from the trough were also measured to determine whether its chemistry was within the current corrosion technical standards. The two options for inhibitor concentrations in the dissolution water were tested. The tests were designed to address these specific questions:

- 1) What salt solution composition can be expected as the sodium hydroxide concentration of the dissolution water is varied from 0.01 M to 1 M?
- 2) Is the composition of the salt solution produced within the corrosion chemistry technical standards?
- 3) Do any of these techniques result in excessive "channeling" or "short-circuiting" of the flow of dissolution water?
- 4) Do these techniques produce a horizontal saltcake profile?
- 5) How long is it necessary to wait to ensure that the salt solution is saturated before beginning removal?
- 6) How much salt is dissolved by a given quantity of dissolution water?
- 7) Do insolubles localize in a particular region of the trough?

After the salt solution chemistries were analyzed, the current technical standards for fresh waste storage and its application to waste removal operations were reviewed. Although the corrosion mechanism of concern remains the same (i.e., stress corrosion cracking), the temperature at which the modified density gradient will be performed is significantly lower than that for storage of fresh waste. The lower temperature may require less inhibitor to prevent stress corrosion cracking. Plans for future corrosion tests which will investigate this variable are described in this document.

3.0 Experimental

3.1 Apparatus

The salt dissolution tests were performed in a trough constructed of Lexan™ that was 36 inches long, 15 inches high, and 3 inches wide (see Figure 1). Grooves, that were 1/4" deep and 1/8" wide, were spaced 1" apart along the sides and bottom of the trough. The grooves prevented preferential flow of the solution along the walls of the trough.

Solutions were added and removed from the trough with a peristaltic pump. The flow rate capacity of the peristaltic pump was between 1-100 ml/min. A stainless steel tube, which was approximately 15" long and 0.0785" inside diameter, was attached to 1/4" diameter TYGON™ tubing to provide a sturdy outlet line that would simulate the transfer jet. A second stainless steel tube was designed for criticality studies. The tube was bent in a U-shape at the bottom (see Figure 2) to simulate the fixed transfer jet which will be utilized during Phase I of the salt dissolution demonstration [5]. For the studies on dissolution of perched salt, a centrifugal pump with a flow rate capacity of 1 liter/min was utilized. Two tests were performed with different sized tubing attached to the pump: 1) 3/4" diameter TYGON tubing and 2) 0.0935" diameter stainless steel tubing. The velocity of the jet from the TYGON tubing was approximately 0.2 ft/s, while the velocity

from the stainless steel tubing was approximately 12 ft/s. Type K thermocouples were inserted into the saltcake to detect temperature changes during salt dissolution.

An apparatus was also designed to measure the density of the salt solution in-situ. A copper cylinder, which was 1/4" in diameter and 1/8" long with a mass of 1.0 g, was attached to a thin copper wire. The cylinder was coated with wax to prevent degradation during the tests. The length of the wire was adjustable so that the density at different levels could be measured. During the tests, the cylinder was suspended from a Mettler™ balance perched above the trough. The measurements made during a test included the weight of the cylinder while it was submerged in the salt solution and the height of the midpoint of the cylinder. The following equation, derived from Archimedes principle, was used to calculate the density:

$$\text{Density} = \frac{W_{\text{air}} - W_{\text{sol}}}{V_{\text{cyl}}} \quad (1)$$

where W_{air} is the weight of the cylinder in air, W_{sol} is the weight of the cylinder in solution, and V_{cyl} is the volume of the cylinder. These measurements were compared to the density of the salt solutions removed from the trough.

3.2 Saltcake Preparation

The saltcake was prepared from the sodium salts listed in Table 2. The amounts were chosen such that the composition of the soluble saltcake solids would be similar to the salt samples obtained from Tank 41H [6]. The primary components of the soluble solids are sodium nitrate, sodium carbonate, sodium hydroxide and sodium nitrite.

Sludge solids were also added to the saltcake to simulate the insoluble solids present in the saltcake. Batch 1 simulated sludge prepared at TNX was utilized for this purpose. The composition of the sludge is shown in Table 3. The primary elemental components of the sludge include iron, sodium, aluminum, and manganese.

Preparation of the saltcake involved several steps. Initially, NaOH is dissolved in 2 liters of deionized water, while in a separate beaker $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is dissolved in 500 ml of deionized water. The $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is slowly added to the NaOH solution while the solution is stirred. The solution was then heated and stirred as the remaining sodium salts are added to the mixture. The solution was stirred until the solids dissolved. Deionized water was added until the total volume of solution was 3 liters. The solution was then heated to boiling ($\sim 110^\circ \text{C}$) to evaporate the solution to 80% of the original volume ($\sim 2400 \text{ ml}$). Approximately 0.5 g of the Batch 1 sludge was added to the mixture after 500 ml of the solution had evaporated. This amount of sludge produced a saltcake which contained approximately 0.7 wt.% insoluble solids. After evaporation, the solution was poured into the trough. Fans were placed along the sides of the trough to cool the solution by air convection. This method of heat removal was designed to simulate the function of the cooling coils in the waste tanks. The solution was allowed to cool and crystallize overnight. The next day the layer of liquid present above the saltcake solids was removed from the trough and evaporated to approximately 80% of its original volume before returning it to the trough. This step was designed to simulate evaporation cycles that occur in the tank farm. Due to time constraints, only one evaporation cycle was performed. Three batches of solution were evaporated each day so that approximately 3" of saltcake formed in the trough. The procedure was repeated until 10-12" of saltcake had formed in the trough.

3.3 Test Procedures

Four dissolution techniques were investigated:

- 1) Drain-Add-Sit-Remove (DASR)
- 2) Modified Density Gradient
- 3) Continuous Salt Mining.
- 4) Simulated water jet to remove perched salt

These tests were performed with 1 M sodium hydroxide or inhibited water (0.01 M sodium hydroxide and 0.011 M sodium nitrite) as the dissolution water. Table 4 summarizes the tests that were performed by technique and the type of dissolution water. Each of these techniques are described below.

Drain-Add-Sit-Remove - This procedure was originally designed to simulate an option for Phase I salt removal from Tank 41 [7]. This technique is illustrated in Figure 3. Figure 3a shows the initial condition of the saturated saltcake. A hole approximately 1" in diameter and 2-4" beneath the surface of the salt was cored to insert the stainless steel suction tube. The hole was located 4" from the right hand edge of the trough. Interstitial liquid was removed from the hole until the pump suction could draw no more liquid. Figure 3b shows the resulting damp saltcake at the completion of this step. Dissolution water was added to the top of the saltcake at a location 4" from the left hand edge of the trough (see Figure 3c). The amount of dissolution water varied from an amount approximately equal to that which was drained from the saltcake to 2-4 times that amount. Methyl red, an indicator, was added to the dissolution water so that the flow pattern of the dissolution water could be traced during the test. Methyl red is yellow-orange in the alkaline solutions utilized for the tests. The salt solution and saltcake were allowed to sit for 24 hours for further dissolution. The salt solution was then removed from the trough until the pump suction could draw no more liquid (see Figure 3d).

Modified Density Gradient - This procedure was designed to simulate an option for Phase III salt removal from Tank 41. This technique is illustrated in Figure 4. A hole approximately 1" diameter was cored to within 1/4" of the bottom of the trough for the stainless steel suction tube. This hole was also located 4" from the right hand edge of the trough. Two liters of dissolution water was then added to the top of the saltcake (see Figure 4b) at a location 4" from the left hand edge of the trough. Salt solution was removed from the trough until the top of the solution was at the same level as the saltcake (see Figure 4c). The salt solution and saltcake were allowed to sit for 24 hours to allow further dissolution (see Figure 4d). Two additional liters of dissolution water were then added to the top of the saltcake and the cycle was repeated until almost all of the saltcake was dissolved.

