LA-UR-01-6913

THE ACTINIDE SOURCE-TERM WASTE TEST PROGRAM (STTP)

Final Report

Prepared for the DOE-Carlsbad Field Office

Fall 2001

VOLUME III

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I. Summary of Volume III; STTP Results and Discussions

- All waste drums selected for the STTP tests contained > 5 gm of Pu per 55-gal drum.

- All homogeneous wastes were comminuted to allow greater mixing and contact of the brine with the waste to shorten the time of determining the influence of the waste on the behavior of actinides in the brine.

- Soluble salts of Th, U, and Np were added to all test containers. Nd was added to all test containers except the six test containers (LS-10, 11, 12, and 37, 38 and 39) with added Am-241.

- About 75 mg of Am-241 as a soluble salt was added to the Portland Cement test containers LS-10, 11 and 12, and the Pyrochemical Salt tests LS-37, 38 and 39. In both cases, the Am precipitated in the basic brine solution and was not re-solubilized during the entire test period.

- Fe mesh was added to each STTP liter-scale and drum-scale test container except the three sets LS-7, 8, 9; 10, 11, 12; 37, 38, and 39. The Fe mesh was packed into flow through polypropylene bottles to allow brine to have free access to the Fe mesh. However, D&D of the liter-scale test containers showed that most of the Fe mesh containers were filled with finely divided sludge that limited the contact between the brine and the Fe mesh. **A hard black coating, identified as magnesioferrite, formed on the surface of the Fe mesh that prevented corrosion or dissolution of the Fe mesh. This occurred in all test containers**.

- Fe mesh did not appear to maintain a reducing environment in most test containers. Pu (V) and (VI) was present in four test containers with Fe mesh present.

- A mixed microbial inoculum (100-150 ml) of anaerobic brine-containing sediments consisting of 20% lake brine and 30% muck pile salt solution from the WIPP environs along with 50% G-Seep Brine from the WIPP was added to each test container. The microbes appeared to die off rather quickly in the STTP test containers.

- Nitrate and phosphate were added to three drum-scale tests (DS-10, 11 and 12). Nitrate was essentially totally destroyed in the two Brine A experiments (DS-10 and 11) and was not affected in the Castile Brine experiment (DS-12). The mechanism for destruction of nitrate was thought to be from alpha-particle activity that radiolytically destroyed the nitrate that was in solution. **The reason the Brine A experiments resulted in destruction of nitrate and the Castile Brine had no effect is not known.**

- Organic solvents were added to LS-13, 14, and 15. The organic solvents generated very high concentrations of particles and colloids that did not contain actinides. Nitrates in the two Brine A experiments (LS-13 and 14) were totally destroyed and the nitrate in LS-15 with Castile Brine was less affected. This finding points to an energy transfer that may include Mg in the Brine A test. Higher concentrations of H_2 and CO_2 were present in LS-13 and 14 and not so high levels were in the headspace of LS-15, a Castile Brine experiment. Once again, this points to an energy transfer mechanism that could include Mg in Brine A and lack of a radiolytic energy transfer in Castile Brine. **These results accentuate one of many differences in Brine A and Castile Brine chemistry.**

- Bentonite was added to LS-31, 32, and 33 and to DS-4, 5, and 6. Bentonite was effective in maintaining a very low concentration of soluble actinides in all six test containers. The tests with added bentonite had relatively lower concentrations of particles (colloids) that ranged from 10^8 to 10^{10} particles per liter. Typical particle concentrations ranged from 10^{10} to10^{11} particles per liter.

- Envirostone tests with high levels of nitrates (30,000 to 36,000 ppm) also had very high concentrations of N_2O (20 to 40 $^v/_o$) but not high levels of CO_2 in the headspace of the test containers. These test containers with high concentrations of N_2O had lower levels of H_2 in the headspace.

- The drum-scale tests with massive metals did not result in significantly higher concentrations of Pu or other actinides. The soluble Fe concentration increased from <0.1 ppm to 558 ppm in LS-13 (Brine A) and <0.1 to 110 ppm in LS-14 (Brine A), and did not increase (<1 ppm) in LS-15 (Castile Brine). The pcH decreased in LS-13 from pcH 8.19 to 5.45 and in LS-14 from 7.78 to 6.62. The pcH in the Castile Brine test LS-15 did not significantly decrease during the test period (7.86 to 7.74). These results show the Brine A resulted in greater concentrations of soluble Fe than Castile Brine. The pcH in Brine A tests decreased while the pcH in Castile Brine did not. **These results strongly point out the difference in the chemistry of Brine A and Castile Brine.**

- The STTP tests contained comminuted homogeneous wastes and a selection of heterogeneous wastes immersed in brine, therefore, the experiments are applicable to WIPP Disposal Rooms that would be partially or completely filled with brine. **Such a brine-filled containment in the WIPP would require a geologic upheaval or an extensive human intrusion scenario. The probability of either of these two scenarios is very low.**

- Pu present as a salt or non-fired oxide in the waste is probably the major form that would be soluble in WIPP brines. Medium-fired or high-fired Pu oxides would have minimal solubility in basic WIPP brines. Metallic Pu is not expected to be in the waste.

- The wastes included in the STTP studies to determine the chemical behavior of the waste and associated actinides Th, U, Np, Pu and Am, were comminuted forms of the homogeneous wastes Portland Cement, Envirostone and Pyrochemical Salts. This effectively speed up chemistry in the repository by several hundred or thousand years. The heterogeneous waste forms were a mixture of combustible wastes and three tests contained massive metal.

- Actinides were not solubilized in brine in contact with Portland Cement or were solubilized and immediately precipitated. Soluble concentrations in Portland Cement tests were in the low ppb range.

- Only U was solubilized to any extent in tests with comminuted Envirostone. Pu, Am, Np, Th, and Nd were essentially not solubilized in the Envirostone tests.

- Envirostone tests with added organic solvents resulted in increased actinide solubilization but concentrations were low relative to pyrochemical salt tests. **Organic solvents resulted in much higher particle concentrations (~10^{13} particles/liter) but the particles did not contain actinides.**

- There were two forms of pyrochemical salt wastes tested, Direct-Oxide Reduction (DOR) salts and Oxygen Sparging (OS) salts. The chemistry of the two salt wastes were considerably different as shown later in this report.

- Test containers with Pyrochemical salt wates contained higher loadings of Pu (0.38 to 11.1 gm) relative to other STTP tests. The concentration of soluble actinides in pyrochemical salt wastes was significantly higher than other STTP tests.

- The liter-scale pyrochemical salt tests with added bentonite resulted in very low levels of soluble actinides and relatively low particle concentrations (10^9 to 10^{10} particles/liter). These tests also had very low Ca and Fe concentrations.

- Pyrochemical salt tests with added chelators and calcium hydroxide (96 gm) resulted in significant solubilization of actinides in Castile brines but much lower concentrations in Brine A experiments. The high Mg concentration in the two Brine A tests (LS-34 and 35) combined with chelators to lessen the impact while in the Castile Brine test, LS-36, the chelators were free to solubilize actinides because of the low Mg content. The concentration of Mg in LS-36 at a pcH of 11.2 was < 20 ppm because of the formation of $Mg(OH)_2$. The Ca concentration of 9000 ppm, 90,000 ppm and 65,000 ppm in LS-34, 35 and 36, respectively did not have an impact on solubilization. The ionic strength of all these pyrochemical salt tests, especially Brine A, was very high. Overall, the impact on solubilization of actinides with chelators in comminuted homogenous wastes was considerably less effective than the heterogeneous wastes in the drum-scale tests.

- Pyrochemical salt tests with added soluble Am-241 (75 mg) did not result in significant solubilization of actinides (LS-37, 38, 39). The Am was immediately precipitated in all three tests and did not resolubilize.

- The highest levels of soluble actinides in the STTP was found in LS-27, a Castile Brine experiment with DOR pyrochemical salt wastes at a pcH of ~11.0. D&D of the test container showed that all of the comminuted pyrochemical salts were available to the brine because the interaction of comminuted waste with brine did not form a cemented mass as was seen on many of the other pyrochemical salt waste tests. LS-27 had relative high concentrations of soluble Fe (16-243 ppm) during the test period. Pu (V) was identified in LS-27 but not Pu (VI). An explanation for the presence of Pu (V) is given in this report.

- The highest levels of Pu (VI) were identified in LS-26, a Brine A experiment with DOR pyrochemical salt at a pcH range of ~7.5 to 8.4. The Pu concentration increased slowly at first but more rapidly after about one year and Pu (VI) was identified that persisted for about one year. LS-26 was unique in that only Pu and Am increased in concentration while all other actinides and Nd remained at low levels. In contrast to LS-27, LS-26 had very low levels of soluble Fe (0.1 to 4 ppm) during the test period. LS-26 was the only test that exhibited a positive Eh. An explanation for the presence and eventual reduction in Pu (VI) is given for this test container.

- LS-28 was a DOR pyrochemical salt test in Brine A with ~60 bar of CO_2 pressure added to the headspace of the test container. The pcH of LS-28 had decreased to 4.48 while the Pu had increased to 90,942 ppb. All other actinides and Nd increased during the same period. A slurry of MgO was added to the test container which increased the pcH to 7.7 and the concentrations of Pu and all other actinides were reduced by 90 to 95%. However, a year after addition of MgO, the concentrations of Pu and Am with all the other actinides had increased significantly (Pu from 18,097 to 197,984 ppb) and Pu (VI) was identified in one sample about 27 months after addition of MgO. LS-28 had soluble Fe concentrations that ranged from 1 to 165 ppm during the test period and ~50 ppm in the sample with Pu (VI). An explanation for the presence of Pu (VI) in LS-28 is given in this report.

- LS-36 was a DOR pyrochemical salt test in Castile Brine with a rather high pcH of 11.2. Six chelators each at a concentration of 100-154 ppm was added to the test container. The concentration of soluble actinides, especially Pu, in LS-36 was relatively high and the Fe concentration typically ranged from 30 to 100 ppm. **Pu (V) was identified in LS-36 and this was somewhat surprising because the test had to overcome 101 ppm of added ascorbate as a chelator and a strong reductant and the reducing strength of the added microbial inoculum to achieve an oxidizing environment. The soluble Fe concentration did not maintain a reducing environment.**

- The drum-scale tests were not opened up as part of the D&D process and the condition of the waste or Fe mesh was not established. This decision was based on the increased time and effort as well as the considerable cost for accomplishing this D&D effort.

- The drum-scale tests with combustible and massive metal wastes all contained very low levels of actinide activity. The exception was the three drums (DS-7, 8 and 9) with chelators. **The chelators were considerably more effective at solubilizing all actinides in the drum-scale tests relative to the liter-scale tests with added chelators.**

- The drum-scale tests with massive metal (DS-13, 14 and 15) developed very high levels of H_2 during the entire test period.

- Phosphate added to DS-10, 11 and 12 as a microbial nutrient disappeared rather quickly after the beginning of the experiment. Phosphate concentrations for the two Brine A experiments were reduced to less than detectable within one month while detectable levels of phosphate persisted for about two months in Castile Brine experiment DS-12. **This may have been**

influenced by the higher Mg content in Brine A experiments and exemplified the difference in the radiolytic behavior in Brine A and Castile Brine.

- Phosphate added to the drum-scale tests containing chelators near the end of the test period was very effective in reducing the concentration of all actinides by > 90%. **It was interesting that Fe was also significantly reduced (>90%) in the Castile Brine experiment with chelators but was not effective in reducing the soluble Fe concentration in the DS-7 and 8 with Brine A.** This finding could explain the effectiveness of higher concentrations of Mg in lessening the effectiveness of chelators in solubilizing actinides in the WIPP.

- Radiolysis of brine resulted in the production of much H_2 that accumulated in the headspace of all test containers. **H_2 was found to not have an influence in maintaining a reducing environment.** H_2 is quite insoluble in brine and rises to the headspace of the test container rather rapidly. N_2O is very soluble in brine and is expected to be a reducing agent when nitrate is radiolytically converted to N_2O. Radiolytically generated O_2 remained in the brine as a combined radical and rarely was seen in the headspace except in tests with high loadings of Pu or Am.

- H_2 was a radiolytically generated gas that was the primary gas found in the headspace of STTP test containers except in the tests with high levels of nitrates. All other gases were in trace quantities relative to H_2 and N_2O.

- CO_2 was a radiolytically produced gas from alpha-particle irradiation of organics within the brine. The alpha-particle range in brine is a few microns and does not generate much CO_2 as evidenced by the < 1% CO_2 in the headspace of all test containers except LS-13 and 14 with > 4000 ppm total organic carbon added as organic solvents. LS-13 and 14 accumulated 4-5 $^{v}/_{o}$ and LS-14 about 3 $^{v}/_{o}$ CO_2 in the headspace of the test containers. **Test containers with < 2000 ppm organics typically generated < 1 $^{v}/_{o}$ CO_2.**

- Radiolytic generation of hypochlorite in concentrated brine (~5 M NaCl) is a well known process as reported in the literature. Formation of hypochlorite is dependent on the radiation levels (> 2 GBq/l) and the concentration of chloride (> 4 molar) in the brine. Alpha activity from Pu soluble in brine plus Pu loading in the waste for Pyrochemical Salts would achieve a level of 2 to 10 GBq/liter. So production of hypochlorite is certain to occur in the STTP test containers that contain > 1 gm of Pu-239. Hypochlorite can act as a powerful oxidant in acid (hypochlorous acid) or basic solution (hypochlorite). Both have been shown to stabilize Pu (VI) in Brine A and Castile Brine.

- Radiolytic generation of peroxide in high concentration brines occurs because of the dissociation of the H_2O molecule in brine to form peroxides. Peroxide is a strong oxidant in weak acid and basic solutions of Brine A and Castile Brine and will stabilize Pu (VI) in both solutions but is less effective in neutral solutions. An excess of peroxide can result in reducing Pu (VI) or reducing the concentration of Pu as a precipitate in Brine A and Castile Brine. This may be the cause of the eventual diminution of Pu (VI) in LS-26 and 28.

- A combination of radiolytically generated hypochlorite and peroxide could well serve as an oxidant to oxidize Pu (IV) to Pu (V) and (VI) in weak acid, neutral and basic Brine A and Castile Brine solutions. As the hypochlorite and peroxide concentrations become greater and greater, Pu can be either reduced or act as precipitants to reduce the Pu activity in an STTP test. **This mechanism could limit the concentration and lifetime of Pu (VI) in specific environments in the WIPP.**

- An explanation for the formation of Pu (VI) is STTP Pyrochemical Salt tests is given in a sequential manner as follows.

Formation of Pu (V) and Pu(VI) in STTP Pyrochemical Salt Tests; Sequential Order of Reactions

Pyrochemical Salt Wastes Consist of:

1. DOR (Direct-Oxide Reduction)
2. OS (Oxygen Sparging)

↓

1. **DOR: High concentration of Ca and Cl^-**
   OS : High concentration of Na and K and Cl^-

↓

2. **DOR: High loading of Pu and Am; high activity**
   OS : Lower loading of Pu and Am

↓

3. **DOR: Pu (V) and Pu (VI) Identified**
   OS : No oxidation Observed

↓

4. **Pu (IV) is stabilized by $SO_4^{=}$**

↓

5. **Sulfate in DOR tests precipitated as $CaSO_4$**
   K_{sp} of $CaSO_4$ is 7.1 x 10^{-5}

↓

6. **Nitrates as source of nitrite and N_2O**
   Not available in pyrochemical salt tests

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Formation of Pu (V) and Pu(VI) in STTP Pyrochemical Salt Tests; Sequential Order of Reactions (continued)

↓

7. **High chloride (6 to 11 Molar) predominates in Pyrochemical salt tests**

↓

8. **DOR: Fe concentrations are high; F^- complexation of Fe in acid solution strong; metal hydrolysis effect and amphoterism effect in high basicity solutions.**
OS : Fe concentrations are low

↓

9. **DOR: Total colloid concentration high**
OS : Total colloids 10x to 100x lower than DOR
DOR: Colloids high in Pu, Sr, Ca, SO_4
OS : Colloids low in Pu, Sr, Ca, SO_4

↓

10. **DOR: High Ca and Mg release Pu from $SO_4^{=}$ to Cl^-**
OS : Sulfate remains to stabilize Pu (IV)

↓

11. **DOR: High loading of Pu and Am produce radiolytic OCl^- and peroxides in basic solution and > 5 M chloride**

↓

12. **DOR: Pu (IV) is susceptible to oxidation**
OS : Pu not so susceptible to oxidation

↓

13. **Pu (V) and Pu (VI) Identified in DOR tests**

↓

14. **Pu (VI) Concentration Disappeared**

- A comprehensive study was conducted to determine the concentration and stability of colloids in the STTP experiments. The data showed there was a very low population of Pu bearing colloids. Field Flow Fractionation studies verified this finding and further showed for one test container (LS-27) that there was no activity in the different particle sizes outside of what was defined as a soluble species (<10 nm diameter particles). **This was considered to be an important finding because colloids as a vehicle for transport of actinides does not appear to be a problem for the WIPP. Also, colloids do not seem to be stable in the Brine A and Castile Brine environment of the WIPP.**

- The liter-scale tests were loaded with about 2.5 liters of brine and the pressured tests were loaded with ~ 2 liters of brine. The drum-scale tests were loaded wit about 50 gals (190 liters) of brine. All tests were rotated to agitate the brine and waste to achieve mixing to optimize the amount of leaching that could occur during the rotation period. Agitation was conducted weekly for about 5 years. During the final one to two years, the test containers were left in a quiescent mode. Recognizing that the brine in the repository would be in a relatively quiescent mode, a study comparing the analytical results for actinides after the rotation mode was compared with results after the quiescent mode. Most test containers showed little change between the two modes with concentrations in general being a little lower to significantly lower after the quiescent mode. The test containers showing greater concentrations were as follows: LS-16 showed a significant increase of most actinides; LS-25 showed a Pu increase from 40 ppb to 250 ppb; LS-34 showed a Pu increase from 13.5 ppb to 87 ppb; and LS-37 showed a significant Pu increase from 194 to 5500 ppb. The drum-scale test DS-12 showed a significant increase of all actinides while DS-09 showed a significant decrease of all actinides.

- Sulfate is considered to be an anion that stabilizes Pu (IV), especially when the sulfate concentration predominates over other anions. The concentration of sulfate ranged in Portland Cement tests up to 14000 ppm, Envirostone tests up to 18000 ppm, Pyrochemical Salt tests with Oxygen Sparging waste up to 9000 ppm and Direct Oxide Reduction waste had a range of 50 to 250 ppm. The drum-scale tests showed sulfate from 4700 to 48000 ppm. It is apparent that Direct Oxide Reduction Pyrochemical Salt wastes had concentrations of sulfate that were far lower than other wastes. The high Ca concentration in the DOR salt tests (30,000 to 120,000 ppm) reduced the sulfate concentration by precipitation of the sulfate as $CaSO_4$. The addition of $Ca(OH)_2$ to LS-34, an OS test, resulted in a lower sulfate concentration (800 ppm) than the other OS tests (4600 to 9000 ppm).

- The pressurized liter-scale tests with Portland Cement (LS-4, 5 and 6) showed higher concentrations of U and LS-6, a Castile Brine experiment, showed a higher concentration of Pu (up to 638 ppb) than other Portland Cement tests. The U was expected to increase because of the higher carbonate concentrations in the tests with CO_2 pressure. **Interestingly, the pcH of the Portland Cement did not decrease and go acid as was thought might happen.** The buffering capacity of comminuted Portland Cement must be significant to remain basic after 5-6 years with 60 bars of CO_2 pressure.

- The pressurized liter-scale tests with Pyrochemical Salt wastes showed significantly higher concentrations of all actinides. LS-28 showed a relatively higher Pu concentration after addition of MgO (up to 197,000 ppb of Pu). Th, Np, U, and Am also had higher than usual concentrations in the presence of CO_2. The pcH decreased to slightly acid conditions in all three Pyrochemical Salt tests. The headspace gas in LS-28 showed a concentration of ~ 50% H_2 after being pressurized with 60 bars of CO_2 for over two years. The H_2 is believed to be from radiolytic degradation of brine. The Pyrochemical Salt tests with added CO_2 pressure were all DOR salt tests. The presence of Pu colloids or microprecipitates was evident by the spectroscopic analyses of filters and Pu was associated with $SrSO_4$, however, the concentrations of colloidal-bearing Pu were very small.

- The two liter-scale tests with Pu (VI) were LS-26 and LS-28. LS-26 was a Pyrochemical Salt test with a loading of 4.06 grams of Pu and 2.25 mg of Am in a Brine A. The pcH for LS-26 ranged from a pcH of 7.5 to 8.4 with an average pcH around 8.0 The Pu concentration started at 42.9 ppb and in creased to 3996 after one year of testing. The Pu and Am concentration increased rapidly to 70,826 ppb on 12/02/96 and a sample was analyzed and found to contain 63,413 ppb Pu and Pu (VI) was identified on the 03/24/97 sample. Pu (VI) persisted for about 1 ½ years till 11/02/98 when the total Pu concentration dropped to 5642 ppb. The upward trend that occurred was attributed to the presence of soluble Pu (VI). The eventual downward trend in concentration is attributed to precipitation of Pu (VI) or reduction of Pu (VI) to Pu (IV) and subsequent precipitation of Pu (IV) as a hydrated PuO_2 or Pu hydroxide. According to the results of experiments conducted at LANL by Runde and VanPelt, Pu (VI) can be reduced or precipitated by peroxide within 18 months in Brine A at pH 7-10. Also, peroxide generated by alpha radiolysis that exceeds a few ppm will result in precipitation of Pu as a Pu (VI) hydroxide or a reduced form of Pu hydroxide. The stability or instability of Pu (VI) in the presence of peroxide or hypochlorite in acid, neutral and basic solutions of 5m NaCl Brine A and Castile Brine is summarized below.

Table 1. Study of Peroxide and Hypochlorite in Brine Solutions

Brine A	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Stable > 18 months	Stable > 18 months
7 – 8	Stable > 3 days but reduced at 18 months	Stable > 3 days but < 18 months; white precipitate formed
8 – 10	Stable > 3 days but reduced by 18 months	Slow-partial reduction up to > 18 months; white precipitate formed

Castile Brine	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Very stable > 18 months	Stable > 18 months
7.0 – 7.5	Stable for 6 days and partially stable for 18 months	Stable > 18 months
7.5 – 8.0	Partial reduction to Pu (V) in 6 days	Stable > 18 months precipitate forms
9.0 – 10	Partial reduction on first day; mostly stable for > 18 months	Slow-partial reduction but mostly stable for > 18 months; precipitate forms

5 M NaCl	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
2 – 4	Pu (VI) to Pu (V) in < 7 days	Stable > 18 months
7 – 8	Pu (VI) reduced in < 7 days	Slow-partial reduction then stable for > 18 months
8 – 10	Pu (VI) reduced in < 7 days	Pu (VI) slowly-partially reduced and then stable for > 18 months

Because LS-26 was a Brine A experiment at a pcH of 7.6 to 8.1, Pu (VI) is shown to be unstable on a long-term basis in the presence of peroxide and hypochlorite with the formation of white precipitate at neutral and basic pH. Pu (VI) is more stable in basic pcH than neutral and LS-26 may have been on the verge of being basic enough to be stable. LS-28 was on the acid side of neutral where Pu (VI) is much more stable in Brine A with both hypochlorite and peroxide.

- There were several liter-scale tests that showed a cemented mass at the bottom of the test container. The cemented solid was very hard and resembled Sorel Cement (magnesium oxychloride). None of the Portland Cement or Envirostone tests had the cemented solid, but at least 7 Pyrochemical Salt tests had the cemented solid at the bottom of the test container as determined by visual examination of the test containers. The cemented mass was very hard and could not be penetrated with a sharp screwdriver. The hardened cement would have trapped actinides that also precipitated with the components of the Sorel Cement and would not be made available to the brine.

- Fe mesh was added to 30 liter-scale test containers and corrosion of the Fe wire strands was evident in LS-19, 22, 23 and 24, four Envirostone tests with a pcH range of 6.8 to 8.2. The Fe mesh was irretrievably embedded in hard cement in three Pyrochemical Salt test containers, LS-32, 34 and 36. **The Fe mesh in all test containers had a hard black coating that protected the Fe strands from corroding in both Brine A and Castile Brine.**

- Strontium present in STTP brines because of addition as part of the ingredients or as an impurity in Ca and Mg added to make Brine A and Castile Brine was a key carrier of Pu in Portland Cement, Envirostone, and Pyrochemical Salt tests, but showed no correlation in drum-scale tests. This conclusion was established by observing the correlation of Sr, S, and Pu in the 5 micron, 1.2 micron, and < 10 nm filters with a Wavelength Dispersive X-ray Fluorescence technique. The correlation between Pu and $SrSO_4$ was especially noted in the Pyrochemical Salt tests. Fe as a precipitate or colloid was essentially not present in the Pyrochemical Salt tests and did not have a correlation with Pu filtered out on the filters. $SrSO_4$ is expected to be an efficient carrier of Pu because $BaSO_4$ is a classic method of scavenging and carrying Pu in aqueous systems. $SrSO_4$ could be a most important compound for entrainment (not precipitation) of Pu in certain wastes within the WIPP. Of course, Sr would have to be present in the WIPP salt formations.

II. Applicability of STTP; Chemical Actinide Transport in the WIPP

The primary concern of actinides in the WIPP is the concentration and transport of the soluble or colloidal form actinides in the wastes emplaced in the WIPP Disposal Rooms by any mechanism or process that results in concentrations of actinides in the accessible environment or outside the administrative boundaries of the WIPP. Probably the two primary mechanisms or processes of transporting actinides are by chemical or physical means. Establishing the possibilities of physical transport of actinides in the WIPP was beyond the scope of the STTP. However, establishing the dynamics of actinide transport by chemical means, namely, as soluble actinide species or colloids, was considered to be within the scope of the STTP. Three conditions that could be present in the WIPP after waste has been placed in the WIPP Disposal Rooms could be characterized as follows. The condition of WIPP disposal rooms:

1) could be essentially dry or free of brine pockets;
2) could be partially brine loaded or contain enough free brine to moisten the waste; or
3) could be significantly brine loaded so the waste would be partially or completely immersed in brine.

The most conservative condition would be the third condition of partial or complete immersion because this would require future human intrusion scenarios or a geologic upheaval that would change the characteristics of the entire area.

The first condition would result in a condition of no chemical transport because a chemical carrier that could transport soluble chemical species or colloids from the repository would not exist.

The second condition would be similar to the first because there would be insufficient liquid pressure or driving force to sustain a continuous or semi-continuous flow of brine carrier and therefore soluble actinides or colloid bearing actinides out of the repository.

The third condition, which has a rather low probability, presents the possibility of solubilizing actinides within the waste by free flow brine and transporting the soluble or colloidal species to the accessible environment. It was this condition for which the STTP was designed to provide experimental information, according to an established technical requirements document and test plan. The experiment was to use only actual homogeneous and heterogeneous waste forms. The experiments were to be conducted with brine that was similar to the brine found in the Salado Formation (Brine A) and also brine found in the Castile Formation (Castile Brine). The 36 non-pressurized homogeneous waste experiments were conducted in 3 liter vessels, while the 15 heterogeneous waste experiments were conducted in 246 liter (65 gallon) vessels. Six tests were pressurized to 60 bars with CO_2 and contained in 2-liter vessels. The experiments were conducted in sets of three (2 Brine A and 1 Castile Brine). Several chemical additives were added to different tests to gain technical information on the influence of certain chemicals that might be found on actual waste to solubilize, transport, or alternatively to immobilize otherwise transportable or mobile actinide species. The three major transuranic content codes (TRUCON codes) used for the homogeneous wastes were TRUCON 111-211 as Portland Cement tests, TRUCON 112/212, 113/213, 114/214, and 126/226 as Envirostone tests, and TRUCON 124/224 as Pyrochemical Salt tests. All tests were maintained at 30 °C, the approximate temperature in the WIPP, for the entire test period of 5-6 years.

Significant Transport Parameters

Solubility of Pu and Am in TRU waste

The transport of mobile species of Pu and Am require that the two actinides are solubilized to some extent in the brine phase to be available for transport as a soluble or colloidal species. The solubility of the Pu and Am in brine under WIPP relevant conditions can be governed by the form of the Pu. STTP data has shown that soluble Am concentrations followed or tracked the soluble Pu concentrations in essentially every test that had higher Pu concentrations. In six liter-scale tests (LS-10, 11, 12, 37, 38, and 39) with Am-241 added in a soluble form, the Am-241 precipitated immediately after addition and did not resolubilize at any time during the test period. The concentration of Am followed the increase and decrease of Pu in all tests including the six tests pressurized with 60 bars of CO_2. This indicates that as Pu present in the actual waste solubilized, Am was solubilized by the same mechanism from the same matrix. The forms of Pu that can be present in the TRU waste shipped to the WIPP can be categorized as follows:

1) Pu metal – This form is not expected to be in most TRU waste and has probably oxidized to a non-fired Pu oxide. Pu, as a finely divided metal or non-fired Pu oxide, is solubilized quite easily by strong anions or chelators.

2) Pu salt – Pu present as a salt such as chloride, nitrate, sulfate, or fluoride is soluble to a large extent based on the anion or chelating species in the brine. This form of Pu is not expected to represent a significant portion of the waste streams except for select canisters. Pyrochemical salt wastes could have significant quantities of Pu salts.

3) Pu oxide (non-fired) – This is the form of Pu that can be a major source of contamination in both homogeneous and heterogeneous TRU waste streams. The first three Pu waste forms are the most likely to solubilize in WIPP type brines. This waste stream consists of Pu that has oxidized at ambient temperatures or less than 200 °C.

4) Pu oxide (medium-fired) – This is a waste form that is generated by oxidizing Pu of > 400 °C which can be the primary contaminant in both homogeneous and heterogeneous wastes. This waste form will not dissolve in a slightly acidic, neutral, or basic medium or with strong chelators. This form of Pu is refractory and generally requires a strong anion such as fluoride in a > 1 Molar acid heated to greater than 40 °C for an extended period of time (several hours). Based on the STTP results, the only waste that showed significant solubilization of Pu was certain experiments with pyrochemical salt wastes and the heterogeneous waste stream with added chelators.

5) Pu oxide (high fired) – This waste stream is a specialized form of highly refractory Pu oxide that is difficult to dissolve even in concentrated nitric acid with fluoride. This form of Pu is not soluble in WIPP type brine under WIPP conditions.

The forms of Pu that can be solubilized in WIPP brines under WIPP conditions will probably precipitate as Pu hydrate or polymer that reduce the concentrations of soluble Pu to much lower levels. However, once solubilized the Pu can remain solubilized in an anionic, chelated, or oxidized form. Certain soluble species of Pu can be present as or associated with colloids that are readily transportable. The conditions and chemistry of the brine must be favorable for colloids to form rather than non-transportable precipitates. Soluble Pu species that precipitate are generally no longer available to be metathesized to a transportable form. The enhancement of transportability of actinides by major influencing variables has been summarized for the major waste streams tested in the STTP in Table I. A review of the solubilization level is categorized on a relative basis as follows:

Designation	Solubilization Level
Very Low (VL)	< 50 ppb
Low (L)	50-500 ppb
Medium (M)	500-5000 ppb
High (H)	5000-100,000 ppb
Very High (VH)	>100,000 ppb

The categorization and designation of total colloid particles per liter of brine is as follows:

Designation	Total Particles/Liter
VL	10^{9}
L	10^{9}-10^{10}
M	10^{10}-10^{11}
H	10^{11}-10^{12}
VH	10^{12}-10^{13}

The two above designation will be used in the following data tables for liter-scale and drum-scale tests according to the test matrix.

Table 2. STTP Liter-Scale test Matrix

	LS-01	LS-02	LS-03		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic process sludge	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1

	LS-04	LS-05	LS-06		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge with CO_2	
Brine	A	A	CASTILE	Portland Cement	10:1 / 3:1 / 2:1

Continued on next page

	LS-07	LS-08	LS-09		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge without Fe	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	LS-10	LS-11	LS-12		
TRUCON	111/211	111/211	111/211	Solidified aqueous inorganic sludge w/o Fe; Am-241 added	
Brine	A	A	CASTILE	Portland Cement	10:1 / 2:1 / 2:1
	LS-13	LS-14	LS-15		
TRUCON	112/212	112/212	112/212	Absorbed organic liquids	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-16	LS-17	LS-18		
TRUCON	113/213	113/213	113/213	Absorbed aqueous laboratory waste	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-19	LS-20	LS-21		
TRUCON	114/214	114/214	114/214	Cemented inorganic particles	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-22	LS-23	LS-24		
TRUCON	126/226	126/226	126/226	Cemented organic sludge	
Brine	A	A	CASTILE	Envirostone	2:1 / 2:1 / 2:1
	LS-25	LS-26	LS-27		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	LS-28	LS-29	LS-30		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts with CO_2	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	LS-31	LS-32	LS-33		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts with brine – equilibrated bentonite	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1
	LS-34	LS-35	LS-36		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts with $Ca(OH)_2$ and chelators	
Brine	A	A	CASTILE		3:1 / 3:1 / 3:1
	LS-37	LS-38	LS-39		
TRUCON	124/224	124/224	124/224	Pyrochemical Salts without Fe; Am-241 added	
Brine	A	A	CASTILE		2:1 / 2:1 / 2:1

Table 3. STTP Drum-Scale Test Matrix

	DS-01	DS-02	DS-03	
TRUCON	116/216	116/216	116/216	Combustibles
Brine	A	A	CASTILE	
Waste (lbs)	43	59.1	47.2	
Total (lbs)	740.2	728.4	720	

	DS-04	DS-05	DS-06	
TRUCON	116/216	116/216	116/216	Combustibles and brine – equilibrated bentonite
Brine	A	A	CASTILE	
Waste (lbs)	72.6	85.5	76.6	
Total (lbs)	765	723	746	

	DS-07	DS-08	DS-09	
TRUCON	116/216	116/216	116/216	Combustibles with chelators
Brine	A	A	CASTILE	
Waste (lbs)	122.6	51.55	56.65	
Total (lbs)	783.4	726	720.6	

	DS-10	DS-11	DS-12	
TRUCON	116/216	116/216	116/216	Combustibles and sodium nitrate/phosphates
Brine	A	A	CASTILE	
Waste (lbs)	66.4	48.6	66.4	
Total (lbs)	728	754.6	717	

	DS-13	DS-14	DS-15	
TRUCON	117/217	117/217	117/217	Metals
Brine	A	A	CASTILE	
Waste (lbs)	171.4	136.8	162.2	
Total (lbs)	867.4	846.2	860	

Table 4. Factors That Influence Actinide Transport
PORTLAND CEMENT

	Liter-Scale ID								
Soluble Pu Concentration Level	*1*	*2*	*3*	*7*	*8*	*9*	*10*	*11*	*12*
VL	X	X	X	X	X	X	X	X	X
L									
MED									
H									
VH									
Pu Solubilization Basis									
Added Chelators	0	0	0	0	0	0	0	0	0
Radiolytic Oxidants	0	0	0	0	0	0	X	X	X
Unknown	-	-	-	-	-	-	-	-	-
*Colloid Formation**									
Pu	0	0	1	0	0	0	0	0	0
Fe	0	11	15	0	2	7	0	7	7
Sr	4	13	15	3	15	12	2	15	8
Total Particles/Liter	L	M	M	L	L	L	L	L	L

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

No Fe mesh added to LS-7, 8, 9, 10, 11, 12
No Nd added to LS-10, 11, 12
^{241}Am added to LS-10, 11, 12

Table 5. Factors That Influence Actinide Transport
ENVIROSTONE

	Liter-Scale ID											
Soluble Pu Concentration Level	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*22*	*23*	*24*
VL					X		X	X	X	X	X	X
L	X	X	X			X						
MED				X								
H												
VH												
Pu Solubilization Basis												
Added Chelators	0	0	0	0	0	0	0	0	0	0	0	0
Radiolytic Oxidants	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	-	-	-	X	-	-	-	-	-	-	-	-
Added Organics	X	X	X	0	0	0	0	0	0	0	0	0
High Nitrate					X		X	X	X	X	X	X
*Colloid Formation**												
Pu	14	11	0	6	14	12	6	0	0	6	6	5
Fe	17	14	5	10	16	8	9	16	3	15	12	13
Sr	2	4	1	8	7	10	7	7	2	16	9	13
Total Particles/Liter	VH	VH	VH	L	L	L	L	M	L	M	L	L

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

Fe mesh added to all tests
Organic solvents added to LS-13, 14, 15

Table 6. Factors that Influence Actinide Transport
PYROCHEMICAL SALT

	Liter-Scale ID											
Soluble Pu Concentration Level	*25*	*26*	*27*	*31*	*32*	*33*	*34*	*35*	*36*	*37*	*38*	*39*
VL							X				X	
L	X			X	X	X				X		
MED								X				X
H		X							X			
VH			X									
Pu Solubilization Basis												
Added Chelators	0	0	0	0	0	0	X	X	X	0	0	0
Radiolytic Oxidants		X							X	X	X	X
Unknown		X	X									
DOR (X) or OS (0)	X	X	X	0	0	0	0	X	X	X	0	0
*Colloid Formation**												
Pu	9	17	16	8	10	14	11	2	16	8	0	13
Fe	0	0	0	3	5	6	0	0	2	6	1	0
Sr	15	13	16	0	4	3	0	3	14	15	2	5
Total Particles/Liter	M	H	H	L	L	L	L	M	M	L	L	L

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

Bentonite added to LS-31, 32, 33
Chelators and Calcium hydroxide added to LS-34, 35, 36
^{241}Am added to LS-37, 38, 39
No Fe or Nd added to LS-37, 38, 39
Pu (V) and (VI) identified in LS-26, 28, 36

Table 7. Factors that Influence Actinide Transport
PRESSURIZED TESTS

	Liter-Scale ID					
	Portland Cement			*Pyrochemical Salt*		
Soluble Pu Concentration Level	*4*	*5*	*6*	*28*	*29*	*30*
VL						
L	X	X	X			
MED			X			X
H					X	
VH				X		
Pu Solubilization Basis						
Added CO_2	X	X	X	X	X	X
Radiolytic Oxidants				X		
Unknown				X	X	
MgO				X		
*Colloid Formation**						
Pu	0	0	0	3	3	3
Fe	1	1	0	1	2	1
Sr	0	0	0	3	0	0
Total Particles/Liter	M	M	L	VH	H	M

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

Pu (VI) identified in LS-28
MgO added to LS-28

Table 8. Factors That Influence Actinide Transport
DRUM-SCALE TESTS (D1-9)

	Drum-Scale ID								
Soluble Pu Concentration Level	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
VL	X	X	X	X	X	X			
L									
MED							X	X	X
H									
VH									
Pu Solubilization Basis									
Added Bentonite				X	X	X			
Added Chelators							X	X	X
NO_3 Decrease	X	O	X	X	X	O	O	O	O
*Colloid Formation**									
Pu	0	0	0	1	0	1	13	13	3
Fe	15H	17H	18H	15H	19H	19H	12L	14	11L
Sr	0	0	0	0	0	2	0	0	1
Total Particles/Liter	L	M	L	M	M	L	M	H	H

* Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

10 kg of Bentonite (Brine equilibrated) added to DS-4 and DS-5
10 kg of Bentonite (non-equilibrated) added to DS-6
Chelators added to DS-7, 8, 9
$NaNO_3$ (159 g) and NaH_2PO_4 (258 g) added to DS-10, 11, 12

Table 9. Factors that Influence Actinide Transport
DRUM-SCALE TESTS (D10-15)

	Drum-Scale ID					
Soluble Pu Concentration Level	*10*	*11*	*12*	*13*	*14*	*15*
VL		X	X	X	X	X
L	X					
MED						
H						
VH						
Pu Solubilization Basis						
Added metals				X	X	X
Added $NaNO_3$ and NaH_2PO_4	X	X	X			
NO_3 decrease*	X*	X*	0			X*
*Colloid Formation***						
Pu	12L	14L	10L	1L	9L	1
Fe	20VH	23VH	18H	19MED	20MED	18MED
Sr	1	0	0	0	0	0
Total Particles/Liter	MED	MED	L	H	L	L

* NO_3 reduction rapid and complete

** Indicates the number of individual samples that contained either Pu, Fe, or Sr as identified by Wavelength Dispersive X-ray Fluorescence Spectroscopy on 5 micron, 1 micron, and 10 nm filter papers.

Notes:

$NaNO_3$ (159 g) and NaH_2PO_4 (258 g) added to DS-10, 11, 12
DS-13, 14, and 15 were massive metal tests

III. STTP Test Matrix

Liter-scale Tests

This sludge is described as Los Alamos 111A, concreted aqueous waste. This waste was a mixture of radioactive liquid waste from analytical operations in the CMR, process waste from TA-55, and industrial waste from throughout the Laboratory. It began as a corrosive and radioactive liquid waste that was neutralized essentially to a basic slurry with powdered $Ca(OH)_2$, ferric sulfate, and a flocculation aid. This treatment precipitated and carried the actinides and other soluble metal ions into a slurry. This slurry was solidified in 55-gallon drums with various portions of Portland Cement, vermiculite, and sodium silicate. The pH of the Portland Cement waste was driven by the calcium hydroxide concentration and is generally 9-11.

LS-1, 2, 3

Solidified Aqueous Inorganic Process Sludge, TRUCON 111/211, (LS 1-3)

These experiments would establish the effectiveness of Portland Cement to retain actinides precipitated by addition of ferric sulfate and $Ca(OH)_2$ and a flocculation aid. The comminuted Portland Cement immersed in Brine A and Castile Brine should have a different basicity in the two brines; pcH 8-10 in Brine A and pcH 10-13 in Castile. The results from this experiment will allow comparison between a Brine A test with a brine to solid ration of 10:1 and 2:1. There was an addition of Fe mesh, Th, U, Np and Nd. These experiments should establish a reference background of Eh from basic Portland Cement tests.

LS-4, 5, 6

Solidified Aqueous Inorganic Process Sludge, TRUCON 11/211 with CO_2 at 60 Bar (LS 4-6)

The composition of these sludges is similar to LS 1-3. These tests will be conducted with a headspace pressure of about 60 atmospheres (870 psig) with CO_2. The pressurized test containers will be sampled for brine at pressure and filtered at pressure. It is reasonable to assume that the actinide solubilities, especially U, could be affected by carbonate complexation and decreased pcH. The increased carbonate complexation might solubilize the ferric sulfate, which would increase the concentration of soluble iron and provide more chemical sites for entrainment of $Fe(OH)_3$. The results from these tests could be directly compared with LS 1-3.

LS-7, 8, 9

Solidified Aqueous Inorganic Process Sludge, w/o Fe, TRUCON 111/211, (LS 7-9)

Corroding steel in the disposal rooms provides a possible sink for actinides through sorption. However, CO_2 in the rooms might passivate steel by forming a surface layer of siderite ($FeCO_3$), which would render much less iron oxide available for actinide sorption. These experiments test the effect the removal of iron oxides from the system, elimination sorption of actinides by the Fe oxide phases. These experiments would be similar to LS 1-3 but without added Fe mesh and could be directly compared with LS 1-3 to determine the effect of Fe under these conditions.

LS-10, 11, 12

Solidified Aqueous Inorganic Process Sludge w/o Fe, TRUCON 111/211; ^{241}Am added (LS 10-12)

In addition to providing a source of sorbants, corrosion of steel also lowers brine Eh in its vicinity. Without steel (or other active metals), the oxidizing effects of radiolysis may dominate the Eh of the system. These experiments measure actinide concentration, and possibly speciation, under the most toxic conditions reasonably attainable in the rooms. The addition of about 75 mg (257 mCi) of Am-241 to each test container would be expected to increase radiolytic decomposition of brine to yield greater concentrations of peroxide and hypochlorite. The basicity of the Portland Cement is expected to precipitate the actinides including the added Am-241 and higher Eh may solubilize some of the precipitated actinides. The extent of radiolysis may be determined by the rate of hydrogen generation and eventual accumulation in the headspace.

Envirostone Liter-scale Tests

Envirostone is the commercial name of Envirostone gypsum cement and is a white solidification agent that was used to solidify evaporator bottoms and other sludge wastes that could contain both inorganic and organic solvents or salts. The composition of Envirostone is 80-90% calcium sulfate, 15-20% melamine-formaldehyde resin and 0-0.1% ammonium chloride. Envirostone is not as basic as Portland Cement and the results of these experiments should provide information about the effect of a high calcium and sulfate matrix with mild basicity on actinide chemistry.

LS-13, 14, 15

Absorbed Organic Liquids, Envirostone, TRUCON 112/212 (LS 13-15)

The experiments with Envirostone have added organic solvents and residues and will determine if high concentrations of organic solvents and reagents in the brine significantly promote dissolution or suspension of actinides. If the waste contains exclusively solvent residues, their effect will be minimal. However, if chelating agents, extractants, or detergents are present, their effect on actinide concentration could be significant. These experiments will also establish the effect of colloidal suspensions on actinide concentrations.

LS-16, 17, 18

Absorbed Aqueous Laboratory Waste in Envirostone, TRUCON 113/213 (LS 16-18)

These are laboratory wastes that have been neutralized or made slightly basic and solidified with Envirostone. The high salt content and possible high organic content including chelating agents may increase actinide solubility. The possible high nitrate content in these wastes should provide information on the effect of radiolytic degradation of nitrates.

LS-19, 20, 21

Cemented Inorganic Particulates (Sludge) in Envirostone, TRUCON 114/214 (LS 19-21)

This waste form is process residue from evaporator bottoms and other discardable solutions, process leach solids, ash, filter cakes, salts, metal oxides, fines, etc. These tests will determine the effect of increased pcH and particulate from process waste streams. Similar to LS 16-18, there may be high concentrations of nitrate in these experiments.

LS-22, 23, 24

Cemented Organic Sludge Solidified with Envirostone, TRUCON 126/226 (LS 22-24)

These wastes are process residues from evaporator bottoms and other discardable solutions, process leached solids, ash, filter cakes, salts, metal oxides, fines, etc. This waste has been immobilized in Envirostone with a possible presence of chelators. These tests have the potential for high concentrations of nitrates.

Pyrochemical Salt Liter-scale Tests

The Pyrochemical Salt waste added to the STTP test containers was obtained directly from TA-55 (the technical area where LANL's nuclear materials are handled) waste drums. The Pyrochemical salt waste streams were from two major operations, direct oxide reduction and oxygen sparging of electrorefined plutonium metal and salts. The Pyrochemical salt waste contained high-fired MgO crucibles entrained with salts used for direct oxide reduction. For the STTP, the crucibles and any salt lumps were comminuted, including other salt flux ingredients. It was expected that the Pyrochemical salt waste would be high in sodium chloride, potassium chloride, calcium chloride, magnesium oxide, magnesium chloride, fluorides, and some residual unreacted calcium metal and calcium oxide.

The Pyrochemical salt process was initiated to directly reduce PuO_2 to Pu metal by heating to ~800 °C with Ca metal in a MgO – Y_2O_3 crucible containing $CaCl_2$ or some other salt matrix. The direct oxide reduction was followed by an electrorefining process including oxygen sparging to eliminate Na or K developed at the electrorefining cathode. The Pyrochemical salts used for STTP contained higher concentrations of ^{239}Pu and ^{241}Am relative to Envirostone and Portland cement tests.

LS-25, 26, 27

Pyrochemical Salt Wastes, TRUCON 124/224 (LS 25-27)

The Pyrochemical waste forms used for the STTP tests were the wastes developed from the Direct-Oxide Reduction (DOR) process or the Oxygen Sparging process and included pieces of MgO crucibles that had been ground up.

The waste from the DOR process could contain $CaCl_2$, CaF_2, Ca metal, CaO, and magnesia (MgO) from the MgO crucible. The Pyrochemical salt wastes from DOR and O_2 sparging processes generally contain relatively higher levels of Pu and Am which could result in increased levels of brine radiolysis and perhaps more oxic conditions from oxidizing products of radiolysis. If unreacted Ca remains in the waste or if higher concentrations of CaO or $Ca(OH)_2$ are in the waste, the brine become more basic upon dissolution of the Ca or Ca compounds. LS-25, 26, and 27 were Pyrochemical salts from the DOR process.