Continuous Salt Mining - This procedure was designed to simulate an alternate method for salt removal from Tank 41. This technique is illustrated in Figure 5. Two holes were cored into the saltcake for this test approximately 28" apart. The depth of the holes ranged between 3-4" below the initial saltcake level. Dissolution water and salt solution were added and removed simultaneously from the trough through these holes. The rates of addition of dissolution water and removal of salt solution were adjusted to maintain the liquid level in the trough just above the saltcake level during the test. The ratio of salt solution removed to dissolution water added observed in previous tests was utilized to determine this flow rate ratio. Two different criteria were set for discontinuing the test: (1) the density of the salt solution decreased below 1.32 and (2) approximately 1 liter of solution which had a density less than 1.32 had been collected. The latter criteria

provided data on the composition of unsaturated solutions. Chloride ion was added to the dissolution water to detect the breakthrough of the salt solution at the transfer jet location.

Simulated Water Jet. If the saltcake was not submerged beneath liquid, "bridging" across the width of the trough occurred and had left the saltcake perched above the salt solution (see Figure 6). This phenomenon was also observed between the cooling coils during density gradient dissolution in Tank 10 (see Figure 7) [3]. For tank 10, dissolution water was added until the bridged saltcake was covered with solution. After several days, the solution was removed and the saltcake had been dissolved. This test was designed to simulate a high pressure water jet which would dislodge the perched saltcake. The desire was to dislodge the saltcake and minimize the amount of dissolution water added to the trough. The perched saltcake was approximately 1" thick and stretched across the length of the trough. A 3" gap between the perched saltcake and the saltcake bed existed prior to each test. Two jet velocities were tested, 0.2 ft/s and 12 ft/s. Dissolution water was added until the perched saltcake collapsed into the trough or the saltcake was submerged beneath liquid (see Figure 8). The amount of water that was added was measured and compared with the amount of water necessary to submerge the perched saltcake.

The tests were performed in seven separate troughs as shown in Table 5. Multiple techniques were utilized in the first two troughs. The order the techniques were performed was chosen to simulate the expected order the technique would be utilized during the Tank 41 demonstration. Therefore the salt solution chemistry results and the flow visualization results for the simulated water jet technique and some of the DASR tests may have been impacted. The modified density gradient technique was performed in a separate trough. The technique was repeated until nearly all of the salt was removed. The final four troughs were utilized to study the effect of the removal rate on the localization of insolubles at the transfer jet. Test NCSE38M investigated the use of the modified transfer jet vs. the straight tube transfer jet.

Table 5 also depicts the variables for the test. The variables included the drainage rate, the addition rate, the removal rate, and the position of the transfer jet relative to the initial salt level. Two methods were considered for scaling the laboratory flow rates to the expected rates for the Tank 41 demonstration. The first approach was to scale the laboratory tests so that the ratio of the volumetric flow rates were proportional to the volumes of salt that were to be dissolved.

$$\frac{\text{Volumetric Flow Rate Trough}}{\text{Volumetric Flow Rate Tank 41}} = \frac{\text{Volume of Salt in Trough}}{\text{Volume of Salt in Tank 41}} \quad (2)$$

Calculations showed that a 100 gpm flow rate in the tank was proportional to approximately 6 ml/min in the trough. Flow rates between 1.7 ml/min and 6 ml/min were calculated by this method. A second approach was to assume that the flow rates should be a function of the saltcake surface area for a constant dissolution rate [1].

$$\frac{\text{Volumetric Flow Rate Trough}}{\text{Volumetric Flow Rate Tank 41}} = \frac{\text{Surface Area Trough}}{\text{Surface Area Tank 41}} \quad (3)$$

In effect this latter equation ensures that the change in solution level with time for the trough was the same as that of the tank. Calculations showed that a 100 gpm flow rate in the tank was proportional to approximately 50 ml/min. Flow rates between 10-50 ml/min were calculated by this method. In actuality, neither of these methods can completely scale the velocity distribution in the trough to the velocity distribution in the tank. For example, the slower velocities are similar to the velocities far away from the removal site,

while the higher velocities simulate the velocity distribution closer to the removal site. The tests will show, however, the effect of increasing the velocity on the profile of the saltcake, amount of salt dissolved and localization of insolubles.

The depth of the transfer jet relative to the top of the saltcake is also an important variable. At greater depths, interstitial liquid will be removed sooner which will dilute corrosion inhibitors present in the salt solution during the latter stages of salt removal. On the other hand, at shallower depths "short circuiting" of the dissolution process may occur. Initial depths that were used for this study are shown in Table 5.

4.0 Results

4.1 Observations on Dissolution Phenomena

The dissolution phenomena was unique for each of the techniques. A schematic of the dissolution processes is shown in Figure 9. In this section a description of the phenomena and their impact on salt solution strength, saltcake profile, localization of insolubles, and dissolution time will be presented.

Drain-Add-Sit-Remove

The initial stage of the DASR technique involved draining the saltcake of interstitial liquid until no more liquid could be removed. The damp saltcake had the appearance of snow at the completion of the drainage phase (see Figure 3b). The saltcake generally slumped approximately 1/2" from its original level and contained a few channels. Slower drainage rates removed a greater percentage of the available interstitial liquid than faster drainage rates. At completion of this stage, the interstitial liquid would re-establish its equilibrium level at a higher level above the outlet line at the faster rates than with the slower rates. This simply means that the resistance of the saltcake to fluid flow establishes a maximum rate at which the solution may be drained. The impact of this observation is that if salt is drained rapidly, less dissolution water will be added (assuming that the amount of dissolution water added is equal to the interstitial liquid removed). Therefore you would remove less salt for each batch that is performed.

As dissolution water was added to the saltcake, initially it penetrated beneath the saltcake to the level of the interstitial liquid. Due to differences in the density between the dissolution water and the interstitial liquid, the dissolution water floated and began to flow horizontally through the saltcake (see Figure 9a). The dissolution water dissolved saltcake and mixed with the entrapped interstitial liquid as it flowed across the trough. The saltcake near the addition location dissolved rapidly.

After the saltcake from above the addition point dissolved, it was observed that the saltcake profile began to slope gently upward for a distance of about 10-12 inches, before leveling off at the original saltcake level (see Figure 3c). This phenomenon is likely due to stratification between the salt solution and dissolution water as the method proceeds. The fresh dissolution water being added does not immediately contact the saltcake and, therefore, must flow horizontally some distance from the addition point before contacting saltcake.

Evidence for this stratification was gathered by performing in-situ measurements of the density during the addition stage. Table 6 lists the density of the salt solution relative to the initial salt level. The table shows that below the original saltcake level the solution is saturated while solution that was above was at various degrees of saturation. These densities were measured within 24 hours after the dissolution water was added. Waiting

for longer periods of time will likely allow for more dissolution to occur and thus formation of higher density solutions.

Stratification was most evident in tests in which the amount of dissolution water added exceeded the interstitial liquid removed (Scenario 2 and Test 2). If the amounts of dissolution water added and interstitial liquid removed were equal (Scenarios 1 and 3, Test 1), the salt solution level was just above the original saltcake level. Thus, at the end of the addition phase the liquid was just above the saltcake on the far side of the trough away from the addition location. A smaller range of densities than experienced for Scenario 2 would also be expected. The addition rate seemed to have minimal effect on the appearance of the saltcake profile and the densities measured. This result would seem to indicate that dissolution is instantaneous and saturation is achieved rapidly after the saltcake is contacted with water.

Due to the rapid dissolution rates in the "slushy" saltcake of the tests, the 24 hour "sit" stage of the process was probably unnecessary. However, if hard chunks of salt remain attached to the cooling coils or equipment in the tank, the "sit" stage will provide extra dissolution time necessary to remove these chunks. During this time, the level of the saltcake that was 18-36" away from the addition location decreased 1/4-1/2". This result indicated that some dissolution and settling of saltcake occurred during this stage. There was no change in the saltcake level near the addition location indicating that the liquid in direct contact with the salt cake was saturated. The saltcake at this location also appeared less compact than that at the other end of the trough.