LS-28, 29, 30

Pyrochemical Salt Wastes with Added CO_2, TRUCON 124/224 (LS 28-30)

This test has Pyrochemical salt wastes from the DOR process as discussed in "Pyrochemical Salt Wastes" just above, but with added CO_2 pressure at about 60 bars (~870 psig). Any basicity from the Ca compounds should be neutralized by the CO_2 headspace. The bicarbonate and carbonates formed from the CO_2 may increase the solubility of actinides, especially uranium, but may also increase solubility of iron.

LS-31, 32, 33

Pyrochemical Salt Wastes with Brine-Equilibrated Bentonite, TRUCON 124/224 (LS 31-33)

These tests contain wastes from the oxygen-sparging process with added brine-equilibrated bentonite. The O_2 sparging process resulted in wastes as discussed in the "Pyrochemical Salt Wastes with Added CO_2" section above but also contained oxidized salts (Ca, Na, K) generated by the electrorefining process. The results from these tests could indicate the effectiveness of brine-equilibrated bentonite, a potential backfill material, in removing actinides from solution by adsorption and indicate whether the bentonite itself presents a significant source of colloids. These tests could also determine the effectiveness of bentonite as an actinide sorbent in the presence of high concentrations of divalent ions (particularly Ca^{2+}), which compete with the actinides for sorption sites on the clay particles.

LS-34, 35, 36

Pyrochemical Salt Wastes with $Ca(OH_2)$ & Chelators, TRUCON 124/224 (LS 34-36)

This set of tests consists of LS-34 with Pyrochemical salt wastes from the O_2 sparging process and LS-35 and 36 with wastes from the DOR process. All three tests have added $Ca(OH)_2$ to increase the basicity of the brine and to determine the effect of the basic solution on generated CO_2 and increased carbonate production. Major chelators have been added to the three test containers. These tests should indicate the solubilizing effect of major chelators on actinides in a basic solution. The results of these experiments can be compared to the results of the drum-scale tests with added chelators, DS 7-9.

LS-37, 38, 39

Pyrochemical Salt Wastes with added ^{241}Am, TRUCON 124/224 (LS 37-39)

This set of tests consists of LS-37 with Pyrochemical salt wastes from the DOR process and LS-38 and 39 with wastes from the O_2 sparging process. All three tests have added ^{241}Am, which may render the system more oxic and provide an indication of Pu-238 effects on brine chemistry. The oxidizing products of radiolysis such as O_2, H_2O_2, or OCl^- if they are stable in the high brine solutions may enhance corrosion of iron that could in turn actually provide a reducing effect on the system. These tests may provide an indication of the redox chemistry with increased radiolysis. Fe mesh was excluded from these tests.

The test matrices for drum- and liter-scale test containers include all combinations of solubility-influencing variables judged sufficiently different to require testing. The two test matrices were developed by collaborative effort between SNL and LANL.

IV. Drum-Scale Test Waste and Pu Content

The waste loaded into the drum-scale tests were Transuranic Content Code 116 (Heterogeneous Combustible or debris type waste) and 117 (Massive metal wastes). The criteria for the drums was that the waste must contain greater than 5 grams of Pu in a 55-gal drum. Also, the entire contents of a single 55-gal waste drum was to be loaded into each STTP all-titanium drum-scale test which had a volume of ~65 gal. There was to be no mixing of waste from different 55-gal waste drums. The waste that was selected for each test drum to meet the type of waste and the total Pu content is given below.

Table 10. STTP Drum-Scale Pu Contents

Drum #	LA No.	TRUCON Code	Pu-52 (gm)
DS-1	54546	116	7.10
DS-2	52896	116	8.15
DS-3	54129	116	8.19
DS-4	52114	116	9.11
DS-5	53565	116	9.38
DS-6	52410	116	10.78
DS-7	52047	116	11.60
DS-8	54409	116	14.94
DS-9	54174	116	16.25
DS-10	52878	116	16.44
DS-11	53217	116	16.45
DS-12	53211	116	16.70
DS-13	54371	117	12.74
DS-14	52109	117	8.19
DS-15	54871	117	16.22
		Total	182.24

Drum-Scale Tests

DS-1, D2, D3

Combustibles, TRUCON 116/216 (DS 1-3)

Of significance in these drum-scale tests are the effects of cellulose degradation on actinide concentration. Aerobic oxidation and fermentation will lower system Eh. Denitrification may produce complexing agents such as citrate and lactate. Complexing agents from decontamination activities may already be present in the waste and will make up the bulk of complexing agents withdrawn in the leachate at early times.

DS-4, D5, D6

Combustibles with Bentonite Backfill (DS 4-6)

The results from these experiments can be compared directly with those from tests, DS 1-3. These results will indicate the effectiveness of brine equilibrated bentonite, a reference backfill, in removing actinides from solution by adsorption and indicate whether the bentonite itself presents a significant source of colloids.

DS-7, 8, 9

Combustibles with Added Chelation Agents (DS 7-9)

Although fermentation and denitrification of cellulose are predicted to yield complexing agents, this condition conceivably may not occur during the time frame of the STTP. These experiments test how actinide solubility is affected by a system containing both “naturally occurring” ligands (such as lactate) and ligands introduced as part of the waste stream (such as EDTA). As it is not reasonable to assay drums for chelating agents as part of waste selection, these drums must be prepared by spiking the ordinary combustible waste with the major chelators described in “Addition of Chelators.”

These tests will follow ligand concentration over time to observe if microbial activity can act as a sink or source of complexing agents.

DS-10, 11, 12

Combustibles with Added Nitrate and Phosphate, TRUCON 116/216 and 111/211 (DS 10-12)

In denitrification, cellulose or its fermentation products are oxidized by bacteria capable of using nitrate as an electron acceptor. The NO_3 is in turn reduced to N_2 or NH_3. Denitrifying bacteria can oxidize organic acids to α-hydroxy acids, which are effective complexing agents. The presence of nitrate in process sludges may be significant in promoting this process in combustible waste.

In these experiments, nutrients in the form of sodium nitrate and sodium phosphate are added to the test containers to study their effect on microbial activity. $NaNO_3$ and NaH_2PO_4 was added at the 0.01M level for the 210 liter volume, 180 and 300 grams, respectively.

DS-13, 14, 15

Metals, TRUCON 117/217 (DS 13-15)

Metals capable of corroding under anoxic conditions can reduce system *E*h below the stability limit of water, possibly stabilizing Pu(III) in solution. Both iron (from mild steel) and aluminum will anoxically corrode in brines. Less active metals such as copper and lead may also corrode if H_2S (from sulfate reduction) is present. A protective polyethylene liner was added to these drums to prevent damage to the test container walls during rotation.

V. Commentary on STTP Liter-Scale Tests

PORTLAND CEMENT

The soluble actinides and Pu in the Portland Cement tests were all categorized as “very low” for all non-pressurized tests. Am-241 was added to LS-10, 11, and 12, and no apparent solubilization occurred as a result of enhanced oxidation from radiolytically produced oxidants. Nitrate reduction occurred in all Portland Cement tests. Calcium concentrations were very high for all Brine A tests and very low for Castile Brine tests. Sulfate was very high for Castile Brine tests and relatively low for Brine A tests. There were essentially no Pu bearing colloids in any Portland Cement tests although there were Fe and Sr bearing colloids without actinides. The concentration of total particles per liter was categorized as low (7 tests) and medium (2 tests), but the particles did not contain actinides.

Overall Comment: There was no analytical evidence that there was significant actinide solubilization or production of mobile colloids in Portland Cement tests.

ENVIROSTONE

The analytical results from Envirostone show the Pu concentrations were categorized as “very low” (7 tests), “low” (4 tests), and “medium” (1 test; LS-16). LS-16 is perhaps the only test that was on a trend of actinide increase (except for U which was on a definite decrease, (14583 ppb to 182 ppb) with Pu increasing from 208 to 1187 ppb. The Pu concentration of 1187 ppb in LS-16, is the highest of the Envirostone tests but can be considered to be relatively low overall. LS-13, 14, and 15 had added organic solvents that had increased total particles per liter that did contain a significant number of Pu bearing colloids, but these were at relatively low levels. Most of the colloids were Fe bearing, and some were associated with Sr. In general, the Envirostone Brine A tests had 1100-2700 ppm of soluble Ca while the Castile Brine test had 600-780 ppm Ca. The sulfate concentrations of the Brine A tests were 4000-9000 ppm, while the Castile Brine tests were 12000-17000 ppm. The nitrate concentrations all decreased during the test period. And certain tests such as LS-13, 14, and 18 showed very large decreases so that the nitrates were essentially totally destroyed. The destruction of nitrate, an oxidant, to nitrites N_2O and N_2 by chemical, microbial, or radiolytic degradation is significant because the intermediate species are reductants that will maintain a reducing environment during the nitrate destruction process. Nitrous oxide, a gaseous product from the radiolytic degradation of nitrate is very soluble in brine and will promote a reducing condition during the test period. The Envirostone tests were noted for the high starting concentrations of U that in all cases decreased to very low levels at the end of the test period. Np was initially high in LS-15 (7753 ppb), LS-18 (1557 ppb), and LS-21 (5311 ppb), but these three tests ended up at <100 ppb.

Overall Comment: There was no analytical evidence that Envirostone tests resulted in significant solubilization of Pu and other actinides. Except for LS-17 and 18, there was minimal production of Pu bearing colloids, and even LS-17 and 18 had sporadic concentrations on the filter papers. Fe was a very prevalent colloid and Sr was present in most tests for colloids.

PYROCHEMICAL SALTS

The tests with pyrochemical salts had the highest content and concentration of Pu and Am in both what was in the waste and what was solubilized. The concentrations of soluble Pu in the non-pressurized tests were categorized as follows:

Very Low	2 tests (LS-34 and 38)
Low	4 tests (LS-25, 31, 33, and 37)
Medium	3 tests (LS-32, 35, and 39)
High	2 tests (LS-26 and 36)
Very High	1 test (LS-27)

To understand the chemistry that occurred in the pyrochemical salt tests, it is necessary to recognize the difference in the two major pyrochemical salt waste forms, namely, Direct Oxide Reduction (DOR) and Oxygen Sparging (OS).

The waste from the DOR process was obtained from a process that mixed and heated PuO_2 in a salt flux of $CaCl_2$, CaO, and Ca metal in a ceramic crucible made of refractory MgO and 3% Y_2O_3. This mixture was heated up to about 840 °C to convert the PuO_2 to Pu metal. The Pu metal button was removed from the mixture, and for STTP, the crucible, $CaCl_2$, and residual Ca metal was comminuted and became DOR pyrochemical salt waste in LS-25, 26, 27, 28, 29, 30, 35, 36, and 37. The key to this waste is that the $CaCl_2$ is very high leading to a high concentration of Ca and chloride ions.

The waste from the OS process was obtained during the process of purifying impure Pu in a heated NaCl-KCl salt flux by electrodepositing the Pu on the cathode electrode of the electro-refiner. After a pure Pu metal product was electro-deposited on the cathode, some K and Na from the NaCl-KCl mixture were also reduced to metallic Na and K on the cathode. This mixture was sparged with oxygen to oxidize the K and Na metal to the oxide and eventually converted back to the chloride. After removal of the Pu metal, the remainder of the salts became the OS waste stream that was comminuted and used for STTP tests. Some OS experiments also contained $CaCl_2$ from O_2 sparging experiments that had $CaCl_2$ as part of the salt flux.

The pyrochemical salt tests with DOR wastes were very high in $CaCl_2$ and may have had some residual Ca metal or CaO. The OS wastes were very high in KCl and NaCl and may have had some Ca as $CaCl_2$ or CaO.

As part of the preparation for the tests with pyrochemical salt wastes, Brine A and Castile Brine were added to the comminuted waste forms. Brine A is principally $MgCl_2$ but also contains lower quantities of sulfate as sodium sulfate, bromide as NaBr, and Ca chloride and Sr chloride as salts. Castile Brine is primarily NaCl but there is a high concentration of sulfate as $NaSO_4$.

When DOR experiments with very high levels of $CaCl_2$ were mixed with Brine A and Castile Brine, the very high Ca concentrations resulted in precipitation of most of the sulfate as $CaSO_4$ and other Group II cations, such as Ba and Sr sulfates. This would result in DOR pyrochemical salt tests with low sulfate concentrations and very high Ca and chloride concentrations. The concentrations of nitrate in pyrochemical salts were very low for all tests because this is not a part of the waste stream. Also, if any nitrate had been resent, it would be destroyed by heating with Na, K, or $CaCl_2$. The sulfate concentrations in the OS tests that were not so high in $CaCl_2$ except for LS-34 and 38 were as high as expected based on the relative sulfate concentrations in Brine A and Castile Brine. So basically, sulfate was at low concentrations for DOR salt tests and at higher levels of OS salt tests.

Pu sulfate ($Pu(SO_4)_2$) is a strong Pu complex that tends to stabilize Pu in the Pu (IV) oxidation state especially, in a basic medium. However, the absence or very low concentration of sulfate in the DOR tests reduced the potential for stabilization of Pu as Pu (IV) sulfate in these tests. Oxidized forms of Pu as Pu (V) and (VI) were identified in LS-26, 27, 28 and 36. All four of these tests were DOR salt tests with very high calcium and low sulfate concentrations. None of the OS wastes showed oxidized Pu species. Any low concentration of nitrate was quickly destroyed as a source of radiolytic nitrite and N_2O which are both reductants. The very high chloride content in the DOR tests enhances the possibility of oxidation to the Pu (V) and (VI) states in the absence of a stabilizing anion. The presence of Pu bearing colloids or microprecipitates was a characteristic of essentially all the pyrochemical salt tests. The filters from DOR tests had high concentrations of Ca whereas the filters from OS tests had low concentrations of Ca. The filters from DOR tests were all high Pu bearing filters with Sr and sulfate associated with the Pu while filters from OS tests had lower Pu, Sr, and sulfate concentrations. The high concentration of all actinides in LS-27, a DOR experiment with Castile Brine, was surprising initially because no explanation was established for this test. LS-27 had a high Fe concentration (generally 100-200 ppm) and Pu (V) was identified in this test container. The pyrochemical salt tests were characterized by the absence of Fe in most of the filters even though the presence of soluble Fe in many tests was significant. The high radiolytic activity in the pyrochemical salt tests could have produced sufficient oxidants to oxidize the Fe^{2+} to the Fe^{3+} state which is much more insoluble and will not act as a reductant in the chemistry of soluble and insoluble Fe.

Liter-scale test number 27 was anomalous in that this test container had high concentrations of all actinides from the start of the experiment. This can be explained by the D&D observation that in LS-27 (and LS-26) there was no solidified or cemented mass and all the comminuted waste was available to all the brine throughout the test period. This was not the case in most pyrochemical salt tests. Soluble Fe was high in LS-27 but very low in LS-26 which had high levels of Pu (VI). Liter-scale tests LS-31, 32, and 33 were oxygen-sparging tests that had added bentonite that may have been the reason for the lower concentrations of Pu in these tests. LS-31 had a definite trend up from 1.4 ppb at the start to 275 ppb near the end of the test period. LS-32 started very low (3.9 ppb) and peaked at 697 ppb half-way through the test and then trended down to 156 ppb near the end of the test. Liter scale test LS-33 in Castile Brine started very low at 2.7 ppb and leveled off at about 135 ppb through the end of the test period. Liter-scale tests

LS-34, 35, and 36 contained added chelators and calcium hydroxide. LS-34 was an oxygen-sparging test while the other two tests with chelators and $Ca(OH)_2$ were Direct Oxide Reduction tests with very high levels of calcium (9000, 80000, and 80000 ppm, respectively). LS-34 and 35 had very high levels of Mg while LS-36 had very low levels of Mg. The high Ca and Mg in LS-34 and 35 appeared to mitigate the solubilizing effect of the chelators, but L36 had very high levels of solubilized Pu. The combination of low Mg content and very high levels of chloride allowed the chelators to be effective in solubilizing actinides in LS-36. The combination of high Ca, Mg, and chloride did not enhance solubilization of actinides by the chelators.

The addition of Am-241 to LS-37, 38, and 39 did not seem to enhance solubilization of Pu significantly.

Overall Comment: There were several unknown factors about the chemical and radiolytic behavior of the pyrochemical salt wastes including the presence of Pu (VI) in LS-26 and 28. However, a comprehensive examination of the test data including observations from the D&D process has led to explanations of why these tests acted as they did. It is now understandable why the Direct Oxide Reduction tests were the only tests that had oxidized forms of Pu and why the oxygen sparging tests did not. The overall impact of these tests experiments has shown that the presence of oxidized forms of Pu is limited to a very small percentage of wastes under very specific conditions that are rather unique. The lessons learned from the behavior and chemistry of DOR and OS pyrochemical waste forms can be extended to mitigate the oxidative potential of other high level wastes including high Pu-Am content oxide residues. The effect of chelators in LS-34 (OS and Brine A), LS-35 (DOR and Brine A), and LS-36 (DOR and Castile Brine) provides a diverse set of conditions to establish that LS-34 and 35 did not significantly solubilize Pu and other actinides whereas LS-36 (OS and Castile Brine) showed the effectiveness of chelators solubilizing Pu under the conditions of high Ca and chloride and low Mg.

PRESSURIZED TESTS

The STTP pressurized liter-scale tests were conducted in specifically designed containers with a 2-liter volume and a pressure of 60 bars (870 psig) of CO_2. The 6 pressurized tests consisted of three Portland Cement tests and three pyrochemical salt tests. The pyrochemical salt tests were all from the Direct Oxide Reduction (DOR) processes conducted at TA-55.

Portland Cement

The three Portland Cement tests contained different amounts of waste; LS-4 (204 g), LS-5 (612 g) and LS-6 (907 g). The brine to solid ratio was 10:1. 3:1, and 2:1, respectively. The Pu concentration in LS-4 started very low (1.6 ppb) and increased with each sampling period to 255 ppb; LS-5 did not have a trend and varied to 184 ppb; and LS-6 had an up and down trend with a maximum of 638 ppb. The U concentration was about 10000 ppb, 500 ppb, and 4000 ppb, respectively. There were very low concentrations of all other actinides. The pcH range was 7.2-7.4, 7.0-7.4, and 7.5-7.9 for the three tests, respectively. There were no filters with Pu colloids or microprecipitates. There was a medium level of particles per liter in the three tests. The three different quantities of wastes did not seem to have an impact on these tests.

Overall Comment: The pressurized Portland Cement tests showed that there was essentially no significant solubilization of actinides other than U. Even with 780 psig of CO_2, the pcH remained above pcH 7.0 for all the tests. There were no mobile Pu bearing colloids identified during the test period.

Pyrochemical Salts

The three pressurized pyrochemical salt tests, LS-28, 29, and 30, contained 920 g, 920 g, and 902 g of Direct Oxide Reduction process waste, respectively. The brine to solid ratio was 2:1 for all three tests. LS-28 and LS-29 were both Brine A experiments and had very high levels of Pu concentrations. LS-28 contained one of the highest inventories of Pu on the STTP (10.61 g) and LS-29 was also very high with 4.34 g. LS-30 had a considerably lower inventory of 2.01 g. LS-30 was a DOR waste experiment with Castile Brine at a pcH range of 5.9-6.6. Generally, Castile Brine experiments are low Ca and low Mg experiments, but LS-30 was a high Ca, high Mg experiment with a Pu concentration that leveled off at about 1000 ppb with no apparent trend.

LS-29 was a DOR waste experiment with Brine A at a pcH range on the acid side of neutral of 4.7 to 5.7. This test had a very high content of Ca (180000 ppm) as $CaCl_2$ and about 22000 ppm of Mg. The high Ca concentration resulted in a low sulfate concentration. The Pu concentration increased from 161 ppb to 8444 ppb as the pcH dropped to 4.73.

LS-28 become one of the most notorious experiments of the STTP matrix because it had a very high Pu inventory with a high soluble Pu concentration that was rapidly increasing. MgO was added to this test in February 1997, and the pcH increased from 4.48 to 7.70, and the concentrations of actinides and Fe decreased substantially. However, in time, actinides and Fe concentrations increased rather rapidly, and Pu (VI) was identified on May 17, 1999 when the Pu concentration achieved a peak of 197,984 ppb. All other actinides increased in concentration during the same period. LS-28 was a DOR experiment with Brine A with a very high Ca concentration (120,000 ppm) and Mg concentration (16,000 ppm) and a very low concentration of sulfate (60 ppm) and nitrate (21 ppm). With a low sulfate and nitrate concentration and a very high Ca and chloride concentration as $CaCl_2$, the Pu in LS-28 was susceptible to oxidation. The question concerning LS-28 was whether the addition of MgO enhanced the potential for oxidation of Pu.

The presence of mobile colloids or microprecipitates was evident in essentially all filters. The Pu in the filters was associated with $SrSO_4$ and was less associated with Fe precipitates. The number of particles per liter of brine in the 3 pressurized liter-scale tests was very high for LS-28, high for LS-29, and medium for LS-30. The addition of MgO to a brine pool in LS-28 resulted in precipitation of the MgO as sorel cement that blocked the test container and about half-way down and effectively divided it into two parts.

Overall Comment: The pressurized tests with pyrochemical salts (DOR) showed that Pu was solubilized in the three tests. The buffer capacity of Portland cement to maintain the pcH in the basic range was not characteristic of pyrochemical salt wastes as had been observed in the Portland Cement tests. LS-28 had the highest concentration of soluble Pu after LS-27. It had very high concentrations of Ca and chloride as $CaCl_2$ and very low concentrations of sulfate and nitrate. The Fe soluble concentration had increased from 19 to 165 ppm prior to addition of MgO, but Pu (VI) was identified during a period of 1.1 to 2.5 ppm Fe. LS-28 was the only test other than LS-26 that showed Pu (VI). It was the only test with added MgO. The MgO was solidified by the Brine A in such a way that there was no communication of the top portion of brine with the brine near the bottom of the test containers. This isolation led to a small brine pool near the top of the test container that was radiolytically very active and with other chemical additions resulted in the formation of oxidized Pu as Pu (VI). The pressurized tests with pyrochemical salts did have Pu colloids available for transport.

VI. Commentary on STTP Drum-Scale Tests

The 15 drum-scale tests utilized the total content from individual drums for each test. The 15 tests consisted of four sets of three drums of combustible wastes (TRUCON 116) and one set of massive metal tests (TRUCON 117). The drum-scale tests with heterogeneous or debris waste including the three massive metal tests were all categorized as tests with "very low" levels of soluble Pu except for the tests with added chelators and $Ca(OH)_2$ were categorized as "medium" wastes based on results from the tests. The first four sets of drum-scale tests were designed to study the chemical and radiolytic degradation effects of cellulose and carbonaceous materials in TRU wastes immersed in brine and how the degradation intermediates or products might influence the concentrations of soluble or colloidal forms of actinides. The last set of experiments in the drum-scale matrix was to determine the effects of massive metal on the chemistry and concentration of actinides in brine. Drum-scale tests DS-1, 2, and 3 were tests with combustibles in Brine A (DS-1 and 2) and Castile Brine (DS-3). Drum-scale tests DS-4, 5, and 6 were tests with combustibles with added bentonite. DS-4 and 5 in Brine A had 10 kg of brine-equilibrated bentonite, while DS-6 in Castile Brine had 10 kg of bentonite that was not brine-equilibrated. DS-7, 8, and 9 were tests with combustible wastes with added chelators without $Ca(OH)_2$. The five chelators added to DS-7, 8, and 9 at a concentration of about 160 ppm were:

1) Acetamide,
2) Sodium acetate,
3) Trisodium citrate dihydrate,
4) Oxalic acid dihydrate, and
5) Ammonium thiocyanate.

Ascorbic acid was added to the liter-scale tests as a chelator but was not added to the drum-scale tests. Calcium hydroxide was added to the liter-scale tests to assure the pcH was basic so all the chelators would dissolve.

DS-10, 11, and 12 were tests with combustibles with added $NaNO_3$ and NaH_2PO_4 which were to be nutrients for the microbial inoculum added to the test containers. There were 159 g of added $NaNO_3$ and 258 g of added NaH_2PO_4. DS-13, 14, and 15 were massive metal tests in Brine A and Castile Brine.

The drum-scale tests with combustible waste only (DS-1, 2, and 3) gave results that showed essentially no solubilization of Pu for all three tests. DS-1 had <10 ppb Pu; DS-2 had <30 ppb Pu; and DS-3 had <10 ppb Pu for the entire test period. The pcH ranged from 7.0-8.0 for all three tests. There was no Pu bearing colloids or microprecipitates in DS-1, 2, or 3 and also no Sr bearing colloids. Fe was prevalent in high quantities in essentially all filters but Pu was not carried with the Fe.

The drum-scale tests with combustible waste with added bentonite (DS-4, 5, and 6) showed essentially no solubilization of actinides (generally <10 ppb) at a pcH range of 7.0-7.7. There did not appear to be any difference in the chemistry of the brine-equilibrated and non-brine-equilibrated bentonite. The non-brine-equilibrated bentonite in Castile Brine generally showed <10 ppb in all actinides while the brine-equilibrated tests (DS-4 and 5) showed some solubilization of U and Np. There was essentially no Pu bearing colloids or microprecipitates in the filters from these tests.

The drum-scale tests with combustibles with added chelators and calcium hydroxide (DS-7, 8, and 9) showed great solubilization of all actinides throughout the test period. All the actinides were solubilized to high levels at the beginning of the tests and remained at high levels for the entire test period. The major decrease in concentration for all actinides in DS-7, 8, and 9 occurred when phosphate was added to these drum-scale tests. The added phosphate was quickly reduced in concentration due to precipitates of elemental phosphates. The presence of mobile colloids or microprecipitates was very evident in the drum-scale tests with added chelators in that most of the filters contained Pu bearing colloids. Fe bearing colloids were at lower levels than the rest of the drum-scale tests. Phosphate additions were made to the drum-scale tests with chelators to reduce the actinide concentrations for waste disposal purposes. Drum-scale 7 was an experiment in Brine A and chelators that contained 700 ppm Ca, 32000 ppm Mg, 4700 ppm sulfate, and 33 ppm nitrate. The Pu concentration was generally high for most actinides. Drum-scale test 8 was a Brine A experiment with chelators that contained 800 ppm Ca, 32000 ppm Mg, 48000 ppm sulfate, and 836 ppm nitrate. The Pu concentration peaked at 4310 ppb, and all other actinides were very high as well. Drum-scale 9 was a Castile Brine experiment with chelators that contained 600 ppm Ca, 700 ppm Mg, 17000 ppm sulfate, and 540 ppm nitrate. The Pu concentration peaked at 2667 ppb, and all other actinides were very high as well.

The drum-scale tests with combustible wastes with added sodium nitrate and sodium dihydrogen phosphate showed the effect of three major processes on the chemistry of these wastes.

The addition of phosphate to the drums reduced and maintained actinides at a very low level. However, the phosphate tended to complex all cations and precipitated and disappeared within a few weeks.

The addition of nitrate to these tests showed a very interesting process that was later found to exist in most liter-scale and drum-scale tests. The nitrate in DS-10 and 11 (Brine A) essentially disappeared due to either radiolytic, chemical, or microbial degradation or a combination of all three processes. The degradation products of nitrate, an oxidizing agent, are nitrites and N_2O, which are reductants. An associated by-product is N_2 which has no chemical effect. The addition of nitrates and phosphates as nutrients for the microbial inoculum added to the drums was not conclusive. There did not seem to be significant microbial activity that affected the chemistry of the tests other than the reduction of nitrate. The drum-scale tests with added nitrate and phosphate did show a significant population of filters with Pu bearing colloids or microprecipitates. There was a very large population of Fe bearing colloids. There was essentially no Sr bearing colloidal particles.

The drum-scale tests with massive metals were conducted to establish the effect of massive metals on the chemistry of the actinides in brine and to establish the rate of corrosion of massive metals in brine. DS-13, 14, and 15 showed essentially no solubilization of Pu during the entire test period. There was some solubilization of U and Np in all three tests but at low levels. The pcH dropped from 8.1 to 5.95 in DS-13 and from 7.78 to 6.71 in DS-14 during the test period. DS-15 in Castile Brine did not show a similar decrease in pcH (7.9-7.7). The Fe concentrations in the Brine A tests from DS-13 increased to a concentration of 558 ppm. In DS-14, the Fe concentration increased to 110 ppm during the test period. DS-15 in Castile Brine did not show any solubilization of Fe (<1 ppm) for the entire test period. There was a reduced level of Pu bearing colloids in the three tests and the Fe bearing colloids were very high as could be expected.

VII. Brine Replacement During Sampling

Samples of about 40-50 ml of brine were periodically taken from each test container in the STTP. Some samples were less in volume because of plugging of the sampling syringe needle that occurred during sampling and some were sampled fewer times during the test period because of the difficulty in sampling. Pressurized liter-scale samples were only sampled 7 or 8 times during the test period and the sample volume varied from 10 to 30 ml. There was no replacement brine added to the pressurized tests. A maximum of about 27 samples of brine was taken from each of the non-pressurized test containers and the volume of sample extracted was replaced with fresh Brine A or Castile brine as appropriate. This means that a maximum of about (50) (27) = 1350 ml of brine was sampled from an estimated volume of about 2,500 ml or about 54%. So the soluble contents of the waste such as nitrate would be diluted by 54% by the replacement brine. However, the soluble constituents in the brine would be replenished by the replacement brine and any constituents that precipitated early in the test would be continually replaced by the fresh brine.

VIII. Addition of Actinides to STTP Test Containers

The waste streams added to the STTP test containers were all from the Los Alamos National Laboratory inventory of wastes. The criteria for waste drums to be used for the STTP matrix is that each waste drum must contain at least 5 grams of Pu. ^{241}Am should accompany the total Pu but a criteria is not established for Am. There is no criteria to limit the quantity of ^{240}Pu and ^{241}Pu. There is no need to include waste containing ^{238}Pu because of the added difficulty in handling, sampling, and analyzing samples with the very high radioactivity levels of ^{238}Pu. The chemical effects expected to result from ^{238}Pu in the wastes will be induced by addition of about 75 mg of ^{241}Am to six different liter-scale test containers. Because the WIPP is expected to have wastes contaminated with Th, U, and Np, all the liter-scale and drum-scale tests are spiked with soluble salts of these actinides. Neodymium was also added to select test containers as a chemical analogue or surrogate for ^{241}Am.

The following is a list and description of the added actinides and neodymium:

Neodymium

Neodymium was added as $NdCl_3$ directly to the test containers at the WCRRF. The glass vial containing the $NdCl_3$ was not added to the test container.

Thorium

Thorium was added as a water solution of $Th(NO_3)_4 \cdot 4H_2O$ to a glass vial containing other actinides. The glass vial was placed in each test container. The Th was 99.99% pure and was present as ^{232}Th.

Uranium

Uranium was added as a nitric acid solution from a high purity specimen of depleted U metal (100%). The metal was dissolved in 16 N HNO_3 heated with a trace of HF. An aliquot of the U solution was placed in a glass vial containing other actinides. The glass vial was placed in each test container. The U was ^{238}U.

Neptunium

Neptunium was added as a Np salt solution after dissolution of NpO_2 by a sealed reflux dissolution system. Concentrated HCl with a few drops of HNO_3 and HF was used to dissolve the NpO_2. Aliquots of the dissolved oxide were added to glass vials containing other actinides. An aliquot of the solution was placed in a glass vial with other actinides. The glass vial was placed in each test container. The Np was ^{237}Np. The Np solution from the dissolved NpO_2 was added to each liter-scale test container, the Np added to the drum-scale tests was dissolved form specimens of Np metal. The metal was dissolved in concentrated HCl with a few drops of HNO_3 and HF. The 15 specimens of Np metal weighed 5 gm.

Americium

Americium was added as an Am solution after dissolution of AmO_2 in 0.5 ml 12 N HCl with two drops 16 N HNO_3 and two drops of HF. An aliquot of the solution was placed in a glass vial and evaporated to damp dryness. Each of the six glass vials had a radiation reading of about 800 mR/hr β, γ at contact. The AmO_2 was about 82.2% Am and remainder Pu. The vials with Am were added to each select test container along with the vials containing the other actinides.

Table 11. Actinides Added to STTP Liter-Scale Test Containers

Test Containers	*Nd (mg)* *	*^{232}Th (mg)*	*^{238}U (mg)*	*^{237}Np (mg)*	*^{241}Am (mg)*
1, 2, 3	45	75	75	75	0
4, 5, 6	30	75	75	75	0
7, 8, 9	45	75	75	75	0
10, 11, 12	0	75	75	75	75
13, 14, 15	45	75	75	75	0
16, 17, 18	45	75	75	75	0
19, 20, 21	45	75	75	75	0
22, 23, 24	45	75	75	75	0
25, 26, 27	45	75	75	75	0
28, 29, 30	30	75	75	75	0
31, 32, 33	45	75	75	75	0
34, 35, 36	45	75	75	75	0
37, 38, 39	0	75	75	75	75

* Nd added as $NdCl_3$ for a concentration of about 15 mg/L for nonpressurized tests, assumption of 3L; 15 mg/L for pressurized tests, assumption of 2L.

Table 12. Actinides Added to STTP Drum-Scale Test Containers

Test Containers	*Nd (mg)* *	*^{232}Th (mg)*	*^{238}U (mg)*	*^{237}Np (mg)*	*^{241}Am (mg)*
1, 2, 3	3.69	5	5	5	0
4, 5, 6	3.69	5	5	5	0
7, 8, 9	3.69	5	5	5	0
10, 11, 12	3.69	5	5	5	0
13, 14, 15	3.69	5	5	5	0

* Nd added as $NdCl_3$ for a concentration of about 24.37 mg/L, assuming 151.4 L (40 gal).

IX. Addition of Chelators to STTP Tests

The effect of chelators on chemicals with complexing functional groups was expected to be present in a portion of the wastes destined for the WIPP. Most of these complexing agents are expected to be in the combustible or debris waste but some complexing agents could be solidified in the Envirostone waste so to study the impact of chelators on the chemistry of the tests, a set of complexing agents were added to both the homogeneous wastes (pyrochemical salt tests LS-34,35, and 36) and the heterogeneous wastes (DS-7, 8, and 9). The chelators were the same for the two wastes except the pyrochemical salt waste tests had added ascorbate, a strong reducing agent, and the drum-scale tests did not have ascorbate. The chelators were added in acid or neutral salt form to a separate vessel and dissolved in a slightly basic medium prior to addition to the 3 liter-scale tests and 3 drum-scale tests. The chelators, especially citrate, were expected to solubilize actinides that otherwise might not have solubilized in the basic medium in the test containers.

Calculation of Concentration of Chelators in STTP Liter and Drum-Scale Test Containers

Liter-scale test containers with added chelators and 96.2 gm of $Ca(OH)_2$ are:

LS-34 Oxygen sparging pyrochemical salts
LS-35 Direct oxide reduction pyrochemical salts
LS-36 Direct oxide reduction pyrochemical salts

The concentration of chelators added to the liter-scale test containers assume a brine volume of 2000 ml.

The drum-scale containers with added chelators are DS-7, 8, and 9, which are loaded with TRUCON Code 116/216, combustibles. The concentration of chelators added to the drum-scale test containers assume a brine volume of 200L.

Table 13. Chelators Added to STTP Tests:

Liter-Scale Tests

Chelator	*LS-34 (mg)*	*LS-35 (mg)*	*LS-36 (mg)*
Acetamide	200	200	202
Sodium Acetate	277	276	277
Trisodium Citrate Dihydrate	308	307	311
Oxalic Acid Dihydrate	285	288	286
Ascorbic Acid	201	202	198
Ammonium Thiocyanate	295	294	295

Continued on next page

Drum-Scale Tests

Chelator	***DS-7 (mg)***	***DS-8 (mg)***	***DS-9 (mg)***
Acetamide	30.2	30.2	30.3
Sodium Acetate	42.0	42.0	42.0
Trisodium Citrate Dihydrate	46.6	46.6	46.6
Oxalic Acid Dihydrate	43.3	43.3	43.3
Ammonium Thiocyanate	44.4	44.4	44.4

Calculations for Liter-Scale Test Containers

Acetamide

$$\frac{(200\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 100\text{ ppm}$$

Sodium Acetate

$$\frac{(277\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 139\text{ ppm}$$

Trisodium Citrate Dihydrate

$$\frac{(308\text{ mg})(1000\text{ ug/ml})}{2000\text{ ml}} = 154\text{ ppm}$$

Oxalic Acid Dihydrate

$$\frac{(285\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 143\text{ ppm}$$

Ascorbic Acid

$$\frac{(201\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 101\text{ ppm}$$

Ammonium Thiocyanate

$$\frac{(295\text{ mg})(1000\text{ ug/mg})}{2000\text{ ml}} = 148\text{ ppm}$$

Calculations for Drum-Scale Test Containers

Acetamide

$$\frac{(30.2\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 151\ \text{ppm}$$

Sodium Acetate

$$\frac{(42.0\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 210\ \text{ppm}$$

Trisodium Citrate Dihydrate

$$\frac{(46.6\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 233\ \text{ppm}$$

Oxalic Acid Dihydrate

$$\frac{(43.3\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 217\ \text{ppm}$$

Ammonium Thiocyanate

$$\frac{(44.4\ \text{gm})\,(1000\ \text{mg/gm})}{200\ \text{L}} = 222\ \text{ppm}$$

X. Addition of Fe to STTP Test Containers

An important parameter that could have a significant effect on the Redox potential in the repository is the presence of iron from the mild steel 55-gallon drums containing the waste. The STTP experiments were designed to be conducted in Ti vessels because high ionic strength brine was expected to dissolve to different degrees many of the proposed containment vessels that might be used to contain the experiments with brine at 30 °C for up to 5 years. Because titanium was not dissolved by the synthetic Brine A and Castile Brine formulations, a means of trying to determine the effect of Fe in the mild steel drums had to be tested. Consequently, all test containers were fabricated from Ti metal and a high surface area mesh was added to each test to simulate the amount of Fe that would be present if the waste were in a 55-gallon drum. The corrodable surface area in a 55-gallon drum was calculated to be about 4 m^2. To simulate this surface area of Fe, an Fe mesh with wire strands of a small diameter and therefore a large surface area was procured and prepared by Sandia National Laboratory for addition to the STTP test containers. The procured material was a No. 10 mesh made with 20 gauge wire and procured from Aggregate and Mining Supply Company of Albuquerque, New Mexico. The material came in rolls three feet wide and had a nominal analyses of elements as follows:

Fe	98.453 %
C	0.679 %
Mn	0.620 %
Si	0.230 %
P	0.012 %
S	0.006 %

It was determined that 2748 in^2 of this mesh would provide about 4 m^2 of surface area in a 55-gallon or 210-liter test drum. For the liter-scale vessels, about 39.25 in^2 would be required. The Fe mesh was cut in approximately 1.25 inch width and 30.0 inch length sections, with a target mass of 102.01 g selected to provide the necessary surface area for the experiments in three liter-scale test containers. This amounted to 39.25 in^2 with an average weight to surface area ratio of 2.599 g/in^2. These cut samples were packaged in 4 ounce Qorpak polypropylene jars with one inch diameter holes cut on the top and bottom of each jar to allow inflow and outflow of brine.

The Fe mesh for the 6 pressurized test containers with a two-liter volume were cut to a target mass of about 68 g and placed in 2-ounce Qorpak polyethylene jars.

The Fe mesh prepared and packaged for the drum-scale tests were cut into 6 pieces that were 36 inches by 12 inches plus one additional piece that was 12 inches by 12.9 inches for a target surface of 2748 square inches. The target weight of Fe mesh was about 7142 g to achieve about 4 m^2 of corrodable steel surface. The accumulated Fe mesh sections were placed in a 5 gallon polyethylene bucket that had 5-inch diameter holes cut in the top and bottom to allow flow of brine through the Fe mesh.

A spectroscopic analysis of the Fe mesh with a Wavelength Dispersive X-ray Fluorescence Spectrometer showed an average constituent analysis of five wires, giving the following data:

Fe	95.4 %
Zn	1.5 %
P	1.43 %
Mn	1.28 %
Si	0.29 %
Cr	0.14 %
C	not analyzed

The presence of zinc was disturbing because it might be a galvanizing constituent or a protective layer. A surface analysis was performed to determine the property of the zinc in the wire by Auger Electron Spectroscopy. The zinc was determined to be a loose protective layer that was discontinuous over the Fe based wire strands. Corrosion on the unprotected Fe strands was visible where the zinc layer was very thin (~200 angstroms) and did not provide total protection of the wire.

XI. Addition of Mixed Inoculum

A batch of mixed inoculum was prepared for addition to each of the 39 liter-scale tests and 15 drum-scale tests. The inoculum consisted of a mixture of ingredients sampled from the WIPP site that contained a diverse mixture of halotolerant microorganisms that survive in the surfacial and supersaline conditions of the WIPP environments. The mixed inoculum batch consisted of the following components.

Table 14. Composition of Mixed Inoculum and Amounts Added to STTP Tests

Component	**Quantity %**	**Liters/drum**
Lake Brine and sediment mixture	20 %	1.06
Muck-pile salt solution	30 %	1.59
G-seep Brine	50 %	2.65
	Total	5.30

The inoculum solution was to be added to the test containers to establish and maintain an anaerobic environment. The anaerobic environment was established by purging the mixed inoculum for 30 minutes with N_2. The mixed inoculum was continually mixed and maintained under a N_2 atmosphere prior to addition to the liter-scale and drum-scale tests. About 100-150 ml of inoculum was added to the liter-scale tests, and about 5.3 liters was added to the drum-scale tests. For the pressurized liter-scale tests, 80-100 ml of inoculum was added to each of the 6 pressurized tests. The quantity of chemical reducing agents added as part of the inoculum injection was not known.

XII. Addition of Nitrate/Phosphate; Effect of Brine Type on Nitrate Reduction

Nitrate was added to three drum-scale test containers along with phosphate as nutrients for the added microbes. Nitrate was added as sodium nitrate ($NaNO_3$) and phosphate was added as sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$). Approximately 159 gm of $NaNO_3$ and 258 gm of $NaH_2PO_4 \cdot H_2O$ was added to each of the three drums. Assuming 50 gallons of brine in each drum, that would give a concentration of 159000 mg/189.25 liters = 840 mg/liter of $NaNO_3$ and 613 mg/liter (613 ppm) of added nitrates. The concentration of nitrate in the waste prior to addition of the nitrate injection is unknown. Nitrate could be expected to be totally soluble in the tests.

Table 15. Reduction of Nitrate in STTP Tests

	DS-10	**DS-11**	**DS-12**
Select Dates	**Nitrate, ppm**	**Nitrate, ppm**	**Nitrate, ppm**
06/19/95	683	441	620
08/21/95	620	325	620
10/10/95	584	260	570
04/15/96	545	31	482
01/21/97	334	**5**	542
06/16/97	103	**6**	477
06/22/98	**20**	**<5**	571
02/08/99	**8**	**<5**	554

The trends apparent in the above data show that nitrate was essentially totally destroyed in the Brine A experiments (DS-10 and 11) and was not affected in the Castile Brine experiments (DS-12). The major difference in the constituents in the Brine A and Castile Brine tests is that there is ~ 30,000 ppm Mg in the Brine A experiments (DS-10, 11) and only ~ 600 ppm Mg in the Castile Brine experiments (DS-12). Another difference is that the sulfate concentration in DS-10 and 11 was ~ 5000 ppm whereas DS-12 (Castile Brine) has a sulfate concentration of 17,000 ppm. It appears that the reduction in the nitrate concentration in the Brine A experiments could be due to lower sulfate concentration or, most likely, the much higher Mg concentration in DS-10 and 11. The mechanism responsible for this reduction may be chemical, radiochemical, or microbial but the overall assessment of the data points to a radiolytic/chemical reduction. There is no explanation why microbes would not be effective in DS-12 and be very effective in DS-10 and 11 for total destruction of nitrate in the brine. The Pu loading for the three drums were quite similar as below.

Table 16. Pu Loading vs. Soluble Pu Concentration

	DS-10	**DS-11**	**DS-12**
Pu Loading	16.44 gm	16.45 gm	16.70 gm
Pu Concentration Potential	* 87,000 ppb	87,000 ppb	88,000 ppb
Soluble Pu Concentration Measured	0-30 ppb	<5 ppb	<5 ppb

* Assumes 50 gal (189.25 Liter) of Brine in test

The above data shows that if the reduction in nitrate was a result of radiolysis that the radiolysis process must have been from alpha particles in the waste that were not dissolved or that dissolved and reprecipitated. If the Pu oxides did not dissolve, they could still be present in the waste as dispersed oxides or be released as dispersed oxides or be released and settled to the bottom of the drum. If the Pu contaminants dissolved and precipitated as hydrated Pu oxide, the precipitate would have settled to the bottom of the drum. Rotation of the drum contents would have enhanced settling of the Pu oxide and precipitates to the bottom of the drum. Any radiolytic degradation of nitrate would have to occur at the bottom of the drum or from Pu particles that are dispersed in the waste.

Assessing the data that shows the destruction of nitrate in the drum-scale tests DS-10 and 11 with Brine A indicates that Mg could have played a key role in enhancing this reaction. The actual mechanism of Mg as an energy transfer agent of radiolytic processes is not known.

The other instance in the STTP where nitrate was essentially totally destroyed was in LS tests with added organics such as LS-13 and 14 (Brine A experiments and less prominent in LS-15, Castile Brine experiments).

XIII. Pu (V) and (VI) in the STTP; An Explanation

The pyrochemical salt tests of the STTP consisted of two principal waste streams from pyrochemical salt processes at TA-55. The two major pyrochemical salt processes were Direct Oxide Reduction (DOR) and Oxygen Sparging (OS). The two waste streams had significantly different processes that yielded parameters that impacted the chemistry of the two different sets of STTP tests with DOR and OS wastes.

The waste from a typical DOR run was to add approximately 200 gm of PuO_2 to a refractory MgO – 3% Y_2O_3 crucible with about 1000 gm of $CaCl_2$ salt and 85 gm of Ca metal. The furnace was heated to ~ 840 °C and the PuO_2 was reduced to Pu metal while the Ca was oxidized to CaO. The Pu metal button would accumulate at the bottom of the crucible and was removed for further processing. The crucible with $CaCl_2$ salts and residual calcium metal and unreacted PuO_2 or $PuCl_3$ would be the DOR waste stream that was comminuted for the STTP DOR experiments. An important parameter was that the waste had a high concentration of $CaCl_{2,}$ high concentrations of Pu salts, and a low concentration of nitrate because nitrate would be destroyed during the high temperature process step with $CaCl_2$ and Ca. The high Ca and chloride concentrations were to be important chemical parameters in the chemistry of the STTP pyrochemical salt tests.

The waste from the OS process was generated during the process of purifying the Pu metal by electrodeposition with a cathode-anode electrode immersed in a heated NaCl-KCl salt flux. During the electrolytic process, NaCl and KCl was also reduced at the cathode to yield Na and K metal. This heated mixture was sparged with O_2 to convert the K and Na to K_2O and Na_2O and eventually the K_2O and Na_2O was converted back to KCl and NaCl.

The salt tests with DOR were characterized by high concentrations of $CaCl_2$ that may have had some residual Ca metal or CaO. The OS wastes were characterized by high concentrations of NaCl and KCl and may have had some K_2O, Na_2O, and CaO.

Preparation of the salt wastes for the STTP at the LANL Waste Characterization, Reduction and Repackaging Facility consisted of comminution of the crucibles, salts, and oxides and weighing out ~ 1320 gm of waste (920 gm for pressurized tests LS-28, 29, and 30; 880 gm for the tests with chelators, LS-34, 35, and 36). Brine was added to the test containers loaded with pyrochemical salt wastes and additives were added prior to final placement and fixing of the lid. A visible reaction of the Ca or CaO was noted during the addition of brine to some of the test containers. Later, a microbial inoculum was added to the sealed test containers at the CMR Building where the tests were to be conducted.

Brine A was added to the two test containers in each set of three tests and Castile Brine was added to the remaining test container from each set so a total of 10 tests had Brine A and 5 tests had Castile Brine. Brine A primarily consists of $MgCl_2$, NaCl, and KCl with some $NaSO_4$, $CaCl_2$, and NaBr. A small amount of $SrCl_2$ and $FeCl_2$ is included in the Brine A experiments. Castile Brine primarily consists of NaCl, $NaSO_4$, KCl, and $MgCl_2$. Lesser amounts of $CaCl_2$ and NaBr are added to the Castile Brine experiments.

The pyrochemical salt tests with Brine A and Castile Brine contain the following soluble constituents contributed by addition of brine.