During the removal stage, saturated salt solution was removed at liquid levels beneath the saltcake, while unsaturated dissolution water was contacted with the saltcake. The removal rate and the depth of the outlet tube impacted the results of this final stage. Saltcake tended to dissolve preferentially near the removal site, thus leaving a slightly humped salt profile. Slower removal rates resulted in the middle of the saltcake being approximately 1/4-1/2" higher than the ends, while faster removal rates resulted in the saltcake at the removal site being approximately 1-1.5" lower than the midpoint. Apparently in order to achieve the high removal rates, a greater ratio of unsaturated solution was drawn down from above the saltcake than permeated through the saltcake. This result was evidenced by the lower ratios of dissolution water added to salt removed and slight decrease in the average density (see Table 7). It should be noted that even at the higher removal rate the density is still well above the minimum required (1.32) and the sodium nitrate concentrations are above 4 M. Again this result indicated that dissolution was a rapid process.

Some "channeling" through the salt was seen during the removal stage. This phenomenon was observed primarily in the vicinity of the removal site. The slower rates tended to produce larger channels which were subterranean and located just above the outlet opening. The hole that was cored for the outlet also remained intact at these lower removal rates. At faster removal rates less channeling was observed and the hole collapsed around the outlet line. Given that the density of the salt solution removed was high during this period, it does not appear that the appearance of channeling has an adverse effect on the salt dissolution process. That channeling does not impact the process is evidence that salt dissolution occurs rapidly once contacted with unsaturated solution.

It was also observed that the ratio of dissolution water added to salt removed increased (and hence the density decreased) as the depth of the outlet line below the saltcake level decreased. This result is shown in Table 7 by comparison of NCSE38 and NCSE38M. This observation is again related to the resistivity of flow through the saltcake requiring a

greater proportion of unsaturated solution from above the saltcake. Therefore, for the shallower depths, the time that the unsaturated solution is in contact with the saltcake was insufficient. The strength of the solution was impacted less by the depth of the outlet when the salt solution was removed at a slow to moderate rate (2-6 ml/min) or if the outlet line was at depths greater than 5". The strength of solution was relatively independent of the removal rate at these depths (see NCSE6, NCSE38, and NCSE100).

The potential for localization of insolubles was also investigated with this technique. The concern was that fissile material could localize in the tank and form a critical mass. Three different rates and two different outlet line depths were tested. At slow rates (1-6 ml/min), no localization of insolubles was observed. The depth of the outlet line had no impact on this result. The insoluble particles settled and formed a thin uniform layer on top of the saltcake during removal. Apparently the velocity of the salt solution was insufficient to carry the insoluble through the saltcake or across the top of the saltcake. Very few salt crystals and insolubles were entrained in the salt solution that was removed.

At a medium flow rate (38 ml/min), localization of insolubles occurred at the outlet line site (see Figure 10). The depth of the outlet line was approximately 3" initially. The region shown in the figure was conically shaped and approximately 1.5 inches at the base and 0.75 inches in height. The concentration of insolubles had increased from 0.7 wt.% in the bulk saltcake to 4 wt.% in this region. A significant amount of salt crystals and insolubles was entrained in the salt solution that was removed. As a consequence, plugging of the outlet line with salt crystals and insolubles also occurred. However, when the outlet line was placed at a depth of 6" and the test performed at this removal rate, no localization of insolubles was observed. Although, salt crystals and insolubles were entrained (~620 ppm) in the salt solution removed and some pluggage occurred during this test.

The test was also performed at a fast flow rate (100 ml/min) at an outlet line depth of 6". No localization of insolubles occurred at the outlet line site. However, a significant amount of salt crystals and insolubles (1000 ppm) were removed with the salt solution. No pluggage of the outlet line occurred during the test. Apparently the velocity of the salt solution at the outlet line was great enough to prevent aggregates of salt crystals and insolubles to form.

The appearance of the saltcake around the outlet line suggests a mechanism for the localization of insolubles. The saltcake formed a conical well around the outlet site which was approximately 6-8" across and 2" deep. The fast removal rate and shallow depth of the outlet line required a significant amount of liquid from above the saltcake in order to supply salt solution for removal. The unsaturated solution dissolved the saltcake in a pattern which followed the flow stream lines. As the saltcake dissolved, the insolubles settled to the bottom of the well. It is likely that the flow rate in the vicinity of the well was high enough to drain the insolubles to the outlet site. This mechanism suggests that the localization observed was a surface phenomenon in the region of the outlet line and not a result of transport of insolubles through the bulk of the saltcake.

For further evidence of this assertion, calculations were performed to determine the velocity distribution in the vicinity of the outlet site. At a removal rate of 38 ml/min and a distance of 2" from the outlet site (a distance outside the conical formation of insolubles), the velocity of the salt solution would be less than 0.05 inches/min. Scaling this velocity to the actual tank, a 75 gpm pump would produce the same velocity at a distance of 14 feet from the outlet line. Although calculations have not been made, it would seem unlikely that there would be enough fissile material within the 14 foot sphere of influence to produce a critical mass and geometry.

Pluggage of the tank transfer jets may not be an issue. The tubing utilized for the tests was 0.0935" in diameter, while the diameter of the transfer jet is on the order of inches. Given that there is a characteristic particle size distribution for saltcake, it seems unlikely that aggregates on the order of inches in diameter will form.

The temperature of the salt solution was monitored at three locations: at the addition site, the middle of the trough, and near the removal site. Sodium nitrate dissolution is an endothermic process and thus a distinct decrease in temperature occurs. After dissolution was complete, the salt solution returns to the ambient temperature. It was desired to use thermocouples in the tank to monitor the temperature and hence the progress of dissolution. If the thermocouple was located at the dissolving interface a 10 °F decrease below the ambient temperature was observed. However, locating this interface was difficult. Most of the saltcake bed remained at the ambient temperature. Given the difficulty in locating the dissolving interface for the trough, it seems unlikely that the dissolution process in the tanks can be monitored with thermocouples.

In summary the DASR method is an effective salt removal method. Optimum operation of this technique would involve a slow to moderate removal rate (20-30 gpm) with the inlet to the transfer jet submerged to a sufficient depth to reduce the potential for short circuiting. The method also retains the interstitial liquid in areas which are below the outlet line. Depending on the depth the outline is positioned for each batch, the transfer jet height may have to be adjusted several times.

Modified Density Gradient

The modified density gradient technique will be tested during phase 3 of the Tank 41 demonstration. The sequence for this technique was to (1) add dissolution water to the top of the saltcake, (2) remove salt solution from the bottom of the saltcake until the dissolution water is just above the saltcake level, (3) allow solution to stand for 24 hours, and (4) repeat the sequence until all the saltcake is dissolved. As shown in Figure 9b, the concept behind this technique is to create vertical plug flow so that the saltcake was dissolved with a horizontal profile. If chunks of hard salt are observed to be hanging from the cooling coils or equipment, it may be beneficial to allow the solution to stand on top of the saltcake prior to removal to allow extra time for dissolution.

Dissolution water added floats on top of the saltcake due to the difference in the densities between the dissolution water and the interstitial liquid. The rate at which the dissolution water was added has no impact on the process, however, the amount of dissolution water added may influence the strength of the salt solution removed. If too much dissolution water is added, particularly near the bottom of the trough, the salt solution removed may not be sufficiently concentrated to meet ITP requirements.