Table 17. Total Constituent Content in Brine A and Castile Brine Tests

	Brine A			Castile Brine		
Brine Constituent	**Total gm/2.5L**	**Salt ppm**	**Element ppm**	**Total gm/2.5L**	**Salt ppm**	**Element ppm**
$MgCl_2 \cdot 6H_2O$	730	292,000	3,5000	9.7	3880	464
NaCl	250	100,000	40,000	654	261,600	103,000
KCl	143	57,200	30,000	18	7,200	3,775
$NaSO_4$	15.5	6,200	5,200	59.3	23,720	20,000
$CaCl_2$	4.2	1,680	607	3.3	3,300	1,200
NaBr	1.3	520	116	2.8	1120	250
$SrCl_2$	0.038	15	8	0	0	0
$FeCl_2$	0.031	12	5	0	0	0

NOTE: The pressurized tests (LS-28, 29, 30) contain about 1500 ml of brine or ~ 60% of the constituents in the non-pressurized tests.

It is evident that the addition of Ca to the DOR pyrochemical salt tests from brine is negligible relative to the Ca added as $CaCl_2$ in the waste. However, the amount of Mg added to each DOR test by the brine A is significant; castile brine tests contained low concentrations of Mg as does the brine. The sulfate concentrations of all tests was very low because of the high Ca content which resulted in precipitation of the sulfate. The K_{sp} for $CaSO_4$ is 7.1×10^{-5}.

The Ca ion concentration in DOR tests varied from 2-4 molar (80,000 to 160,000 ppm). The sulfate concentration in Castile Brine tests due to the brine was ~ 20,000 ppm and about 5,200 ppm in brine A tests. The sulfate concentration in OS tests was generally 5,000-16,000 except when higher Ca concentrations reduced the sulfate to lower concentrations such as LS-38 with a Ca concentration of 60,000 ppm.

Typically, the DOR tests with high Ca ion concentrations precipitated the sulfate to yield tests with sulfate concentrations that were generally less than 200 ppm from a beginning Castile brine concentration of 20,000 ppm and Brine A test concentration of 5,200 ppm.

One of the strongest anionic complexes for Pu in both acid and basic solution is fluoride. The STTP Portland cement tests had fluoride concentrations from 0-40 ppm depending on the test and the Envirostone tests contained fluoride concentrations from 0-250 ppm. The Pyrochemical salt tests contained fluoride concentrations from 0-325 ppm and many of the tests showed a reduction in the concentration of fluoride with time.

Table 18. Fluoride and Fe Concentrations in Pyrochemical Salt Tests

ID	Characteristic	Range of F^-, ppm	pcH	Fe Concentration
25	DOR	50-40	7.8-8.1	<1-6
26	DOR	65-45	7.8-8.1	<1-4
27	DOR, Castile	**39-5**	10.7-11.2	20-240
28	DOR, CO_2	80-70	4.7-7.7	20-165
29	DOR, CO_2	70-80	4.7-5.1	50-1468
30	DOR, CO_2,, Castile	12-20	5.9-6.3	1967-9
31	OS, Bentonite	<10	8.7-9.0	0
32	OS, Bentonite	<10	8.7-9.0	0
33	OS, Bentonite, Castile	<10	9.5-9.8	0
34	OS, Chelators	**325-5**	8.7-9.1	0
35	DOR, Chelators	60-25	8.1-8.3	0
36	DOR, Chelators	**22-2**	11.1-11.4	30-103
37	DOR, ^{241}Am	90-34	7.6-8.0	1-5
38	OS, ^{241}Am	30-17	7.7-8.0	0
39	OS, ^{241}Am, castile	**<10**	9.4-9.8	0

The reduction in fluoride concentration appeared to be most evident in tests with a pcH > 9.0. Castile Brine tests with higher pcH (except the pressurized tests) resulted in reduction of fluoride down to <10 ppm. Bentonite, a clay composed of montmorillonite and beidelite minerals, was effective in eliminating fluoride after the beginning of the test. The high Al content of montmorillonite could be the active agent that complexed fluoride because fluoride has a high affinity (stability constant) for Al at neutral and basic pH.

The concentration of Fe in the pyrochemical salt tests may seem to be sporadic but there is a pattern of chemistry that emerges when the Fe data is evaluated against the parameters of other variables. Fe concentration in the pyrochemical salt experiments is greatest under two different conditions: when the pcH is acidic as in the tests pressurized with CO_2 (LS-28, 29, 30) and when the pcH is very high (> 10.5) in DOR tests in Castile Brine (LS-27 and 36). It was thought that Fe would maintain the repository in a reducing condition but some of the tests with significant concentrations of Fe had oxidized Pu as below.

Table 19. Fe Concentrations in Pyrochemical Salt Tests

ID	Pu Oxidation State	Fe Concentration Range	pcH
LS-26	Pu (VI)	Fe = <1 – 4 ppm	7.8 – 8.1
LS-27	Pu (V)	Fe = 20 – 240 ppm	10.7 – 11.2
LS-28	Pu (VI)	Fe = 20 – 165 ppm	4.7 – 7.7
LS-36	Pu (V)	Fe = 30 – 103 ppm	11.1 – 11.4

One of the puzzling questions concerning Fe in the STTP is that soluble Fe is present in a basic solution at the same time that Pu is soluble and in an oxidized form. This seems like the concentration of Fe and Pu is in contradiction with the K_{sp} of the two cations.

The solubility product constant, K_{sp}, of various reactants shows the solubility that can be achieved by each of the reaction ions relative to the formed solid compound.

Table 20. K_{sp} of Ca, Mg, Fe, and Ba for Relative Comparison

Ca	**K_{sp}**	**Mg**	**K_{sp}**
$Ca(OH)_2$	4.7×10^{-6}	$Mg(OH)_2$	5.6×10^{-12}
$CaSO_4$	7.1×10^{-5}	$MgSO_4$	-
$CaSO_3$	5.0×10^{-6}	$MgCO_3$	6.8×10^{-6}
CaF_2	1.5×10^{-10}	MgF_2	7.4×10^{-11}

Fe	**K_{sp}**	**Ba**	**K_{sp}**
$Fe(OH)_2$	4.9×10^{-17}	BaF_2	1.8×10^{-7}
$Fe(OH)_3$	2.6×10^{-39}	$BaSO_4$	1.1×10^{-10}
FeF_2	2.4×10^{-6}	$BaCO_3$	5.0×10^{-9}

However, the mass action expression for reactants and formed solid compounds requires a heterogeneous equilibrium because more than one phase enters into the expression. The calculated product of ion concentrations given above, are the result from experiments conducted at ideal conditions in low ionic strength solutions with known activity coefficients at neutral pH. The STTP solutions are at extremely high ionic strength solutions with unknown and perhaps indeterminate activity coefficients in a multiple and dynamic electrolyte system that is different for each test. Also, the pcH for each test container is different and certainly not neutral. So we must recognize that the normal equations of state at standard conditions do not apply to the STTP tests (nor to the WIPP). Also, the molar concentration of reactant ions are complicated by the common ion effect as in the case of excess Ca ions relative to sulfate in the following reaction:

$Ca^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrow CaSO_4\,(s)$ *(aq) = aqueous

Theoretically, any reaction equilibrium may be shifted in one direction or another if sufficient reactant or product is added or removed. Perhaps the greatest complication in STTP high ionic strength solutions with multiple reactant ions and salts is the reactions that are competing to form precipitates and reactions that form soluble complexes. The formation of soluble complex ions by the addition of negatively charged ions (ligands) to a central metal ion will compete with the equilibrium that is established between reactant ions to form precipitates. So the formation constants or instability constants for complexation are in competition with the solubility product expression for precipitation.

The above discussion on complexation and precipitation is included in this report to provide an explanation of how an ion like Fe^{3+} in a basic solution can exist in solution with a K_{sp} of 10^{-39}. In solutions with high pcH values, as in some Castile Brine experiments, amphoterism enters into the already complex chemistry as compounds that are highly insoluble in neutral to slightly basic (pcH 7 to 9) conditions begin to solubilize in the more basic solutions. Also, the stability or formation constants of certain ligands compete with the hydroxide radical as the pcH of a test is more or less basic. Generally, the stability constant for inorganic ligands such as fluoride, carbonate and phosphate become stronger as the pH becomes more basic but, sulfate forms strong complexes at neutral pcH and relatively weaker complexes at more basic pcH's (pcH >10). For example, in the presence of EDTA, Ba, Sr, Ca, and Pb precipitate as sulfates at pH 5, but only BaSO4 is precipitated at pH 10. Generally, the hydroxide radical predominates at the higher pH's to either precipitate the metal ion or lead to solubilization due to ion complexation or amphoterism. The presence of high concentrations of Ca and Mg will tend to release Pu from ligand interaction toward the highest anion concentrations, namely, chloride.

XIV. An Explanation of Pu(V) and (VI) in STTP Pyrochemical Salt Waste Stream

Direct-Oxide Reduction (DOR)

$$PuO_2 \xrightarrow[840°C]{CaCl_2,CaO,Ca} Pu + \text{Ca Salts}$$

Oxygen Sparging (OS)

$$Pu/PuO_2 \xrightarrow[\Delta,\ emF]{NaCl,KCl} \underset{\text{cathode}}{Pu + K + Na} \xrightarrow[\Delta]{O_2} Pu + K_2O + Na_2O$$

INFLUENCING PARAMETERS

	DOR	OS
1. Pu(V) and Pu(VI)	LS-26, 27, 28, 36	None
2. Soluble Pu Concentration	Medium -Very High	Very Low-Low
3. Calcium	Very High	Low
4. Sulfate	Very Low	Higher
5. Chloride	Very High	High
6. Pu & Am loading	Very High	Lower
7. Nitrate	Very Low	Very Low
8. Mg (Brine A)	High	High
Mg (Castile Brine)	Low	Low
9. Na and K	Lower	High
10. Soluble Fe concentration	High	Very Low
11. Colloids	High	Low

Parameter No. 1 Pu(V) and Pu(VI)

DOR	OS
Pu(V) LS-27, 36	None
Pu(VI) LS-26, 28	None

Parameter No. 2 Pu Concentration

DOR		OS	
ID	Peak Pu Concentration, ppb	ID	Peak Pu Concentration, ppb
LS-25	127	LS-31	275
LS-26	70, 826	LS-32	697
LS-27, Castile	243, 438	LS-33, Castile	190
LS-28	197, 984	LS-34	50
LS-29	8446	LS-38	19
LS-30, Castile	2226	LS-39, Castile	2599
LS-35	1458		
LS-36, Castile	19963		
LS-37	381		

Parameter No. 3 Calcium
Parameter No. 4 Sulfate

DOS			OS		
ID	Ca, ppm	Sulfate, ppm	ID	Ca, ppm	Sulfate, ppm
LS-25	83000	30	LS-31	1200	4600
LS-26	70000	70	LS-32	800	4800
LS-27, Castile	80000	180	LS-33, Castile	800	9000
LS-28	120000	60	LS-34	9000	800
LS-29	18000	50	LS-38	60000	140
LS-30, Castile	30000	250	LS-39, Castile	700	16000
LS-35	80000	100			
LS-36, Castile	80000	200			
L37	120000	50			

Note: K_{sp} for $CaSO_4$ is about 7×10^{-5}

Parameter No. 5 Chloride Content

DOR		OS	
ID	Chloride, Molar	ID	Chloride, Molar
LS-25	9.1	LS-31	6.3
LS-26	9.0	LS-32	6.3
LS-27, Castile	6.7	LS-33, Castile	5.7
LS-28	10.43	LS-34	6.5
LS-29	10.81	LS-38	7.2
LS-30, Castile	6.4	LS-39, Castile	4.9
L35	7.7		
LS-36, Castile	6.1		
LS-37	9.3		

Parameter No. 6 Pu and Am Loading

DOR			OS		
ID	Pu, g	Am, mg	ID	Pu, g	Am, mg
LS-25	0.38	0.40	LS-31	0.81	0.65
LS-26	4.06	2.25	LS-32	4.10	2.92
LS-27	3.41	1.56	LS-33	1.14	1.10
LS-28	10.61	1.24	LS-34	2.05	2.69
LS-29	4.34	2.38	LS-38	2.77	7.43
LS-30	2.01	2.38	LS-39	4.42	11.50
LS-35	0.45	0.07			
LS-36	11.07	4.94			
LS-37	4.35	1.10			

Note: Portland Cement Pu average = 0.077
Envirostone Average = 1.12

Parameter No. 7 Nitrate Concentration

DOR			OS		
	Nitrate, ppm			Nitrate, ppm	
ID	Start	End	ID	Start	End
LS-25	30	20	LS-31	5250	50
LS-26	40	40	LS-32	1030	28
LS-27	80	35	LS-33	9100	33
LS-28	58	21	LS-34	1020	22
LS-29	15	10	LS-38	30	77
LS-30	26	10	LS-39	2000	219
LS-35	940	20			
LS-36	25	120			
LS-37	960	85			

Parameter No. 8 Mg Concentration

DOR		OS	
ID	Mg, ppm	ID	Mg, ppm
LS-25	22000	LS-31	28000
LS-26	21000	LS-32	30000
LS-27, Castile	<10	LS-33, Castile	400
LS-28	16000	LS-34	23000
LS-29	20000	LS-38	28000
LS-30, Castile	22000	LS-39, Castile	1400
LS-35	24000		
LS-36, Castile	<10		
LS-37	23000		

Parameter No. 9 Na and K Concentrations

DOS			OS		
ID	Na, ppm	K, ppm	ID	Na, ppm	K, ppm
LS-25	7000	20000	LS-31	60000	50000
LS-26	10000	21000	LS-32	70000	55000
LS-27, Castile	44000	5000	LS-33, Castile	100000	40000
LS-28	4000	10000	LS-34	60000	42000
LS-29	2000	12000	LS-38	22000	30000
LS-30	40000	4000	LS-39, Castile	80000	7000
LS-35	20000	26000			
LS-36, Castile	50000	5000			
LS-37	8000	22000			

Parameter No. 10 Soluble Fe Concentration

DOR		OS	
ID	Fe, ppm	ID	Fe, ppm
LS-25	0.1-10	LS-31	0.1-3
LS-26	0.1-4	LS-32	0.1-1
LS-27, Castile	16-243	LS-33, Castile	0.1-1
L28	1-165	L34	0.1-2
LS-29	34-1468	LS-38	0.1-3
LS-30, Castile	10-1967	LS-39, Castile	0.1-1
LS-35	0.1-3		0.1-3
LS-36, Castile	10-103		0.1-1
LS-37	1-20		

Parameter No. 11 Colloids

DOR							
ID	Total Particles	Pu	Sr	Fe	Sulfate	Ca	pcH
LS-25	2×10^{11}	9L	14H	0	15H	High	8.0
LS-26	10^{11}-10^{12}	17H	13M	0	13M	High	8.0
LS-27, Castile	10^{11}-10^{12}	16VH	16H	0	15H	High	11.0
LS-28, CO_2	10^{12}-10^{13}	3H	3M	1L	3M	High	5.0
LS-29, CO_2	2×10^{12}	3H	0-	2L	4M	High	5.0
LS-30, CO_2	3×10^{11}	3M	0-	1M	3M	High	6.4
LS-35, Chelators	10^{10}-10^{11}	1L	3VL	O	15VH	High	8.3
LS-36, Castile/ Chelators	10^{10}-10^{11}	16VH	14H	2M	14H	High	11.2
LS-37, ^{241}Am	10^{9}-10^{10}	8L	15H	6M	13H	High	7.8

OS							
ID	Total Particles	Pu	Sr	Fe	Sulfate	Ca	pcH
LS-31, Bentonite	10^{9}-10^{10}	8M	0	3M	10M	Low	8.8
LS-32, Bentonite	10^{9}-10^{10}	10H	4M	5M	12M	Low	8.8
LS-33, Bentonite	10^{9}-10^{10}	14H	3VL	6M	16M	Low	9.7
LS-34, Chelators	10^{10}	11M	0	0	12M	Med	8.7
LS-38, ^{241}Am	10^{9}-10^{10}	0	2VL	1L	15L	Med	7.8
LS-39, ^{241}Am	10^{9}-10^{10}	13H	5L	0	12H	Low	9.5

Note: L=Low, M=Medium, H=High, VH=Very High

Parameter No. 12 Oxidation Potential

ID	Total Activity, mCi	Cl^-, Molar	pcH
LS-25	25	9.1	8.0
LS-26	259	9.0	8.0
LS-27	217	6.7	11.0
LS-28	662	10.43	5.0
LS-29	277	10.81	5.0
LS-30	133	6.4	6.4
LS-35	28	7.7	8.3
LS-36	703	6.1	11.2
LS-37	531	9.3	7.8

NOTE:
1. pcH < 4 radiolysis of brine yields Cl_2
2. pcH 4 – 7 radiolysis of brine yields HClO
3. pcH > 7 radiolysis of brine yields OCl^-
4. The higher the α-activity the greater the Eh increases
5. > 3 M NaCl + radiolysis oxidizes Pu (IV) to (VI) and Am (111) to (V) in basic solution but not acid solution
6. Pu and Am hydroxide can be solubilized by oxidation
7. Pu α-particle path length in water is ~ 74 microns

Parameter No. 13 Downward Trend of Pu (VI)

The two liter-scale tests with Pu (VI) were LS-26 and LS-28. LS-26 was a Pyrochemical Salt test with a loading of 4.06 grams of Pu and 2.25 mg of Am in a Brine A. The pcH for LS-26 ranged from a pcH of 7.5 to 8.4 with an average pcH around 8.0 The Pu concentration started at 42.9 ppb and in creased to 3996 after one year of testing. The Pu and Am concentration increased rapidly to 70,826 ppb on 12/02/96 and a sample was analyzed and found to contain 63,413 ppb Pu and Pu (VI) was identified on the 03/24/97 sample. Pu (VI) persisted for about 1 ½ years till 11/02/98 when the total Pu concentration dropped to 5642 ppb. The upward trend that occurred was attributed to the presence of soluble Pu (VI). The eventual downward trend in concentration is attributed to precipitation of Pu (VI) or reduction of Pu (VI) to Pu (IV) and subsequent precipitation of Pu (IV) as a hydrated PuO_2 or Pu hydroxide.

According to the results of experiments conducted at LANL by Runde and VanPelt, Pu (VI) can be reduced or precipitated by peroxide within 18 months in Brine A at pH 7-10. Also, peroxide generated by alpha radiolysis that exceeds a few ppm will result in precipitation of Pu as a Pu (VI) hydroxide or a reduced form of Pu hydroxide. The stability or instability of Pu (VI) in the presence of peroxide or hypochlorite in acid, neutral and basic solutions of 5m NaCl Brine A and Castile Brine is summarized on the next page.

Table 21. Study of Peroxide and Hypochlorite in Brine Solutions

Brine A	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Stable > 18 months	Stable > 18 months
7 – 8	Stable > 3 days but reduced at 18 months	Stable > 3 days but < 18 months; white precipitate formed
8 – 10	Stable > 3 days but reduced by 18 months	Slow-partial reduction up to > 18 months; white precipitate formed

Castile Brine	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Very stable > 18 months	Stable > 18 months
7.0 – 7.5	Stable for 6 days and partially stable for 18 months	Stable > 18 months
7.5 – 8.0	Partial reduction to Pu (V) in 6 days	Stable > 18 months precipitate forms
9.0 – 10	Partial reduction on first day; mostly stable for > 18 months	Slow-partial reduction but mostly stable for > 18 months; precipitate forms

5 M NaCl	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
2 – 4	Pu (VI) to Pu (V) in < 7 days	Stable > 18 months
7 – 8	Pu (VI) reduced in < 7 days	Slow-partial reduction then stable for > 18 months
8 – 10	Pu (VI) reduced in < 7 days	Pu (VI) slowly-partially reduced and then stable for > 18 months

Because LS-26 was a Brine A experiment at a pcH of 7.6 to 8.1, Pu (VI) is shown to be unstable on a long-term basis in the presence of peroxide and hypochlorite with the formation of white precipitate at neutral and basic pH. Pu (VI) is more stable in basic pcH than neutral and LS-26 may have been on the verge of being basic enough to be stable.

LS-28 was on the acid side of neutral where Pu (VI) is much more stable in Brine A with both hypochlorite and peroxide.

Table 22. Anion Behavior and Influence on Actinides

ID	Ca, ppm	Mg, ppm	Sulfate, ppm	Nitrate, ppm		Chloride, Molar	Remarks
				Start	End		
LS-01	18000	21000	600	280	150	5.4	
LS-02	40000	<1	400	1550	560	4.8	
LS-03	130	<10	13000	1670	990	4.2	
LS-07	12000	25000	700	250	160	5.5	No Fe mesh
LS-08	36000	2000	400	1800	670	5.0	No Fe mesh
LS-09	120	<10	14000	1300	800	4.3	No Fe mesh
LS-10	12000	22000	800	250	160	5.4	No Fe mesh; ^{241}Am
LS-11	40000	<10	400	1300	660	4.9	No Fe mesh; ^{241}Am
LS-12	120	<10	13000	1300	700	4.3	No Fe mesh; ^{241}Am
LS-13	1150	30000	7000	792	11	5.5	Organic solvent
LS-14	1300	30000	7000	600	8	5.5	Organic solvent
LS-15	650	1000	16000	471	163	4.6	Organic solvent
LS-16	1300	30000	6500	60	10	5.4	
LS-17	1500	30000	6500	23000	11000	5.4	
LS-18	700	1000	16000	3400	134	4.6	
LS-19	1100	25000	9000	51000	28000	5.0	
LS-20	1200	30000	9000	46000	24000	5.4	
LS-21	600	800	17000	47000	28000	4.4	
LS-22	2300	30000	4500	60000	31000	5.3	
LS-23	2700	34000	4000	40000	26000	NA	
LS-24	780	2000	12000	44000	28000	4.4	
LS-25, DOR	83000	22000	30	30	20	9.1	
LS-26, DOR	70000	21000	70	40	40	9.0	
LS-27, DOR	80000	<10	180	80	35	6.7	
LS-28, DOR	120000	16000	60	58	21	10.43	60 bars CO_2; MgO
LS-29, DOR	180000	20000	50	15	10	10.81	60 bars CO_2
LS-30, DOR	30000	22000	250	26	10	6.4	60 bars CO_2
LS-31, OS	1200	28000	4600	5250	50	6.3	Bentonite
LS-32, OS	800	30000	4800	1030	28	6.3	Bentonite
LS-33, OS	800	400	9000	9100	33	5.7	Bentonite
LS-34, OS	9000	23000	800	1020	22	6.5	Chelators and $Ca(OH)_2$
LS-35, DOR	80000	24000	100	940	20	7.7	Chelators and $Ca(OH)_2$
LS-36, DOR	80000	<10	200	25	120	6.1	Chelators and $Ca(OH)_2$

Continued on next page

ID	Ca, ppm	Mg, ppm	Sulfate, ppm	Nitrate, ppm		Chloride, Molar	Remarks
				Start	End		
LS-37, DOR	120000	23000	50	960	85	9.3	No Fe or Nd; ^{241}Am
LS-38, OS	60000	28000	140	30	77	7.2	No Fe or Nd; ^{241}Am
LS-39, OS	700	1400	16000	2000	219	4.9	No Fe or Nd; ^{241}Am
DS-01	700	32000	18000	312	34	5.3	Combustibles
DS-02	500	30000	5000	100	42	5.6	Combustibles
DS-03	400	500	17000	390	40	4.9	Combustibles
DS-04	600	32000	5000	90	20	5.5	Bentonite
DS-05	700	33000	5000	100	20	5.5	Bentonite
DS-06	600	800	18000	140	145	5.0	Bentonite
DS-07	700	33000	4700	38	33	5.5	Chelators and $Ca(OH)_2$
DS-08	800	32000	48000	804	836	5.6	Chelators and $Ca(OH)_2$
DS-09	600	700	17000	503	540	4.9	Chelators and $Ca(OH)_2$
DS-10	600	32000	4900	683	8	5.4	Nitrate/Phosphate
DS-11	500	32000	4900	440	5	5.4	Nitrate/Phosphate
DS-12	300	700	17000	620	554	4.9	Nitrate/Phosphate
DS-13	600	32000	4700	8	0	5.6	Metals
DS-14	700	33000	4900	62	15	5.4	Metals
DS-15	400	800	16000	234	0	4.8	Metals

XV. A Comparison of STTP Final Results for Radioactivity

During the D&D process of STTP test containers, a final sample of brine was taken from each vessel during the disassembly process and total alpha and Am-241 activity was measured on each sample. A comparison of the results of radiochemistry from the final brine sample taken during the D&D disassembly process relative to the final samples taken after rotation of the test containers was terminated is presented. The goal of the comparison was to ascertain whether there were any major changes, particularly significant increases, in activity during the period that the test containers set in a quiescent mode to the D&D timeframe as determined by the total alpha and Am-241 activities in the brine.