During the first batch (Test 4 #1), the initial solution removed was actually interstitial liquid. In fact the lowest dissolution water added to salt removed ratios were achieved due to the fact that the interstitial liquid displaced was included in the amount of salt removed (see Table 7). As the dissolution water contacted the saltcake, dissolution began. The removal rate was slightly faster than the rate at which the saltcake level changed as eventually the top of the liquid reached the top of the saltcake. Given that the liquid was initially 1.1875" above the saltcake, the change of liquid level with time was 0.028 ft/hr, and the time for the liquid to reach the top of the saltcake was 7.3 hours, the change in saltcake level was estimated to be approximately 0.014 ft/hr.

Previous laboratory tests indicate that at the test temperature of 25 °C the saltcake dissolution rate is between 0.5-1.0 ft/hr [8]. Thus from a dissolution kinetics standpoint, removal could actually be performed at a higher rate than performed during the tests. However, fast removal rates do not maintain the vertical flow stream lines through the saltcake bed.

Unsaturated liquid from the above the salt will take the path of least resistance in order to supply the outlet line with the required removal rate. The stream lines will become more diagonal and thus the saltcake profile will slope toward the outlet line site. This observation was made even with the slow flow rate (10 ml/min) as the saltcake sloped approximately 3/4" over the 3 foot long bed. Problems with short circuiting also became significant if the removal rate was too fast. The removal rate became extremely significant during Test 4 as the salt solution from the bottom regions of the trough (last 2-2.5") were more dilute (see Table 6). Thus, slow removal rates for this technique are necessary for two reasons: (1) maintenance of a horizontal profile, and (2) prevention of short circuiting.

The 24 hour sit time allowed further dissolution to occur. The sloping saltcake profile disappeared and a horizontal profile was present after this time period. Unsaturated liquid above the saltcake in the vicinity of the outlet line, floated back over the more dense salt solution that was in the interstices of the sloped saltcake. As the unsaturated solution contacted the saltcake, dissolution occurred and the profile became horizontal. Therefore, with modified density gradient dissolution, allowing the system to sit for a period of time permits the re-establishment of a horizontal saltcake profile.

Localization of insolubles did not occur with this technique. Instead a thin, uniform layer of insolubles formed on top of the saltcake as dissolution proceeded. The slow flow rate and the depth of the outlet line likely prevented localization. Some salt crystals and insolubles were entrained in the salt solution, but not in significant quantities.

Continuous Salt Mining

The continuous salt mining technique is similar to the original density gradient technique, except that the inlet and outlet lines are positioned at the bottom of the saltcake rather than near the top. The concept behind this technique is to form a vertical wall which will displace the interstitial liquid and dissolve the saltcake in a horizontal plug flow fashion (see Figure 9c). In practice, horizontal stream lines are not possible due to the difference in density between the dissolution water and the interstitial liquid. As the dissolution water floats to the top, dissolution occurs along the flow stream lines leaving a slightly sloped profile away from the inlet.

Initially, the salt solution displaced the interstitial liquid. After approximately 1500 ml, the salt solution began to be removed. Unsaturated solution had flowed across the top of the saltcake to within about 8 inches of the outlet and then was drawn down. The evidence for the draw down was the slightly sloped profile toward the outlet line which occurred due to contact of unsaturated solution with the saltcake. As the process continued, the saltcake profile became more horizontal until it was flat at the conclusion of the test. Initially the density and salt solution strength were similar to the other two techniques (see Table 7). However, as with other techniques, dilution of the salt solution occurred near the bottom of the trough. As with previous tests slower removal rates would prevent this short circuiting.

The key step to performing this technique was to maintain the solution level just above the top of the saltcake. To maintain a constant liquid level, the removal rate must be

greater than the addition rate by a factor equal to the average ratio of salt solution removed to dissolution water added that was observed in the tests with the other techniques (1.5). If the removal to addition rate ratio was greater than this value, undercutting of the saltcake occurred and perched saltcake will remain. The addition and removal rates utilized for both Scenario 4 and Test 3 produced salt solutions with high densities (>1.37) until the bottom 2" of salt were reached. Slower addition and removal rates are needed at this stage to prevent short circuiting.

Localization of insolubles was not observed with this technique. As with previous techniques, a thin, uniform layer of insolubles settled on top of the saltcake. Some salt crystals and insolubles were entrained in the salt solution, but not in significant quantities.

This technique was also an effective means of salt removal. However, careful monitoring of the addition and removal rates is necessary to prevent undercutting and dilution. A constant ratio of the removal to addition rate may be utilized for this method, however, each of the rates will need to be reduced as the bottom of the tank is approached.

Simulated Water Jet

The objective of this test was to dislodge the perched saltcake with a minimum amount of dissolution water. A jet velocity of 0.2 ft/s the saltcake was beginning to dissolve and crumble, however, the saltcake was not completely dislodged until it had been submerged in dissolution water. On the other hand, a jet velocity of 12 ft/s dislodged the saltcake well before it was submerged. Thus, velocities of this order of magnitude are necessary to minimize the amount of water added. There are two operational considerations. After the saltcake has been dislodged, care should be taken to make certain that the crumbled saltcake is submerged. Secondly, in the design of the water jet a means of maneuvering the nozzle is necessary. Aiming the jet at one location may not cause the whole section of perched saltcake to dislodge.

4.2 Chemistry Results

The salt solution compositions obtained during tests performed with inhibited water and 1 M sodium hydroxide are shown in Tables 8 and 9, respectively. The term upper region refers to the top 7-9 inches of saltcake in the trough, while bottom region refers to the final 2-3 inches of saltcake. Bottom region data were obtained with the modified density gradient and salt mining techniques.

For the inhibited water tests, the major anions present in the salt solution were nitrate, carbonate, hydroxide, and nitrite. The anion concentrations in the salt solution removed from the upper region were independent of the test technique or the contact time between the dissolution water and the saltcake. These results indicate that the salt solution attains an equilibrium or saturated condition rapidly (i.e., less than 4-5 hours) after the dissolution water contacts the saltcake. It is also interesting to note that there is a 40-80 fold increase in the hydroxide concentration between the dissolution water and the salt solution that is removed. This increase is likely due to the presence of interstitial liquid.

The high hydroxide concentration observed for Test 4 #1, however, was due to the test technique. In this case, the modified density gradient technique, in which liquid is added to the top of the saltcake and removed from the bottom, initially displaces the interstitial liquid. The hydroxide concentration in the removed salt solution is approximately the same as that of the interstitial liquid. The color of the solution also confirmed displacement of the interstitial liquid. The methyl red indicator added to the dissolution

water did not appear in the salt solution until after approximately 1500 ml of solution had been removed.

Table 8 also shows that the concentrations of the major aggressor and inhibitor anions (nitrate, nitrite and hydroxide) in the bottom region decreased to approximately one half their values in the upper region. At the removal rate employed during these tests, it is likely that the ratio of dissolution water from above the saltcake to salt solution permeating through the saltcake was greater than in the earlier tests (i.e., short circuiting). Slowing the removal rate or stopping the removal for a time would allow adequate contact time to achieve higher concentrations.

Table 9 shows the compositions obtained with the 1 M sodium hydroxide dissolution water. As with the inhibited water, the anion concentrations were independent of the test technique. The salt solution compositions were very similar to those achieved with inhibited water as the dissolution water with the exception of the sodium hydroxide concentration. The hydroxide concentration maintained its initial value through most of the tests. These solutions tended to be slightly more dense than the inhibited water salt solutions. This result is likely due to the lower removal rates utilized with these tests.

As with the inhibited water tests, the first test in the upper regions typically displaced interstitial liquid. Therefore the hydroxide concentration was higher during the first test. The concentrations in the bottom region of the trough also decrease to approximately one half their values in the upper region for the same reason mentioned above.

From a corrosion standpoint, the chemistries of the salt solutions produced with the inhibited water were outside the current technical standards for storage, while those produced with the 1 M sodium hydroxide were within the standards. However, the current standards were developed for fresh waste at temperatures near 100 °C [9]. At the lower temperatures, anticipated for these salt dissolution techniques, the inhibitor requirements may be less. Corrosion testing in salt solutions similar to those obtained with the inhibited water are planned to determine if revisions to the technical standard are possible [10].

5.0 Conclusions and Future Plans

In this section a comparison of the four removal techniques will be presented. Differences between the trough tests and the actual tank and future corrosion testing will also be discussed briefly.

5.1 Comparison of Removal Techniques

Salt solutions produced by each of the techniques typically had a density of 1.38-1.4 and had very similar chemistry. All techniques had difficulty maintaining the salt solution strength when the removal rates were too fast and/or the depth of the outlet line was too shallow. Under these conditions, contact between the unsaturated liquid and the saltcake (i.e., short circuiting) is restricted. This phenomenon was particularly apparent at the bottom of the trough.

Table 1 summarizes some of the key aspects of each of the techniques. Due to the shallower depths of the outlet line, the interstitial liquid is retained longer during the DASR technique than the other techniques. From a corrosion standpoint this is desirable as the interstitial liquid has high concentrations of corrosion inhibitors. Each of these techniques produced a relatively horizontal profile. The level profile is important to minimize build-up of saltcake in the corners of the tank. Currently, the plan for DASR is

to place the transfer jet 5-10 feet below the surface of the saltcake and remove horizontal slices. Therefore, a difficulty from an operations standpoint is that the height of the transfer jet will need to be adjusted. A means for mining a hole in the saltcake for the transfer jet post-installation will be necessary. The other two techniques involve fixing the jet at the bottom of the tank.

Slightly faster removal rates may be possible with the DASR technique. More of the dissolution water added immediately contacts the salt than for the other techniques. This last statement is true unless an excess of dissolution water is added above the top of the saltcake (see Scenario 2 and Test 1). The sit time of 24 hours is almost unnecessary for this technique as the salt dissolves rapidly. However, dissolution of hard chunks of salt attached to the cooling coils and equipment may occur during this time. Localization and entrainment of insolubles should not be a problem with any of these techniques provided the removal rates are slow and the outlet lines are at an adequate depth. Even at faster rates, the velocity of the solution is slow at distances far from the transfer jet (greater than 15 feet). Thus entrainment of a significant amount of insoluble fissile material would seem unlikely.

The last two items are concerned with monitoring the process. Since the liquid is drained from the saltcake during the DASR process, there is a potential for the area around the transfer jet to dry and result in the jet "gassing out". This occurrence should not present any hazards or equipment problems provided the jet is disabled shortly after it begins to gas out. The final item refers to monitoring the solution level in order to prevent salt from perching on the cooling coils. The DASR method intentionally lowers the solution level below the saltcake during removal of the salt solution. During the next addition of dissolution water, the solution should cover the saltcake prior to removing salt solution. The modified density gradient and continuous salt mining techniques maintain solution above the saltcake level at all times. The most difficult of these from an operations standpoint would seem to be adjusting the addition and removal rates for continuous salt mining. If the removal rate is too fast relative to the addition rate, the solution level will be beneath the saltcake and perching of saltcake will occur.

A water jet should be an effective way of dislodging any perched salt. A velocity on the order of 10 ft/s is recommended to minimize the amount of dissolution water that is added to the tank. A device for maneuvering the water jet so that all of the saltcake is contacted by the spray will be necessary.

5.2 Differences between Trough and Actual Tank

Table 10 shows a comparison between the average composition of the interstitial liquid in the trough and that in the tank. Examination of the supernate chemistry history for Tank 41 indicates that there were periods when the supernate had a similar composition to that of the interstitial liquid in the trough. Since the mid-1980's, however, the hydroxide concentration has been greater than that of the interstitial liquid. Table 11 indicates that the composition of the interstitial liquid was very similar to that after a single evaporation [8,11]. However, the current supernate concentration in Tank 41 is similar to the liquid composition after two to three evaporation cycles [8,11]. This comparison illustrates the difficulty in simulating the saltcake in Tank 41.

The other major difference is the carbonate concentration of the interstitial liquid in the trough experiments. In order to achieve the concentration of carbonate in the soluble solids, excess sodium carbonate was added to the solution that was evaporated. The mechanism for carbonate formation in the tank is different. Carbon dioxide from the air is absorbed by the waste and then reacts with the free hydroxide in the supernate to form

sodium carbonate [12]. Therefore, one would expect that the saltcake (including interstitial liquid) at the surface would have a higher carbonate concentration relative to the saltcake at the lower levels.

The soluble solids composition was determined from a sample core which was drained of interstitial liquid, dried in an oven at 125 C overnight, and then re-dissolved in 1 liter of dissolution water. A sample core was taken prior to dissolution and after dissolution. For comparison purposes the soluble solids composition for Tank 41 is also included in Table 1. The differences between the nitrite and hydroxide concentrations for Tank 41 and the laboratory test may be explained due to insufficient drainage of the interstitial liquid from the sample core. Therefore, when the salt core was dried, salts that were dissolved in the interstitial liquid crystallized. Crystallization of the interstitial liquid likely elevated the composition of each of the solids components especially the more soluble components.

The change in the saltcake solids composition as dissolution proceeds is shown in Table 12. The two primary constituents of the saltcake were still nitrate and carbonate. However, as more saltcake dissolved the ratio of nitrate to carbonate decreased. This result meant that the sodium nitrate is more soluble than the sodium carbonate. The impact on the salt solution chemistry during most of the trough tests is minimal because there is a large amount of sodium nitrate to dissolve. At the bottom regions of the tank or trough, the smaller amount of sodium nitrate to carbonate may be beneficial from a corrosion standpoint. However, salt dissolution may take longer as the carbonate dissolution rate may be slower.

5.3 Future Corrosion Testing

Stress corrosion cracking (SCC) is a concern in concentrated nitrate solutions such as those produced during salt dissolution. The salt solutions formed after the addition of 1 M sodium hydroxide were all within the current corrosion technical standards for storage of fresh waste, while those formed with inhibited water were outside the standards. As mentioned earlier, it is desirable to utilize inhibited water rather than 1 M sodium hydroxide as this reduces the amount of decontaminated salt solution requiring disposal in the Saltstone facility. There are difficulties in applying the current technical standards to density gradient dissolution in Type III tanks such as Tank 41. First, the temperatures which apply to the majority of the nitrate concentration ranges in the current standards are above 50 °C [9]. The temperatures for density gradient dissolution are typically between 25-50 °C. Tests have shown that the inhibitor requirement for stress corrosion cracking of carbon steel decreased with temperature [9]. Tests will be performed within the expected temperature range for density gradient dissolution and within the concentration ranges of the salt solutions produced with inhibited water.

The second consideration was that earlier tests were performed on ASTM A285 Grade B carbon steel (A285) that was not stress-relieved. The Type III and Type IIIA tanks are stress-relieved and constructed of ASTM A537 Class 1 (A537) and ASTM A516 (A516) carbon steel, respectively. Stress-relief has been demonstrated to mitigate SCC [13] and A537 has also been shown to have superior resistance to SCC compared to A285 [14]. Both A516 and A537 have been shown to have similar resistance to stress corrosion cracking [14]. Thus, concern over SCC of the tank walls is not an issue. However, the distributed cooling coils in the tank are not stress-relieved and are constructed of A106 carbon steel. The heat affected zones near the welds in the cooling coils may be susceptible to SCC. Given that tanks like 41H will be placed back in service following salt removal, it is necessary to assure that SCC of the coils will not occur.