The overall result of this comparison was that there was not any significant increase in activity based on total alpha and Am-241 activity except for the results noted in the summary below.

Summary of Comparison

Portland Cement: No increase in activity during final period.
Envirostone: LS-16 showed an increase in radioactivity during the final quiescent period.
Pyrochemical salt: LS-25, 26, 28, 29, and 34 had increases in either total alpha activity or Am-241 activity during the quiescent period.
Drum-scale tests: No increase in activity during the final period.

Table 23. Comparison of Portland Cement Test Activities

Test Container	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
LS-01	10/14/99	0	0.06	0.06	<0.12	<0.12	8.74
	10/7/99		0.06	0.06	<0.12	<0.12	8.74
LS-03	[*1] 2/22/99	26	0.01	<0.01	<0.12	<0.12	12.92
	[*2] 4/27/01		0.01	0.01	0.17	0.46	12.9
LS-04 CO_2 pressure	9/21/98	32	**15.29**	–	0.92	–	7.34
	5/15/01		0.08	0.21	0.23	0.18	7.20
LS-05 CO_2 pressure	9/21/98	32	0.71	–	0.14	–	7.35
	5/15/01		0.03	0.04	<0.12	0.31	7.02
LS-06 CO_2 pressure	9/21/98	32	**28.01**	–	1.12	–	7.56
	4/27/01		0.07	0.07	0.21	0.44	7.74
LS-07	3/15/99	25	0.26	0.24	<0.12	<0.12	8.75
	4/16/01		0.18	0.14	0.52	0.21	8.85
LS-08	3/15/99	25	0.11	0.09	<0.12	<0.12	9.25
	4/16/01		0.1	0.09	0.15	<0.12	9.44
LS-09	3/15/99	25	0.02	<0.01	<0.12	<0.12	12.97
	4/27/01		<0.01	<0.01	<0.12	0.27	12.92
LS-10 Am-241 added	3/15/99	23	4.29	3.86	3.11	3.04	8.74
	2/22/01		2.25	2.11	1.19	1.15	8.79
LS-11 Am-241 added	3/15/99	23	0.09	0.08	<0.12	<0.12	9.74
	2/22/01		0.05	0.03	0.39	0.3	10.52
LS-12 Am-241 added	3/15/99	23	0.01	<0.01	<0.12	<0.12	12.98
	2/22/01		0.01	<0.01	0.23	0.31	12.92

*1 Final sample taken when rotation of test containers was terminated.
*2 Final sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: Pressurized test containers LS-04 and L06 showed a high coarse alpha activity that was not present in the sample taken 32 months later.

Table 24. Comparison of Envirostone Test Activities

Test Container	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
LS-13 added organics	[*1] 3/1/99	24	4.04	1.71	0.57	0.31	7.07
	[*2] 2/22/01		5.86	5.56	1.1	0.71	7.01
LS-14 added organics	4/15/99	22	10.87	8.23	1.62	1.11	7.11
	1/25/01		13.3	12.91	2.43	2.4	7.22
LS-15 added organics	4/5/99	25	2.01	1.75	<0.12	0.14	7.58
	4/27/01		1.01	1.02	0.34	0.68	6.76
LS-16	2/22/99	23	**424**	**409**	**2.64**	**2.59**	**7.45**
	1/16/01		**1033**	**1027**	**11.0**	**10.2**	**7.47**
LS-17	2/22/99	24	0.70	0.25	0.25	0.18	7.82
	2/22/01		0.97	0.48	0.58	0.76	7.73
LS-18	3/8/99	22	2.34	0.77	1.73	0.94	7.82
	1/25/01		2.78	2.02	2.04	1.5	7.66
LS-19	3/01/99	24	1.56	1.41	1.09	1.13	7.93
	2/22/01		1.75	1.67	1.57	2.01	7.83
LS-20	10/18/99	0	0.17	0.11	<0.12	<0.12	7.81
	10/14/99		0.17	0.11	0.13	<0.12	7.81
LS-21	11/9/99	0	0.44	0.36	<0.12	<0.12	8.11
	11/15/99		0.44	0.36	<0.12	<0.12	8.11
LS-22	2/22/99	26	0.29	0.21	0.25	0.14	7.20
	4/16/01		4.14	0.29	3.87	0.96	7.50
LS-23	3/1/99	24	4.91	5.02	2.98	3.79	7.49
	3/16/01		3.61	3.0	3.61	3.04	7.29
LS-24	2/22/99	26	0.18	0.10	0.13	<0.12	7.76
	4/27/01		0.08	0.06	0.33	0.3	7.70

*1 Final sample taken when rotation of test containers was terminated.
*2 Final sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: LS-16 showed a definite increase in activity during the 23 months of quiescent operation (non-rotation of test containers). This result is consistent with Np, U, Pu, and Am results from an ICP-MS analysis.

Table 25. Comparison of Pyrochemical Salt Test Activities

Test Container	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
LS-25	[*1] 12/6/99	16	0.96	0.66	<0.12	<0.12	8.04
	[*2] 4/16/01		28.66	24.97	0.82	0.72	8.14
LS-26	12/6/99	14	292.1	275	1.3	0.80	8.01
	2/22/01		251	247	77	44.5	8.07
LS-27	12/6/99	14	2825	2277	15.7	15.9	11.16
	1/25/01		1492	1181	155.6	187.8	11.21
LS-28 CO_2 pressure	12/6/99	18	1337	–	19.3	–	5.03
	5/15/01		1683	1767	152.5	141.3	5.19
LS-29 CO_2 pressure	9/20/98	33	360	–	99.8	–	4.73
	6/20/01		1822	1746	56.2	49.9	5.01
LS-30 CO_2 pressure	9/20/98	33	68.4	–	5.8	–	6.59
	6/20/01		70.4	70	1.12	0.99	6.86
LS-31 Bentonite	11/4/99	0	21.12	20.33	1.01	<0.12	8.79
	11/15/99		21.1	20.3	15.19	0.15	8.79
LS-32 Bentonite	12/15/99	0	10.76	10.77	<0.12	<0.12	8.75
	12/15/99		10.8	10.8	1.26	1.16	8.75
LS-33 Bentonite	3/8/99	23	11.37	10.93	<0.12	0.19	9.63
	2/22/01		8.5	8.5	0.46	0.49	9.73
LS-34 Chelators	3/8/99	25	4.68	1.83	0.82	0.44	8.75
	4/16/01		37.6	36.9	1.12	1.13	8.93
LS-35 Chelators	3/8/99	24	13.0	10.1	2.69	2.03	8.31
	3/16/01		14.4	8.8	2.89	2.26	8.26
LS-36 Chelators	3/8/99	22	140.4	126.5	4.0	9.2	11.38
	1/16/01		133	39	40.35	41.17	11.35
LS-37 Am-241 added	3/15/99	22	**15.17**	**13.96**	**0.37**	**0.29**	**7.80**
	1/16/01		**529.5**	**511.5**	**10.59**	**8.05**	**7.76**
LS-38 Am-241 added	3/15/99	22	0.65	0.62	<0.12	<0.12	8.02
	1/16/01		1.32	1.29	0.63	0.22	7.97
LS-39 Am-241 added	3/15/99	22	179.3	175.3	44.70	42.60	9.50
	1/16/01		55.9	53.4	10.19	7.77	9.49

*1 Final sample taken when rotation of test containers was terminated.
*2 Final sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: The radiochemistry results of LS-37 agree with similar increases in concentrations with ICP-MS results. Differences found in LS-26, 28, and 36 do not correlate for the two measurement techniques. LS-27 was interesting because the total alpha activity decreased and Am-241 activity increased.

Table 26. Comparison of Final Drum-Scale Test Activities

Drum Number	Date	ΔT (months)	Total Alpha Activity (nCi/ml)		Am-241 Activity (nCi/ml)		pcH
			Coarse	Fine	Coarse	Fine	
DS-01	*1 2/1/99	28	0.66	0.13	0.36	<0.12	7.70
	*2 6/20/01		0.15	0.10	0.35	0.40	7.71
DS-02	2/1/99	28	0.63	0.13	0.13	<0.12	7.70
	6/20/01		0.07	0.07	0.30	0.28	7.71
DS-03	2/1/99	28	0.01	<0.01	<0.12	<0.12	6.95
	6/20/01		<0.01	0.02	0.26	0.29	6.86
DS-04 Bentonite	2/1/99	28	0.07	<0.01	<0.12	<0.12	7.37
	6/20/01		<0.01	0.03	0.54	<0.12	7.36
DS-05 Bentonite	2/1/99	28	0.06	0.02	<0.12	<0.12	7.16
	6/20/01		<0.01	0.01	0.12	0.56	6.99
DS-06 Bentonite	2/1/99	28	0.02	<0.01	<0.12	<0.12	7.18
	6/20/01		0.02	0.02	0.46	0.64	7.27
DS-07 Chelators	10/18/99	20	6.3	3.7	0.12	0.12	4.99
	6/20/01		1.76	1.64	0.63	0.54	6.33
DS-08 Chelators	10/18/99	20	51.7	51.9	0.40	0.40	6.80
	6/20/01		21.28	20.56	2.71	2.50	6.98
DS-09 Chelators	10/18/99	20	34.2	34.1	0.40	0.30	7.35
	6/20/01		13.52	13.38	1.61	1.84	7.41
DS-10 nitrate, phosphate added	2/8/99	28	2.75	2.42	0.49	0.28	7.45
	6/20/01		0.66	0.49	0.40	0.55	7.31
DS-11 nitrate, phosphate added	2/8/99	28	0.08	0.01	<0.12	<0.12	7.42
	6/20/01		0.01	0.01	0.32	0.44	7.44
DS-12 nitrate, phosphate added	2/8/99	28	0.01	<0.01	<0.12	<0.12	6.21
	6/20/01		0.03	<0.01	0.29	0.23	5.72
DS-13 massive metal	2/8/99	28	0.32	0.29	0.13	0.22	**5.95**
	6/20/01		0.29	0.29	0.26	0.41	**4.34**
DS-14 massive metal	2/8/99	28	0.08	0.05	<0.12	<0.12	**6.71**
	6/20/01		0.07	0.06	0.66	0.69	**5.45**
DS-15 massive metal	2/8/99	28	0.04	0.05	<0.12	<0.12	7.74
	6/20/01		<0.01	0.03	0.63	0.26	7.95

*1 Final brine sample taken when rotation of test containers was terminated.
*2 Final brine sample taken during D&D disassembly process; test container was not rotated during this period (ΔT).

Comments: There was not much change in concentration during the 20 to 28 month quiescent period of STTP. There was a decrease in the pcH in DS-13 and 14 during that period.

XVI. Experimental Study of Pu (VI) Stability/Instability in the Presence of Peroxide or Hypochlorite as Applied to STTP Tests

The radiolytic production of hypochlorite and peroxide in 5 M NaCl has been extensively studied, reported in the literature, and demonstrated in both basic and acidic conditions in solutions with high alpha activity. Also, the effectiveness of hypochlorite in oxidizing precipitated Pu to a soluble form has been reported in experiments conducted in the Federal Republic of Germany. However, the radiolytic behavior of Pu in > 3 M NaCl has been found to significantly differ from the Brine A and Castile Brine solutions synthesized to duplicate WIPP brines. Experiments conducted at LANL by Wolfgang Runde have demonstrated the stability/instability and speciation of Pu (VI) in Brine A, Castile Brine, and 5 M NaCl containing peroxide and hypochlorite in acidic, neutral, and basic pHs.

The experiments were conducted by adding a measured amount (~ 10^{-4} M) of peroxide (3.4 ppm) or hypochlorite (5 ppm) to Pu (VI) in Brine A, Castile Brine, and 5 M NaCl in acidic, neutral, and basic solutions and measuring the UV/VIS spectra on a repetitive basis for several days and up to 18 months to establish the stability or instability of the Pu (VI) in the various solutions.

Table 27. Study of Peroxide and Hypochlorite in Brine Solutions

Brine A	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Stable > 18 months	Stable > 18 months
7 – 8	Stable > 3 days but reduced at 18 months	Stable > 3 days but < 18 months; white precipitate formed
8 – 10	Stable > 3 days but reduced by 18 months	Slow-partial reduction up to > 18 months; white precipitate formed

Castile Brine	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
3 – 4	Very stable > 18 months	Stable > 18 months
7.0 – 7.5	Stable for 6 days and partially stable for 18 months	Stable > 18 months
7.5 – 8.0	Partial reduction to Pu (V) in 6 days	Stable > 18 months precipitate forms
9.0 – 10	Partial reduction on first day; mostly stable for > 18 months	Slow-partial reduction but mostly stable for > 18 months; precipitate forms

5 M NaCl	**Pu (VI) Stability/Instability**	
pH Range	**Peroxide**	**Hypochlorite**
2 – 4	Pu (VI) to Pu (V) in < 7 days	Stable > 18 months
7 – 8	Pu (VI) reduced in < 7 days	Slow-partial reduction then stable for > 18 months
8 – 10	Pu (VI) reduced in < 7 days	Pu (VI) slowly-partially reduced and then stable for > 18 months

The results of the experiments were pertinent in helping to provide an explanation of results that showed the presence of Pu (VI) under certain conditions STTP results and the following conclusions could be made:

1) The stability or instability of Pu (VI) was quite different in 5 M NaCl compared to Brine A and Castile brines, the synthetic brines used to mimic WIPP brines.

2) 5 M NaCl
    a) Hypochlorite effect – Pu (VI) was quite stable in acid, neutral, and basic solutions with hypochlorite for up to 18 months. Partial reduction occurred in basic solution.
    b) Peroxide effect – Pu (VI) was not stable in acid, neutral, and basic solutions with hydrogen peroxide. Pu (V) was detected in acid and neutral solutions but not basic solutions.

3) Brine A
    a) Hypochlorite effect
        1. Pu (VI) was very stable in acid solution for up to 18 months
        2. not stable in neutral solution
        3. somewhat stable in basic solution
    b) Peroxide effect
        1. Pu (VI) was somewhat stable in acid solution with partial reduction up to 18 months.
        2. Pu (VI) fairly unstable in neutral solution
        3. Pu (VI) stable for short term in basic solution but was reduced after 18 months

4) Castile Brine
    a) Hypochlorite effect
        1. Fairly stable in acid solution with partial reduction in 18 months
        2. Fairly stable in neutral solution with partial reduction in 18 months
        3. Fairly stable in basic solution with minimal reduction in 18 months
    b) Peroxide effect
        1. Very stable in acid solution for 18 months
        2. Fairly stable in with partial reduction in neutral solution in 18 months
        3. Very stable with some reduction in basic solution in 18 months

5) Hypochlorite and peroxide at the 10^{-4} M level (3-5 ppm) was added to each experiment; higher concentrations resulted in precipitation of Pu.

6) Precipitation of Pu with **hypochlorite** containing brine
    a) 5 M NaCl
        1. No precipitate in acid solution
        2. No precipitate in neutral solution
        3. A yellow-brown precipitate formed in basic solution

- b) Brine A
    1. No precipitate in acid solution
    2. White precipitate formed in neutral solutions
    3. White precipitate formed in basic solution (this was a voluminous precipitate)
- c) Castile
    1. Very small brown precipitate formed in acidic solution
    2. A brown to yellow amorphous precipitate forms in neutral and basic solutions with NaOCl

7) Precipitation of Pu with **peroxide** containing brine
    - a) 5 M NaCl
        1. No precipitate in acidic solution
        2. Small precipitate in neutral solution
        3. Yellow-brown precipitate in basic solution
        4. Green precipitate in one basic solution; may have had too much peroxide
    - b) Brine A
        1. No precipitate in acidic solution
        2. White precipitate in neutral solution
        3. Voluminous precipitate in basic solution
    - c) Castile Brine
        1. Perceptible yellow-brown precipitate in acidic solution
        2. Brown to yellow amorphous precipitate in neutral solution
        3. Brown to yellow amorphous precipitate in basic solution

8) LS-26 was a Brine A experiment with a pcH of ~ 8. Therefore, oxidation of Pu (IV) to Pu (VI) for about 24 months must have been from radiolytically produced hypochlorite in a slightly basic solution. At neutral pcH, hypochlorite was not effective in stabilizing Pu (VI). Hydrogen peroxide in neutral solution is also not effective in stabilizing Pu (VI) while basic solutions at pcH 9-10 are effected for short times but not on a long term basis. Also, it may be that in neutral solutions that both hypochlorite and peroxide precipitate Pu but can oxidize certain levels of Pu to Pu (VI).

9) LS-27 was a Castile Brine experiment with a pcH around 11.0 and identified Pu (V). Pu (VI) is stabilized by both hypochlorite and peroxide in strong basic solution or a mixture of the two oxidants.

10) LS-28 was a Brine A experiment with identified Pu (VI) for one sample at a pcH of 5.1. Pu (VI) was stabilized in acid solutions of Brine A with hypochlorite (hypochlorous acid) and transitorily stabilized with hydrogen peroxide.

11) LS-36 was a Castile Brine experiment with identified Pu (V) at pcH ~ 11.2. At that pcH level, both hypochlorite and peroxide or mixtures of the two are effective at stabilizing Pu (VI).

12) Addition of peroxide in excess of 10^{-3} to 10^{-4} M can result in immediate reduction of Pu (VI) and formation of a green precipitate that is presumed to be Pu (IV) hydroxide. Addition of excess hypochlorite can also result in precipitation of a Pu (VI) compound, perhaps Pu (VI) hydroxide.

Overall, the results of the experiments provided a better understanding of the STTP results that showed Pu (VI) in the Brine A experiments, LS-26 and 28 under basic and slightly acidic conditions, respectively. Also, the presence of Pu (V) in LS-27 and 36 in Castile brine at pcH ~ 11.1 could be attributed to either hypochlorite or peroxide formation or a mixture of both.

The results of the experiments accentuated the difference of redox chemistry in 5 M NaCl and both Brine A and Castile Brine. The results of the experiments also raises our awareness that serves as a precaution on the relevancy and applicability of explanations derived from experiments conducted under conditions different from what is reality in the WIPP.

XVII. Stability of Pu(VI) in Castile and Brine A

by Wolfgang Runde and Craig VanPelt, LANL

Formation of hexavalent plutonium in concentrated chloride media due to its own alpha radiation has been known for decades. Radiolysis causes the formation of oxidizing species, such as hypochlorite in basic solutions, which subsequently can oxidize plutonium in lower oxidation states to Pu(VI). The kinetics of this autoradiolytic oxidation process depends on many parameters, such as pH, specific activity, and chloride concentration. In the absence or presence of limited concentrations of any reducing agent, high alpha-activities in concentrated chloride solutions will generate oxidizing species that will stabilize Pu(VI). Most of the radiolysis studies reported in the literature have been performed in acidic solutions or in pure NaCl media. WIPP brines are more complex than pure NaCl solutions and contain other cations and anions (e. g. Mg^{2+}, K^+, SO_4^{2-}) that may contribute to solution speciation and redox stability of plutonium. To better understand the behavior of plutonium in high chloride media, we initiated experiments to study the stability of Pu(VI) in brines relevant to the WIPP. We used synthetic brines that were used for the STTP, Castile brine and Brine A, and 5 M NaCl for comparison and varied the pH in the presence of pertinent concentrations of hydrogen peroxide or hypochlorite. The redox agents were added to the brines to obtain approximately 10^{-4} M/L in hydrogen peroxide (3.4 ppm) or hypochlorite (5 ppm) and the pH was very slowly adjusted between pH 2 and 10 by addition of 1 M NaOH or 1 M HCl. Aliquots of an acidic (0.1 M) Pu(VI) stock solution were added to the samples and the absorbance spectra monitored as a function of time. The Pu(VI) concentration was between 10^{-4} and 10^{-5} mol/L (2.4 to 24 ppm) in order to avoid the well known autoradiolytic effects at higher plutonium concentrations.

In the presence of hypochlorite, Pu(VI) observed in the wavelength region 830 to 860 indicates that Pu(VI) in 5 M NaCl and Castile Brine remains stable in solution even after 18 months. The complexation of Pu(VI) and the formation of Pu(VI) hydrolysis products with increasing pH is reflected in the shift of the absorbance maximum towards higher wavelengths. These results confirm the reported effect of hypochlorite to stabilize Pu(VI). While Pu(VI) remains stable in 5 M NaCl and Castile Brine solution, the intensity of the absorbance signals generally decreased over a period of 18 months. This intensity decrease could be caused by changes in solution speciation, reduction of Pu(VI), or precipitation of a plutonium-bearing solid phase. Formation of brown precipitates is observed in Castile brine in acidic, neutral, and basic pH and in basic 5 M NaCl when hypochlorite is added to the solution. Shaking up the precipitate and taking the absorbance spectrum of the suspended solid in solution doubles the Pu(VI) absorbance intensity in comparison to the signal obtained in the absence of the solid phase. This finding reveals that Pu(VI) is contained in the brown solid phase and the precipitation of Pu(VI) contributes to the overall lower soluble plutonium concentration. **This result is very important in understanding the limitations of oxidized forms of plutonium as may occur in the STTP tests.** The formation of a Pu (VI) precipitate in the presence of hypochlorite provides a reasonable explanation of why the concentration of Pu (VI) in STTP LS-26 decreased with time. Further characterization (XRD, XPS, SEM) will provide more information on the nature of the brown solid phase.

In the presence of hydrogen peroxide, Pu(VI) exhibits a different chemistry than in the presence of hypochlorite where Pu(VI) is stabilized in Brine A, Castile, or 5 M NaCl solutions. Plutonium(VI) was observed to be instantly reduced by equimolar amounts of hydrogen peroxide present in 5 M NaCl. In 5 M NaCl, soluble Pu(VI) is observed only within days of reaction time and no absorbance of Pu(VI) is observed after 18 months. In acidic 5 M NaCl, the Pu(VI) signal at around 840 nm disappears and a small peak at about 560 nm suggests the formation Pu(V). The absence of an absorbance peak characteristic for Pu(V) complicates the oxidation state determination of plutonium at neutral and basic pH. In contrast to 5 M NaCl, Pu(VI) in Castile brine is observed in acidic, neutral, and basic conditions after 18 months. Under slightly acidic conditions, the Pu(VI) absorbance was totally stable for a period of 18 months. A measured reduction of Pu(VI) is observed within days of reaction time under neutral and basic conditions, however, between 20% and 40% of the initial Pu(VI) remain in solution after 18 months. In Brine A, Pu(VI) stays in solution only at slightly acidic (pH 3-5) conditions. At neutral and basic pH no absorbance of a Pu(VI) solution species is observed. **This result explains that the oxidation of Pu (IV) to Pu (VI) in the Brine A experiments, LS-26 and 28, was due to hypochlorite formation rather than hydrogen peroxide.** While no precipitation was observed in acidic Brine A, neutral or basic conditions result in the formation of a white solid phase in Brine A. The oxidation state of plutonium in this solid is under investigation. Only in one case was the formation of a green precipitate observed suggesting predominantly Pu(IV) in the solid phase. This precipitation occurred in 5 M NaCl at slightly basic conditions.

The described results indicate the complicated chemistry plutonium may exhibit under different conditions. It is established that the presence of hypochlorite stabilizes Pu(VI) and inhibits reduction of Pu(VI) to lower oxidation states in all investigated brines. The presence of Pu(VI) in the brown solid phase limits the soluble Pu(VI) concentration by the solubility product of this solid. Hydrogen peroxide, however, reacts with Pu(VI) and affects the stability of Pu(VI) significantly, especially in 5 M NaCl. In acidic 5 M NaCl, reduction of Pu(VI) to Pu(V) took place instantly and very low concentrations of Pu(VI) are observed after 18 months. In 5 M NaCl with peroxide, the oxidation state of plutonium is unclear because of the lack of absorbance peaks of Pu(IV) and Pu(V) species. Excess of hydrogen peroxide precipitates Pu(VI) and ultimately reduces Pu(VI) to a lower oxidation state. However, with limited amounts of hydrogen peroxide available, Pu(VI) may be only partly reduced and remains stable in solution for at least 18 months. Most interesting is the different behavior the Pu(VI) exhibits in 5 M NaCl, Brine A, and Castile. While Brine A seemed not to favor Pu(VI) and formation of a white solid phase occurred easily at neutral and basic pH, Pu(VI) was more stable than in 5 M NaCl. Pu(VI) was observed in Castile brine after 18 months independent of pH.

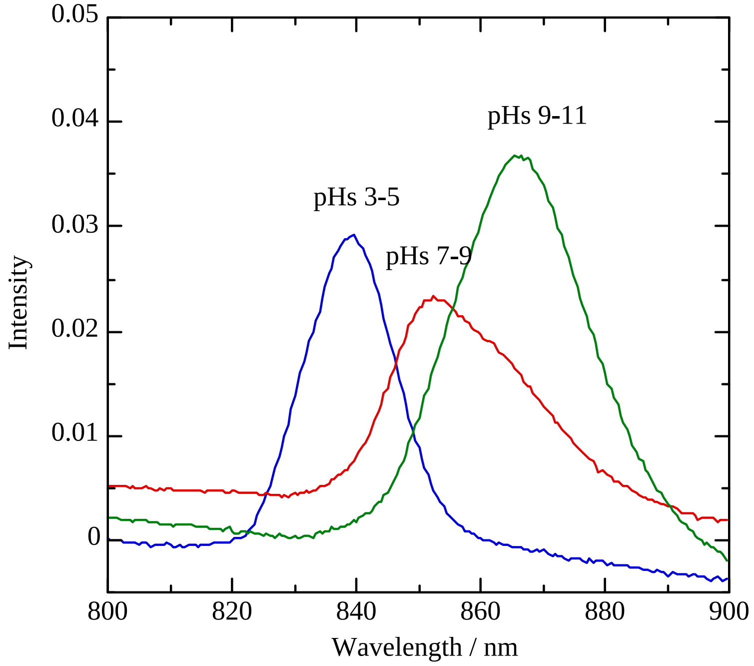


Figure 1. Characteristic absorbance bands for Pu(VI) with varying pH. With increasing pH, complexation of Pu(VI) with anionic ligands in solution shifts the absorbance maximum towards higher wavelength. In the absence of carbonate, formation of Pu(VI) hydroxo species are solution species that will form.

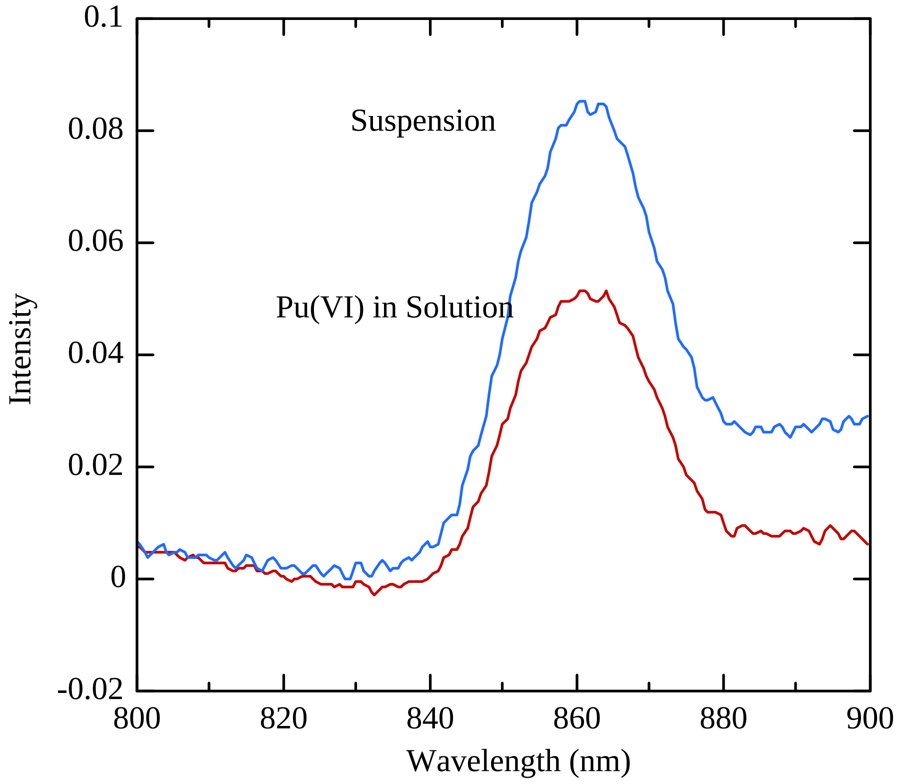


Figure 2. Pu(VI) absorbance in solution and in the presence of the brown solid phase precipitated in most of the Castile and in NaCl solutions. As an example, the Pu(VI) absorbance of alkaline Castile brine in the presence of hydrogen peroxide is shown. The increase in absorbance compared to that in solution indicates the presence of Pu(VI) in the solid phase.

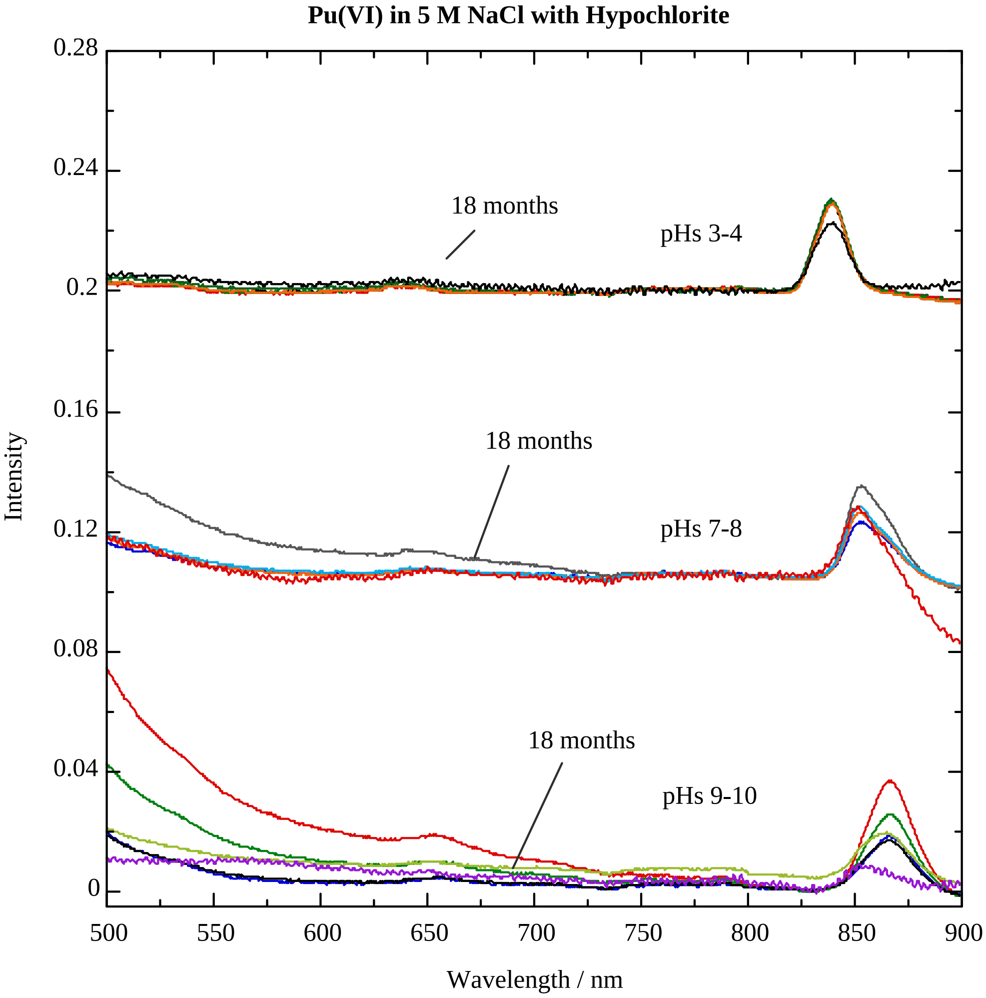


Figure 3. Pu(VI) absorbance spectra in 5 M NaCl in the presence of hypochlorite. The typical Pu(VI) bands are seen in all solutions even after reaction time of 18 months.

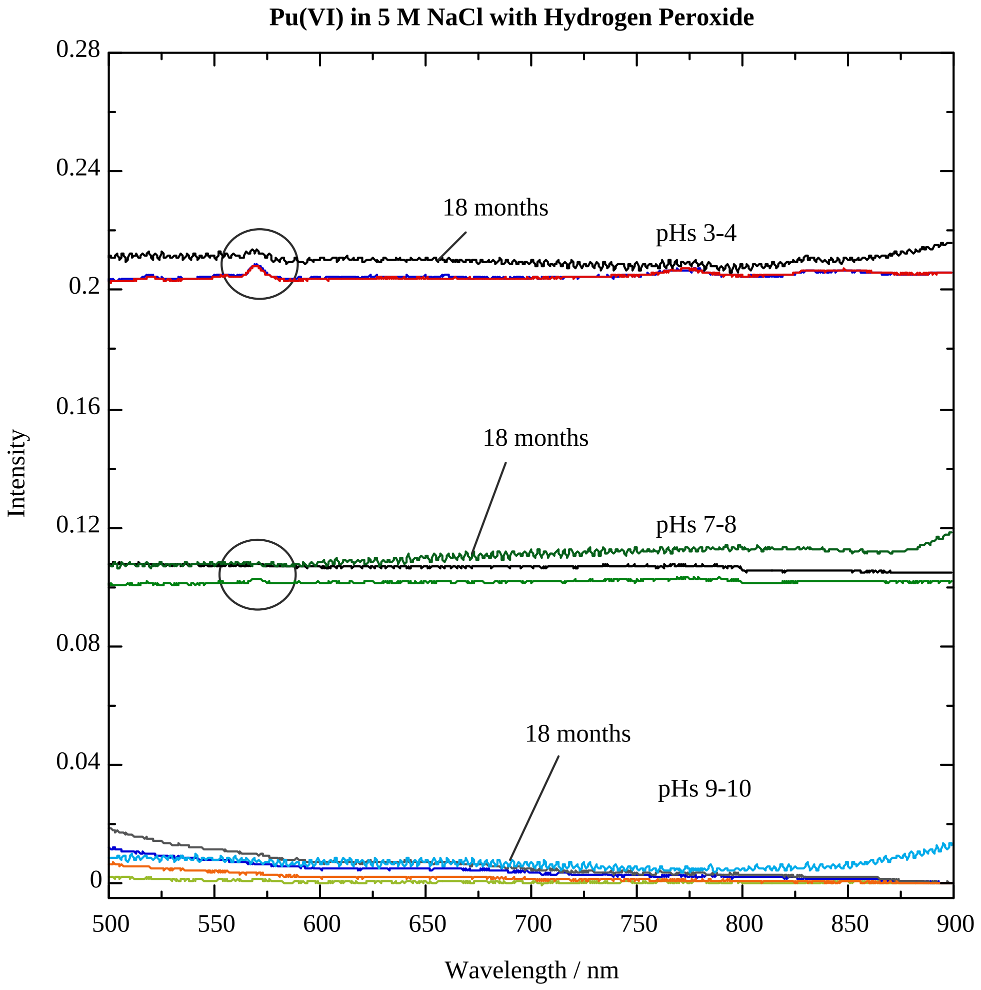


Figure 4. Pu(VI) absorbance spectra in 5 M NaCl in the presence of hydrogen peroxide. Reduction of Pu(VI) occurs instantly and the Pu(VI) bands disappear. The bands at about 550 nm indicate the formation of Pu(V).

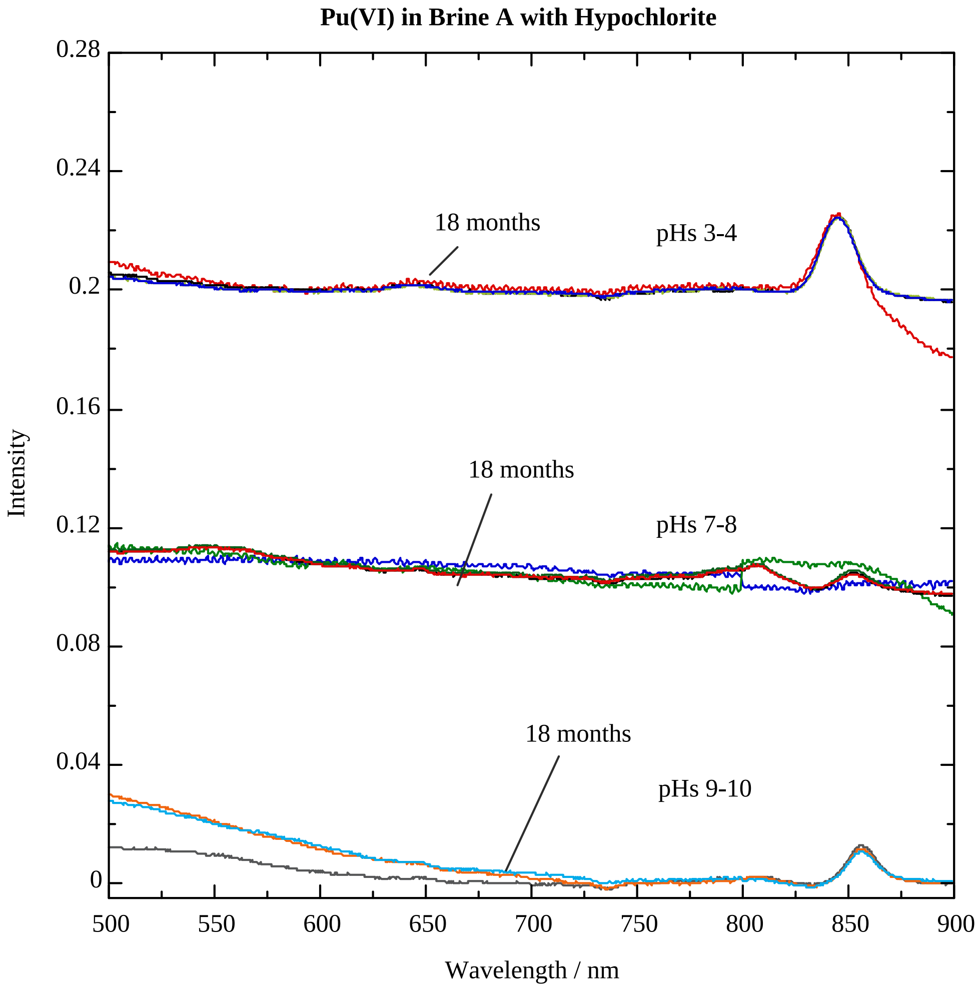


Figure 5. Pu(VI) absorbance spectra in Brine A in the presence of hypochlorite. Even after 18 months Pu(VI) remains in solution. White precipitation is observed at neutral and basic pH.

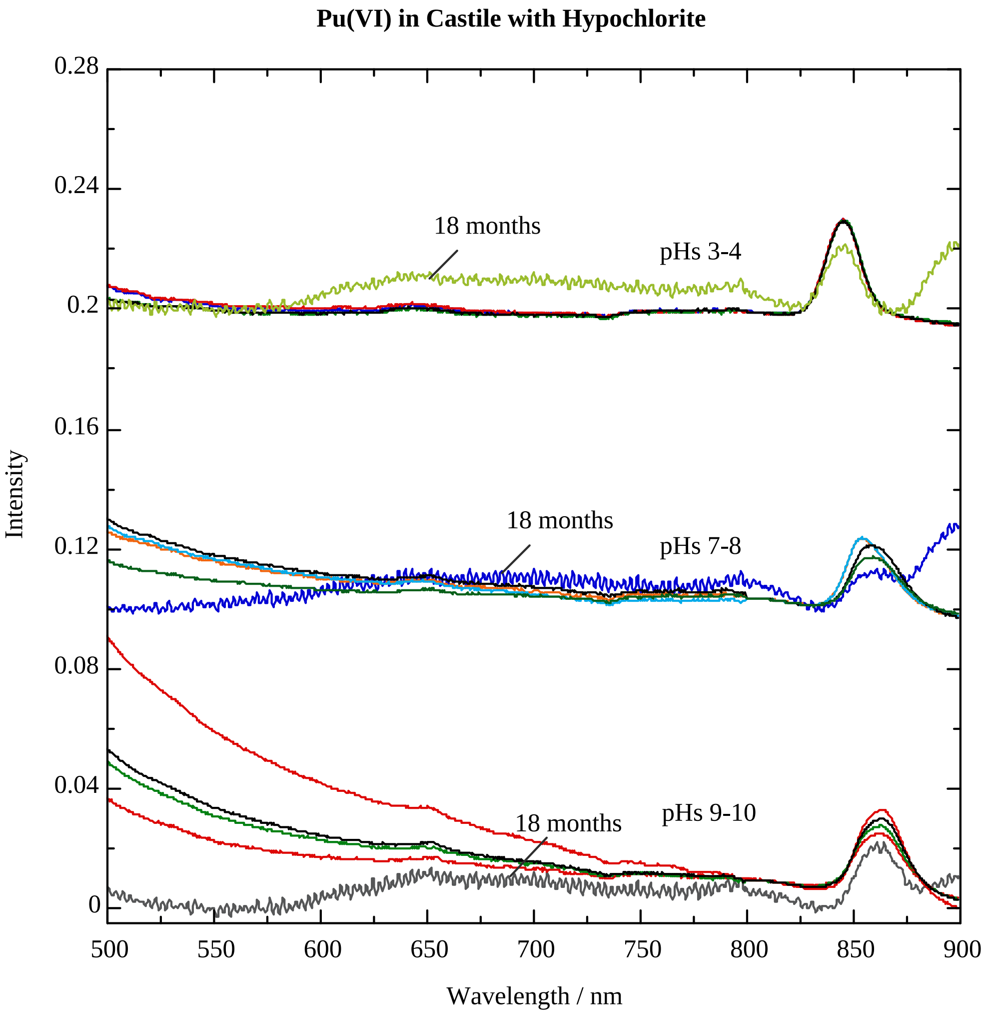


Figure 6. Pu(VI) absorbance spectra in Castile in the presence of hypochlorite. In contrast to Brine A, the characteristic Pu(VI) bands are observed in all Castile solutions with hypochlorite. Except at acidic conditions, precipitations of small amounts of brown Pu(VI)-containing solids are obtained.

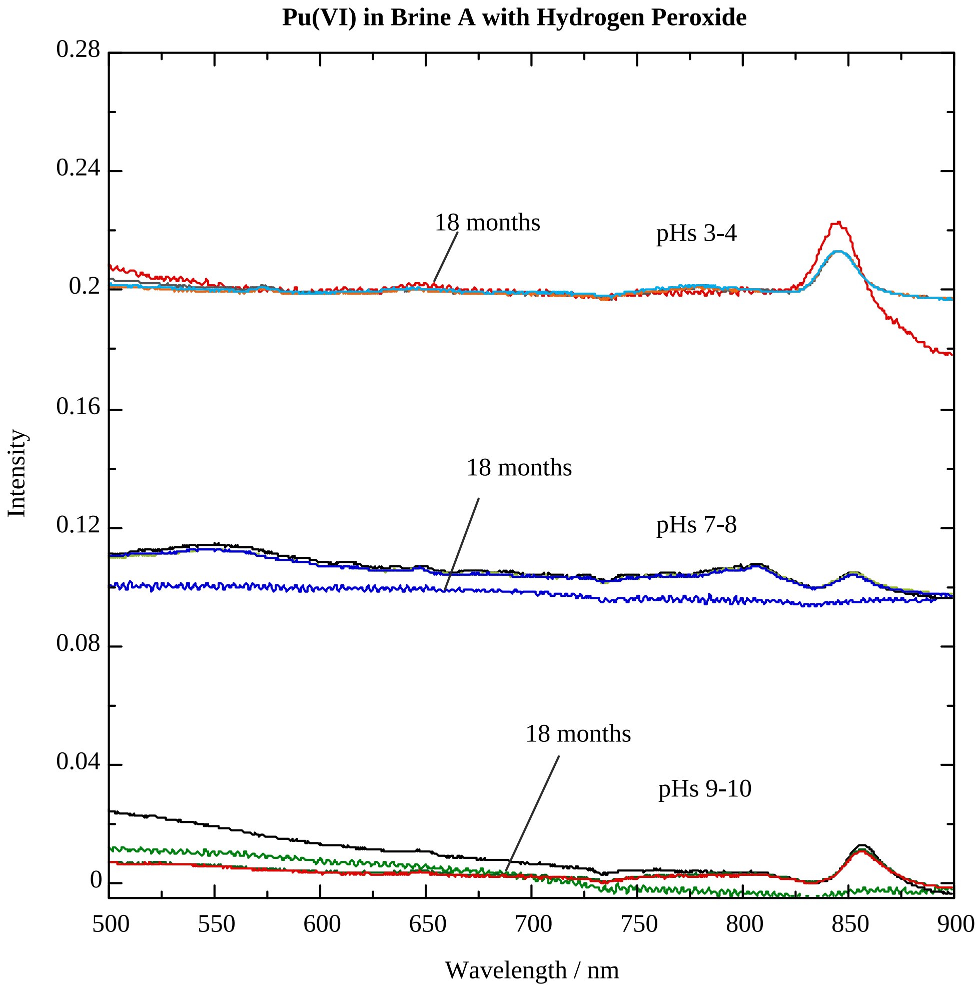


Figure 7. Pu(VI) absorbance spectra in Brine A in the presence of hydrogen peroxide. After 18 months, no Pu(VI) is observed in solution in neutral and basic pcHs; partial reduction in acidic solution at 18 months.

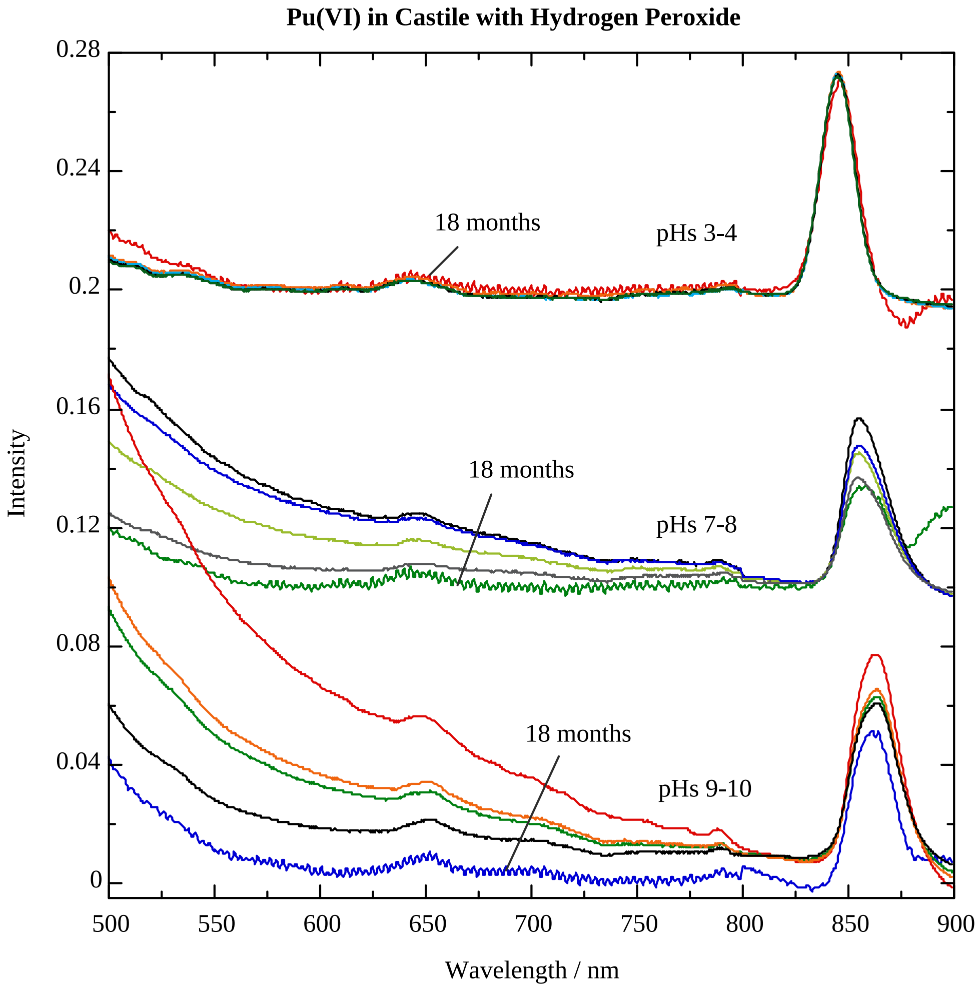


Figure 8. Pu(VI) absorbance spectra in Castile in the presence of hydrogen peroxide. After initial reaction of hydrogen peroxide Pu(VI) remains stable in solution. In contrast to Brine A, Pu(VI) is much more stable in Castile and can be found in solution after 18 months of reaction time.