Two types of corrosion tests will be conducted. The first is constant potential slow strain rate tests. These tests have been performed in the past to establish the technical standards and provide an excellent screening method for the initiation of SCC. A statistically designed set of experiments has been planned for these tests. The variables investigated will include the nitrate, nitrite, hydroxide, and carbonate concentrations and the temperature. The response studied will be the uniform elongation below which SCC is observed.

Coupon immersion tests will also be performed. The coupons will be A106 carbon steel pipe which contains a circumferential weld. The weld filler metal and welding procedure will be the same that were used for the cooling coils in the Type III tanks. The coupons will be immersed for three months in the same solutions that were utilized for the slow strain rate tests. The heat affected zone near the weld will be examined in particular for evidence of SCC.

6.0 Acknowledgments

The author appreciated the comments of W. R. Parish and J. N. Brooke during the formulation and performance of the tests. The laboratory work of A. L. Williams, R. S. Garritano, and R. R. Lathrop was also greatly appreciated.

7.0 Quality Assurance

Test procedures and results were recorded in laboratory notebook WSRC-NB-95-291.

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Table 1. Comparison of Density Driven Techniques

<u>Drain-Add-Sit-Remove</u>	<u>Modified Density Gradient</u>	<u>Continuous Salt Mining</u>
1) Retains interstitial liquid the best.	1) Displaces interstitial liquid faster than DASR.	1) Displaces interstitial liquid the fastest.
2) Produces a level profile.	2) Produces a level profile.	2) Produces a level profile.
3) Need to adjust transfer jet level.	3) Transfer jet is fixed near the bottom of the tank.	3) Transfer jet is fixed near the bottom of the tank.
4) Remove liquid as soon as it reaches the pump site.	4) Needs to be drawn down slowly to prevent "short-circuiting".	4) Needs to be drawn down slowly to prevent "short-circuiting".
5) Insolubles: Slow removal: No localization and minimal entrainment. Medium removal: Localization at shallow jet depths. Pluggage of removal jet. No localization at deeper jet depths. Significant entrainment of salt crystals and insolubles. Fast removal: No localization at deeper jet depths. Largest amount of entrainment of salt crystals and insolubles.	5) Insolubles: No localization and minimal entrainment.	5) Insolubles: No localization and minimal entrainment.
6) Removes saltcake in small horizontal slices.	6) Removes salt solution from the bottom.	6) Removes salt solution from the bottom.
7) More likely to gas pumps.	7) Should not gas pumps.	7) Should not gas pumps.
8) Do not begin removal until liquid covers the saltcake.	8) Need to stop removal when liquid reaches the top of the saltcake.	8) Maintain liquid level above saltcake by adjusting the addition and removal rates.

Table 2. Composition of Soluble Salt Solids in Simulated Saltcake

Component	Tank 41 Salt Solids (wt.%)	Laboratory Initial Salt Solids (wt.%)
NaNO ₃	65.2	50.3
NaNO ₂	1.8	6.2
NaOH	5.5	10.3
Na ₂ CO ₃	23.7	26.6
Na ₃ PO ₄	1.4	2.4
Na ₂ SO ₄	2.1	2.1
Na ₂ C ₂ O ₄	0.3	2.1
NaAl(OH) ₄	0	0

Table 3. Composition of Batch 1 Sludge

Component	wt. %
Aluminum	6.76
Barium	0.012
Calcium	2.67
Chromium	0.18
Copper	0.026
Iron	26.8
Potassium	0.14
Magnesium	1.31
Manganese	2.8
Sodium	10.2
Nickel	0.24
Lead	0.1
Silicon	0.81
Strontium	0.02
Titanium	0.044
Zinc	0.17
Zirconium	0.07
Oxalate	0.194
Carbonate	1.94
Fluoride	0.007
Nitrite	5.86
Nitrate	1.96
Free Hydroxide	2.95
Phosphate	0.84
Sulfate	0.33

Table 4. Experimental Techniques and Dissolution Water Utilized for Laboratory Tests

Technique	Drain-Add-Sit-Remove	Modified Density Gradient	Salt Mining	Perched Saltcake
Dissolution Water				
1 M Sodium Hydroxide	Scenario 1 Scenario 2 Scenario 3		Scenario 4	Scenario 5
Inhibited Water	Test 1 Test 2 NCSE6 NCSE38 NCSE100 NCSE38M	Test 4 #1 Test 4 #2 Test 4 #3 Test 4 #4	Test 3	Test 5

Table 5. Experimental Conditions for Laboratory Tests

Test ID	Trough ID	Drainage Rate (ml/min)	Addition Rate (ml/min)	Removal Rate (ml/min)	Height of Suction Relative to Initial Salt Height (in.)	Initial Salt Height (in.)
Scenario 1	1	17.8	5.1	4.5	-3.5	11
Scenario 2	1	7	5.7	4.3	-2.75	9.75
Scenario 3	1	6.5	5.75	1.7	-6.6	8.1
Scenario 4	1	na	2.8	4.1	-3.0	4
Scenario 5	1	na	1000	1.5	-2.0	3
Test 1	2	4.5	5.9	38	-4.0	9.5
Test 2	2	38	50	38	-3.5	7.5
Test 3	2	na	6.4	10	-4.1	4.4
Test 4 #1	3	na	50	10	-5.4	5.9
Test 4 #2	3	na	50	10	-3.5	4
Test 4 #3	3	na	50	10	-2.5	3
Test 4 #4	3	na	50	10*	-1.9	2.4
Test 5	2	na	1000	na	na	na
NCSE6	4	38	50	6	-6.3	7.5
NCSE38	5	38	50	38	-6.8	8.1
NCSE100	6	38	50	100	-6.8	7.8
NCSE38M	7	38	50	38	-4.5	7.3

na - not applicable

* - Test was interrupted for 12 hours during the removal stage to allow for further dissolution.

Table 6. Density of Salt Solution as a Function of the Height Relative to the Salt Level.

Height Relative to Salt Level (in.)	Density
+ 0.625	1.11
+ 0.5	1.16
+ 0.25	1.26
0	1.34
- 0.25	1.37
- 0.875	1.39
- 1	1.4
- 1.125	1.41
- 1.5	1.43

Table 7. Simulation Results

Test ID	Interstitial Liquid Drained (ml)	Dissolution Water Added (ml)	Salt Removed (ml)	Removal Rate (ml/min)	Ratio of Dissolution Water to Salt Dissolved	Average Density (g/ml)
Scenario 1	1243	1080	834	4.5	1.29	1.39
Scenario 2	695	2625	1989	4.3	1.32	1.39
Scenario 3	2678	3060	1534	1.7	1.99	1.38
Scenario 4	na	4210	1758*	4.1	2.39	1.36
Scenario 5	na	3500	1616*	1.5	2.16	1.36
Test 1	3215	3270	1530	38	2.14	1.35
Test 2	881	1643	927	38	1.77	1.38
Test 3	na	5730	2410**	10	2.38	1.38
Test 4 #1	na	2000	1950	10	1.03	1.39
Test 4 #2	na	2000	2185	10	0.92	1.39
Test 4 #3	na	2000	730**	10	2.74	1.29
Test 4 #4	na	2000	1550*	10	1.29	1.2
Test 5	na	2000	na	na	na	na
NCSE6	3730	3750	2321	6	1.61	1.37
NCSE38	4850	4000	2700	38	1.48	1.37
NCSE100	3375	3375	2823	100	1.2	1.38
NCSE38M	2500	2500	1172	38	2.13	1.29

na - not applicable

* - Stopped test when the density decreased below 1.32.

** - Did not stop test when density decreased below 1.32.

Table 8. Range of Concentrations Obtained from Tests Performed with Inhibited Water as the Dissolution Water

Component	Upper Region Concentration (M)	Bottom Region Concentration (M)
Na ⁺	8-10	4-6
NO ₃ ⁻	4.5-6	2-3.5
OH ⁻	0.4-0.8*	0.1-0.25
NO ₂ ⁻	0.1-0.2	0.04-0.08
CO ₃ ⁼	1.0-1.6	0.6-1.2
Al(OH) ₄ ⁻	0.08-0.15	0-0.04
PO ₄ ³⁻	0.05-0.1	0.1-0.2
SO ₄ ⁼	0.08-0.15	0.02-0.04
C ₂ O ₄ ⁼	0.01	0.02
Density	1.38-1.4	1.15-1.3

* Except for Test 4 #1 where the hydroxide concentration ranged between 1.0-1.3 M.

Table 9. Range of Concentrations Obtained from Tests Performed with IM Sodium Hydroxide as the Dissolution Water

Component	Upper Region Concentration (M)	Bottom Region Concentration (M)
Na ⁺	9-9.5	3.8
NO ₃ ⁻	4.5-6	1.8
OH ⁻	0.9-1.1*	0.87
NO ₂ ⁻	0.1-0.3	0.01
CO ₃ ⁼	1.2-1.6	0.46
Al(OH) ₄ ⁻	0.08-0.15	0.002
PO ₄ ³⁻	0.1-0.3	0.07
SO ₄ ⁼	0.01-0.04	0.02
C ₂ O ₄ ⁼	0.01	0.02
Density	1.38-1.4	1.19

* Except for Scenario 1 where the hydroxide concentration ranged between 1.1-1.4 M.

Table 10. Average Composition of Interstitial Liquid in Simulated Saltcake and Composition of Supernate in Tank 41 as of January 1996.

Component	Simulated Saltcake Liquid Concentration (M)	Supernate Concentration in Tank 41 as of 1/96 (M)	Supernate Concentration in Tank 41 as of 3/82 (M)	Supernate Concentration in Tank 41 as of 2/84 (M)
Na ⁺	9.1	ND	ND	ND
NO ₃ ⁻	4.52	1.93	3.1	3.3
OH ⁻	1.18	6.39	1.3	5.9
NO ₂ ⁻	0.33	1.2	0.3	1.2
CO ₃ ⁼	1.28	0.03	ND	ND
Al(OH) ₄ ⁻	0.15	0.01	ND	ND
PO ₄ ³⁻	0.08	0.016	ND	ND
SO ₄ ⁼	0.16	0.012	ND	ND
C ₂ O ₄ ⁼	0.01	0.0068	ND	ND
Density	1.4	1.37	1.22	1.44

Table 11. Laboratory Data on Evaporated Supernate Compositions.

Component	Goodlett Single Evaporation Liquid Concentration (M)	Goodlett Second Evaporation Cycle Liquid Concentration (M)	Chandler Single Evaporation Liquid Concentration (M)	Chandler Third Evaporation Liquid Concentration (M)
Na ⁺	ND	ND	ND	ND
NO ₃ ⁻	5.03	2.18	4.49	2.71
OH ⁻	2.52	7.6	2.08	4.28
NO ₂ ⁻	ND	ND	0.97	1.94
CO ₃ ⁼	0.18	0.11	0.17	0.22
Al(OH) ₄ ⁻	1.02	2.3	0.76	1.09
PO ₄ ³⁻	ND	ND	0.005	0.01
SO ₄ ⁼	0.07	0.023	0.09	0.07
C ₂ O ₄ ⁼	ND	ND	0.007	0.009
Density	1.49	1.55	1.38	1.43

Table 12. Composition of saltcake at different stages of dissolution.

Component	Laboratory Salt Solids after Partial Dissolution (wt.%)	Laboratory Salt Solids after Nearly Complete Dissolution (wt.%)
NaNO ₃	46.7	27.5
NaNO ₂	0.9	0.3
NaOH	11.5	1.7
Na ₂ CO ₃	37.5	59.9
Na ₃ PO ₄	0.4	1.0
Na ₂ SO ₄	2.6	3.3
Na ₂ C ₂ O ₄	0.4	2.2
NaAl(OH) ₄	nd	4.1

Figure 1. Lexan trough utilized for dissolution tests.



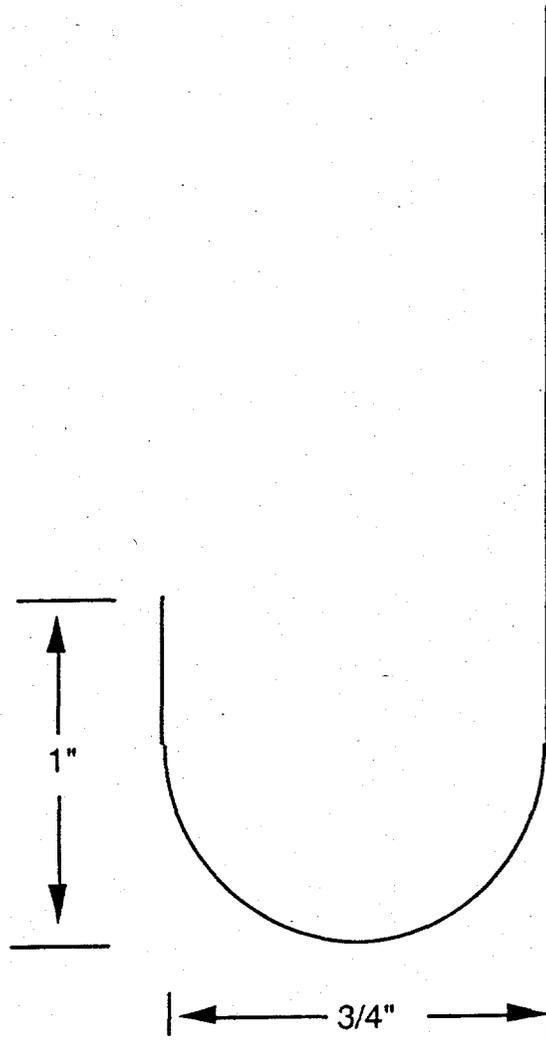


Figure 2. Modified outlet line for criticality studies.

Figure 3. Drain-Add-Sit-Remove Technique: (a) Saltcake prior to dissolution, (b) Drained saltcake, (c) Addition of dissolution water, and (d) Removal of salt solution.

(b)



(3)



(a)



(c)



Figure 4. Modified Density Gradient Technique: (a) Saltcake prior to dissolution, (b) Addition of dissolution water, (c) Removal of salt solution, and (d) Addition of dissolution water for the next batch.

(b)



(a)



(a)



(c)

Figure 5. Continuous Salt Mining Technique: (a) Initial stages of dissolution, (b) Humped region in the middle beginning to form, (c) Saltcake profile beginning to become horizontal, (d) Final condition of saltcake.

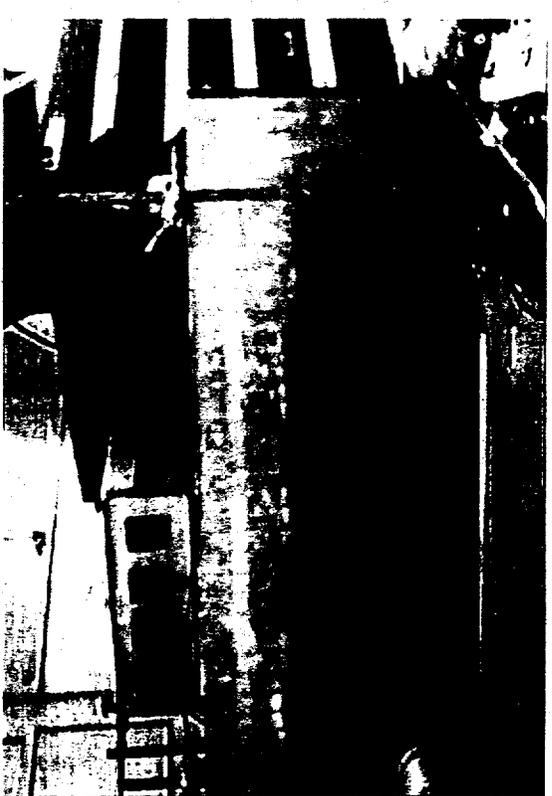
(b)



(a)



(a)



(c)

Figure 6. Perched saltcake during the laboratory tests.

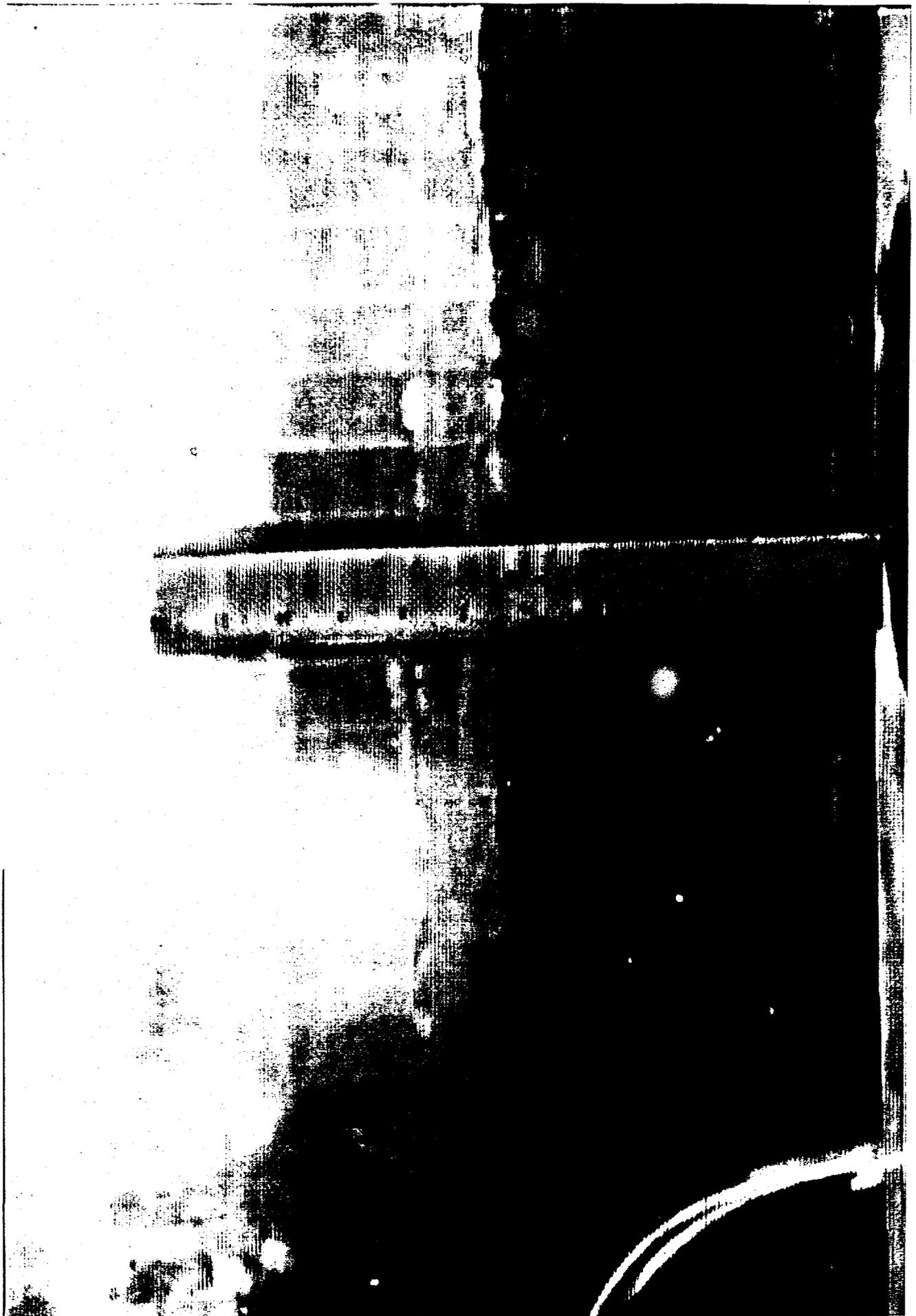


Figure 7. Perched saltcake during density gradient dissolution in Tank 10.

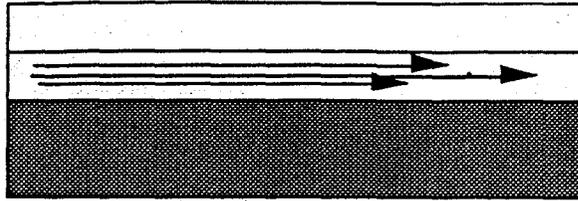


96x00472.01

Figure 8. Water jet simulation to dislodge perched saltcake.



Streamlines for horizontal flow of salt solution in drained saltcake

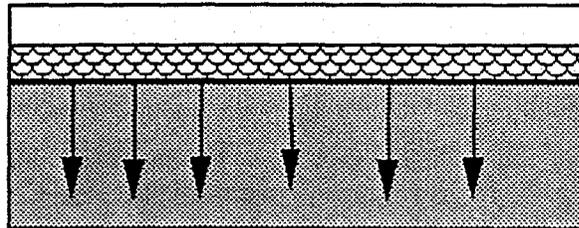


Drained Saltcake and Salt Solution

Saltcake and Interstitial Liquid

(a)

Streamlines for vertical flow of salt solution through saltcake

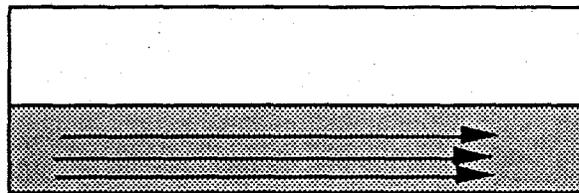


Dissolution Water

Saltcake, Interstitial Liquid and Salt Solution

(b)

Streamlines for horizontal flow of salt solution through saltcake.



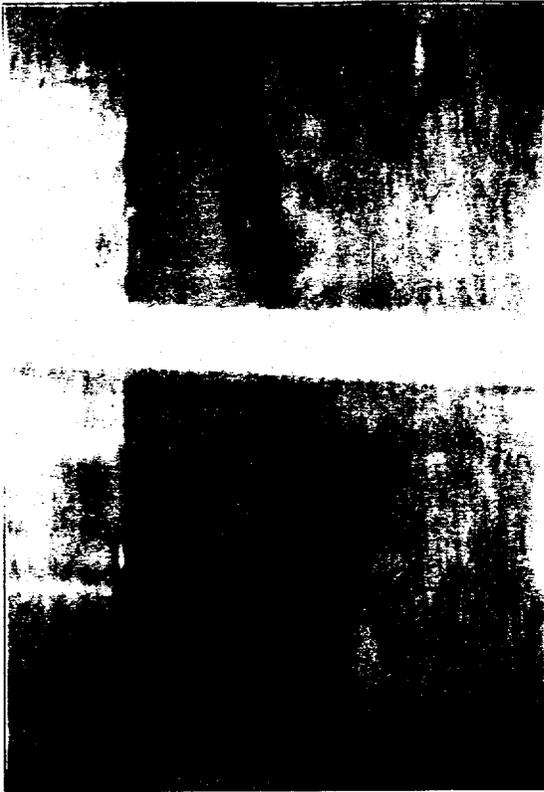
Saltcake, Interstitial Liquid, and Salt Solution

(c)

Figure 9. Schematics of dissolution techniques: (a) Drain-Add-Sit-Remove, (b) Modified Density Gradient, and (c) Continuous Salt Mining.

Figure 10. Localization of insolubles at the outlet line during Test #1.

(b)



(a)



(a)



(c)