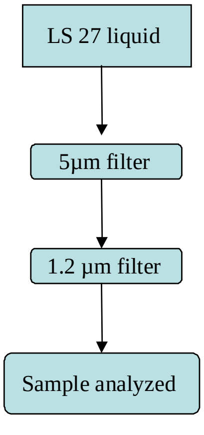
XVIII. Colloidal Study of LS-27 Brine with FFF and ICP-MS

The Castile Brine samples taken from the pyrochemical salt test, LS-27, contained some of the highest levels of actinide activities (except U) of the STTP. The concentration of Pu at 243,438 ppb and Am at 825 ppb on the same sample were the highest in the STTP. The concentrations of Nd, Th, Np, Pu, and Am were high from the first sample taken 5/8/95 and continued to increase to a peak concentration on 10/30/95, then slowly decreased for the remainder of the test. A large number of analyses of different kinds were conducted on LS-27 in an attempt to explain why this particular test had such high actinide activities, especially Pu and Am. The high Pu activity was determined by UV/VIS spectroscopy to have Pu (V) but not Pu (VI). The ratio of Pu (V) to Pu (IV) was not determined.

A sample of Castile Brine was specifically taken to measure the activity associated with colloids in each size fraction of the particle population (10^{11} to 10^{12} particles/liter) from 0 to 350 nm particle size diameters. Studies conducted by measuring the difference in activity of the brine fractions after coarse filtration (1.2 μm) and fine filtration (10 nm) showed that only a small fraction of activity associated with colloids was in the brine between the two filtrations. An attempt to determine the actual particle size fraction that contained the activity attributed to a colloidal fraction was made by isolating different size fractions by a Field Flow Fractionation (FFF) technique and measuring the soluble actinides in each size fraction with an Inductively-Coupled Argon Plasma – Mass Spectrometer (ICP-MS) instrument. The FFF-ICP/MS results showed that all the activity in the sample was associated with the soluble fraction only and that none of the activity was associated with a certain size fraction of particles. There was a rather comprehensive study conducted on LS-27 brine because it had the highest Pu and Am activity. These results verified the results of activities measured on filtered and centrifuged brine that there was essentially no activity associated with a definitive colloid fraction in both all the Brine A and Castile Brine experiments in the STTP. It appears that colloids in the STTP were not stable in the STTP brines because of the high ionic concentrations of a mixture of Group I and II cations and associated chloride anions and, perhaps, the organic content was so low. If the conditions of the STTP are applicable to the conditions in the WIPP, then there would not be stable Pu-bearing colloids or colloidally-based actinide transport mechanisms from the activity in the WIPP repository.

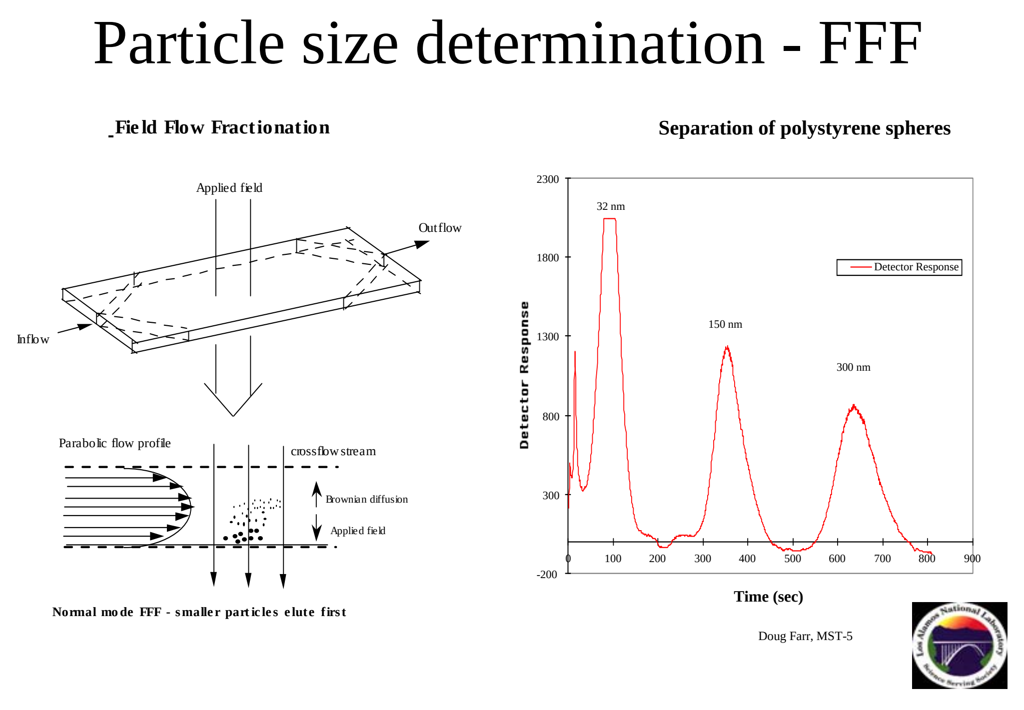
Figure 9.

Analysis of liquid from liter-scale 27 from STTP
Field-Flow Fractionation
and
Inductively Coupled Plasma Mass Spectroscopy



Doug Farr, MST-5

Figure 10.



Particle size determination - FFF

Field Flow Fractionation

Separation of polystyrene spheres

Doug Farr, MST-5

FFF separations are done by flowing a sample and carrier fluid within a flat open channel usually having a rectangular cross section and possessing triangular end pieces where the fluid enters and leaves. The channel dimensions are 20 to 100 cm long and about 1 to 3 cm wide, and 0.05 to 0.5 mm thick. A field, either gravitational, thermal, flow, electrical, or centrifugal, is applied perpendicularly the flat face of the channel. This field drives the sample molecules or particles across the thin channel towards the accumulation wall. The particles (or molecules) establish equilibrium positions in the channel that depend on factors such as how strongly the particles interact with the field and the sample diffusivity.

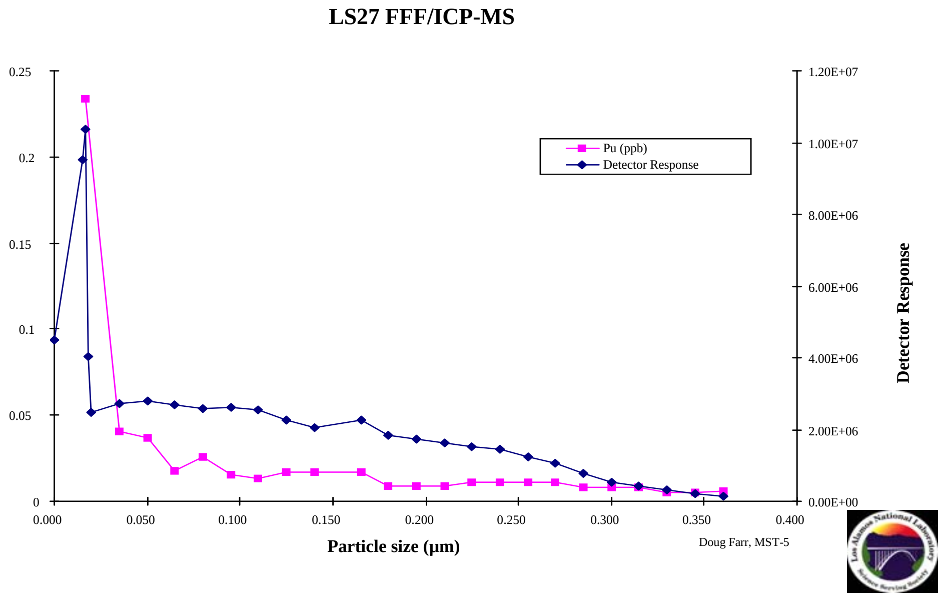
In flow FFF the channel and crossflow streams meet at right angles to each other and are blended. The parabolic channel stream carries the sample towards the outlet while the crossflow, which exits through the semipermeable membrane, drives the sample towards the accumulation wall. The force which drives particles towards the accumulation wall is the viscous force applied to the sample by the crossflow stream, described by Stoke's Law and the Stoke's-Einstein equation:

$$|F| = f|U| = kT|U|/D = 3\pi\mu|U|d$$

When the applied viscous force f|U| is equaled by the opposing effects of diffusion D, the particles equilibrate at a characteristic mean level above the accumulation wall. Each particle size has a different diffusion coefficient and thus will occupy different flow velocity streamlines and elute at different times.

Figure 11.

Solution phase Pu



Field Flow Fractionation (FFF) and Inductively-coupled plasma mass spectroscopy (ICP-MS) show that Pu is in the “soluble” fraction of the coarse-filtered aliquot from liter-scale 27. Pu concentrations were determined by ICP-MS from fractions that were collected as they eluted from the FFF channel. Detector response for the FFF system shows a strong “void peak” at the beginning of the run, around 25 nm. This peak arises from the unretained liquid in the sample and is seen in every fractionation run. The fraction collected from that region contained virtually all of the Pu that was in the sample. Any particles or molecular complexes in that fraction were less than 50 nm in size.

XIX. Reduction of Nitrate

There was a great diversity of starting concentrations of nitrate in the STTP tests as some tests were initiated with < 100 ppm whereas other tests had up to 60,000 ppm nitrate. Nitrate in contact with brine can be considered to be totally soluble in the brine. Many of the test containers showed a decrease in nitrate concentration of about 50% during the length of the test period. The reduction can be expected because about 54% of the brine in the test containers was replaced as part of the sampling and replenishment operation. However, there were certain tests that showed reduction of 80 – 100% of the nitrate and those are the tests that provided information on the destruction of nitrate. A listing of the tests that exhibited significant decreases is given below.

Table 28. Reduction of Nitrate in STTP Tests

Test Container ID	Influencing Variable	Nitrate Reduction, ppm	% Reduction
LS-13	Added organics	792 - 11	98.6
LS-14	Added organics	600 - 8	98.7
LS-18	Envirostone	3,400 - 134	61.0
LS-31	Bentonite	5,250 - 50	95.0
LS-32	Bentonite	1,030 - 28	97.3
LS-33	Bentonite	9,100 - 33	>99.0
LS-34	Chelators	1,020 – 22	98.0
LS-35	Chelators	940 – 20	98.0
LS-37	Am-241	960 – 85	91.0
LS-39	Am-241	2,000 – 219	89.0
DS-10	Added NO_3/PO_4	683 – 8	99.0
DS-11	Added NO_3/PO_4	440 – 5	99.0
DS-15	Metals	234 - 0	100

From the above listing of test containers with significant reduction of nitrates, it is apparent that the reduction occurred in a diversity of liter-scale and drum-scale tests. The cause of the reduction could be chemical, microbial, or radiolytic or a combination of all three. Six Envirostone test containers (LS-19, LS-20, LS-21, LS-22, LS-23, LS-24) had over 40,000 ppm (0.65 molar) of nitrate and up to 40% N_2O in the headspace of the test container. The reaction products of the destruction of nitrate can be different amounts of nitrite, N_2O and N_2 depending on the reduction mechanism. The production of nitrite and N_2O leads to a reducing environment in the brine because nitrite is a reducing agent very soluble in brine that stabilizes Pu in the Pu(IV) oxidation state. N_2O is a gas that has a solubility of ~ 1300 cm^3 per liter of water at 20ºC and is a reductant that would maintain Pu in the Pu(IV) state and preclude oxidation to higher oxidation states. Consequently, nitrate concentrations in the wastes would be a source of reducing agents under certain conditions. The pyrochemical salt tests had very low nitrate concentrations and would not be a source of reducing agents.

XX. Mg and Ca Concentration vs. pcH

Table 29. Mg and Ca Concentration vs. pcH

ID	pcH	Mg	Ca
LS-03	13.0	<10	130
LS-09	13.0	<10	120
LS-12	13.0	<10	120
LS-36*	11.2	<10	80,000
LS-27*	11.0	<10	80,000
LS-02	10.5	<1	40,000
LS-11	10.3	<10	40,000
LS-33	9.6	400	800
LS-39	9.6	1400	700
LS-08	9.1	2,000	36,000
LS-07	8.7	25,000	12,000
LS-01	8.8	21,000	18,000
LS-10	8.7	22,000	12,000
LS-34	8.8	23,000	9,000
LS-31	8.8	28,000	1,200
LS-32	8.7	30,000	800
LS-35	8.2	24,000	80,000
LS-19	8.0	25,000	1,100
LS-26*	8.0	21,000	70,000

* Pu(V) or (VI)

XXI. STTP Anion Results and Trends

Liter-Scale Tests

The anions routinely measured in STTP samples were fluoride, nitrate, phosphate, sulfate, and chloride. A trend in the concentrations of these anions would be indicative of some of the chemistry that would be occurring in the brine. A trend downward would be indicative that a soluble anion could be forming an insoluble precipitate that would settle out and thereby show a decrease in concentration. Also, radiolytic degradation could reduce the concentration of a soluble anion. An increase in the concentration of anions could be indicative of a solubilization of a waste yielding a higher concentration or that the anion was being produced as a radiolytic by-product. In the STTP liter-scale tests, only one increase in concentration of a soluble anion in the brine was found. LS-33, a pyrochemical salt experiment in Castile Brine that had added bentonite showed an increase in sulfate concentration from 6000 to 9000 ppm during the length of the test. No explanation is given for this increase.

Nitrate concentrations tended to decrease in all tests but was significant in at least 8 to 10 test containers as shown in TABLE 1. The decrease in nitrate concentrations in the Envirostone tests, which had the highest concentrations of nitrate, was generally accompanied by an increase in the N_2O concentration in the headspace. The reduction of nitrate concentrations is considered to be from chemical oxidation-reduction reactions, radiolytic degradation, or microbial activity. The significance of the radiolytic or chemical reduction of nitrate is that nitrous oxide, N_2O, and nitrite, which are by-products of the degradation of nitrate are compounds that contain the lower oxidation state of nitrogen and are reductants. This reaction could preclude the oxidation of actinides to higher oxidation states. The higher oxidation states of Pu were not found in Portland Cement and Envirostone tests. Pu (VI) was only found in Pyrochemical Salt wastes which were all low in nitrate salts.

Phosphate was initially present in several test containers but apparently quite rapidly formed precipitates that settled and resulted in the reduction in concentration of phosphate in liter-scale tests.

Fluoride was generally low in concentration and could have formed both insoluble and soluble fluoride complexes. LS-35, 36, 37 and 38 were examples of a significant trend, indicating a reduction in fluoride concentrations.

Table 30. Anion Trends in STTP Liter-Scale Tests

LS-ID	NO_3^-, ppm	SO_4^{-2}, ppm	F^-, ppm	TOC, ppm	pcH	Pu, g
LS-01	282-152 ↓	650-594	28	30	8.8	0.02
LS-02	1400-568↓ ↓	600-416	10	40	10.4	0.11
LS-03	1600-992	14000-12387	12	50	13	0.12
LS-07	256-158	749-800	40	30	8.7	0.03
LS-08	1180-673	700-400	10	60	9.3	0.12
LS-09	1300-816	16000-14000	8	60	13	0.11
LS-10*	250-150	650-770	36	38	8.8	0.02
LS-11*	1000-657↓	600-387	10	40	10.3	0.13
LS-12*	1100-750	14600-13163	8	50	12.9	0.11
LS-13	700-11↓ ↓	7600-7100	38	3200	7.1	3.39
LS-14	600-8↓ ↓	7600-6500	45	3500	7.1	3.47
LS-15	260-163	16000-1500	<10	1200	6.9	0.04
LS-16	60-10	6400-6400	<5	400	7.5	0.62
LS-17	20000-11000↓ ↓	6800-6600	<10	350	7.8	1.47
LS-18	3000-134↓ ↓	15000-15000	20	400	7.8	2.59
LS-19	45000-28000	12000-9000	50	600	7.9	0.51
LS-20	46000-24000	14000-7830↓	110	380	7.6	0.08
LS-21	47000-28000	18000-18000	12	310	8	0.25
LS-22	55000-31000↓	5000-4800	225	450	7.1	0.25
LS-23	38000-26000	3800-3800	250	480	7.3	0.23
LS-24	40000-28000	11000-12000	25	370	7.7	0.5
LS-25	30-30	80-80	36	20	7.9	0.38
LS-26	60-40	70-70	36	20	7.8	4.06
LS-27	40-37	140-170	10	50	11.1	3.4
LS-31	80-50	4800-4500	5	30	8.7	0.81
LS-32	70-30	4700-4800	5	38	8.7	4.08
LS-33	100-33	6000-9000↑	5	30	9.7	1.15
LS-34	73-22	1200-780	5-3	80	8.8	2
LS-35	50-21	103-106	52-25	60	8.3	0.45
LS-36	61-123	160-200	20-2↓	130-50	11.3	11.13
LS-37*	11-85	61-58	90-34↓	30	7.8	4.33
LS-38*	60-70	150-140	30-10↓	40	7.8	2.74
LS-39*	230-220	15000-16000	-	30	9.6	4.48

* Added 75 mg of Am-241

Drum-Scale Tests

The first 12 STTP Drum-Scale test containers contained heterogeneous waste (debris waste) with TRUCON code 116 and DS-13, 14, and 15 contained massive metal components (TRUCON code 117) with some plastic bags.

Three sets of three drum-scale tests (DS-04 through 12) contained additives that were added during the loading at the Waste Characterization, Repackaging, and Reduction Facility. Drum-scale tests D-04, 05, 06 had added bentonite; DC-07, 08, and 09 had added chelators and DS-10, 11, and 12 had added nitrate as $NaNO_3$ and phosphate as NaH_2PO_4. There was 159 g of $NaNO_3$ and 258 g of $Na_2H_2PO_4$ added to DS-10, 11, and 12.

The anions in the drum-scale tests remained fairly constant throughout the test period except for nitrate. Nitrate in most drum-scale tests decreased during the test period due to chemical, microbial, and/or radiolytic processes. The nitrate in DS-10, 11, and 15 were dramatically reduced from 680 to 10 ppm (DS-10) and 440 to 5 ppm (DS-11), and 234 to <5 ppm (DS-15) as shown in TABLE II.

The degradation by-products from reduction of nitrate are reducing agents that will have a significant role in maintaining the waste in the WIPP repository in a reducing condition.

The concentration of sulfate did not change in any of the drum-scale tests. Fluoride was at a very low level during the test period in all drums (1-26 ppm).

Total organic carbon (TOC) increased continuously in all drum-scale test containers, perhaps, due to the chemical or radiolytic degradation of organic-based materials in the waste. The effect of microbial activity on these brine-immersed materials is unknown.

Phosphate was added to DS-10, 11, and 12 and decreased in concentration within 1 to 2 months to less than detectable limits. The concentration of all actinides in the brine remained very low in the experiments with added phosphate.

Phosphate in the form of $NaH_2PO_4 \cdot H_2O$ at a concentration of ~ 3 g per liter was added to DS-07, 08, and 09 to reduce the concentrations of soluble actinides in the drums with added chelators. Typically, the soluble actinide concentrations were reduced by 87 to 95 %.

Phosphate as a soluble complex had a limited lifetime in the brine of these experiments because of the formation of insoluble phosphate precipitates along with actinide phosphates.

A detailed description of the phosphate addition to DS-07, 08, and 09 is given in the document, “Phosphate Addition to Drums 7, 8, and 9 and its Effect on Soluble Actinide Species,” LA-UR-01-3081, May 2001.

Table 31. Anion Trends in STTP Drum-Scale Tests

Drum-ID	Additives	NO_3^-, ppm	SO_4^{-2}, ppm	F^-, ppm	TOC, ppm	pcH	Pu, g
DS-01	none	300-34	5000-4800	2	120-190↑	7.8	7.1
DS-02	none	46-40	5000-5000	5	150-248↑	7.8	8.15
DS-03	none	48-39	18000-17000	<1	130-190↑	7.0	8.19
DS-04	bentonite	90-20	5000-5000	15	110-180↑	7.4	9.11
DS-05	bentonite	46-20	4800-4800	8	650-800↑	7.3	9.38
DS-06	bentonite	150-145	17000-16000	5	230-370↑	7.1	10.78
DS-07	chelators	38-35	5000-5000	20	260-330↑	7.4	11.6
DS-08	chelators	800-800	5000-48000	26	360-540↑	7.2	14.94
DS-09	chelators	500-530	17000-17000	6	475-600↑	7.3	16.25
DS-10*	NO_3^-/PO_4^{-3}	680-10↓↓	4900-4900	12	380-590↑	7.5	16.44
DS-11*	NO_3^-/PO_4^{-3}	440-5↓↓	4700-4800	4	200-300↑	7.5	16.45
DS-12*	NO_3^-/PO_4^{-3}	600-550	17000-17000	2	200-600↑↑	6.5	16.7
DS-13	metals	10-<5	5000-5000	16	40-70↑	6.0	12.74
DS-14	metals	60-15	5000-4900	5	45-88↑	6.8	8.19
DS-15	metals	234-<5↓↓	17000-16000	1	70-137↑	7.8	16.22

* Added 159 gm of nitrate equivalent to 763 ppm

XXII. Effect of Brine Type on Fe after Phosphate Addition

The addition of sodium dihydrogen phosphate (258 gm or ~ 2060 ppm) to the three drum scale tests with chelators (DS-07, 08, and 09) was very successful in reducing the actinides by 90% by precipitation as insoluble phosphates. The precipitation was successful in all tests despite the high stability constant chelators such as citrate and oxalate. However, when the soluble Fe concentration was followed during the same period, a rather curious result was obtained in that the Fe concentration in the brine was not reduced in the tests with Brine A but was significantly reduced (>97%) in the test with Castile Brine (DS-09). There was essentially no difference in the waste for these tests and the pcH was about the same for all three tests. The major difference was the higher concentration of Mg in the Brine A and the higher concentration of sulfate in Castile Brine. The lack of Mg in the Castile Brine test in D09 is what is considered to be the reason that Fe precipitated in this test. This result supports the conclusion that Mg usurped much of the strong chelators by the common ion effect leaving the Fe in the test with less Mg to combine with phosphate and be precipitated. The high ionic strength of Brine A with a high concentration of Mg seems to have had a significant influence in minimizing the effect of soluble chelators on Fe relative to phosphate. This could be a significant finding for mitigating the solubilizing effect of chelators in the presence of high concentrations of soluble Mg in Brine A and Castile Brine in contact with MgO. The concentration of Fe before and after addition of phosphate in the three drum-scale tests is shown below.

Table 32. Impact of Phosphate Addition to Fe in D07, D08 and D09 Tests

	DS-07	**DS-08**	**DS-09**
Date	**Fe, ppm**	**Fe, ppm**	**Fe, ppm**
11-30-98	118	160	218
02-01-99	206	318	352
	Phosphate Added	**Phosphate Added**	
07-22-99	198	-	-
07-22-99	199	-	-
07-29-99	207	-	-
08-09-99	158	176	-
08-09-99	184	-	-
08-25-99	-	-	195
			Phosphate Added
09-20-99	-	55	**5**
10-18-99	138	122	**3**

Table 33. pcH Change after Addition of Phosphate

	PcH Before Addition	PcH After Addition
DS-07	7.5	5.2
DS-08	7.3	7.0
DS-09	7.3	7.4

Ca and Mg concentrations were not affected by phosphate addition.

* 258 gm of $NaH_2PO_4 \cdot H_2O$ is equivalent to ~ 2060 mg/liter or 2060 ppm in the drum-scale brine

XXIII. Phosphate Addition to drum-Scale tests with Chelators; Application to Sulfate

The drum-scale tests with added chelators were at least 2 to 3 orders of magnitude greater in concentration of all soluble actinides and Nd relative to other drum-scale tests. Drum-scale tests DS-7, 8, and 9 were loaded with combustible wastes (TRU CON code 116/216) with DS-7, and 8 containing Brine A and DS-9 containing Castile Brine. Each drum contained Th-232 (4.77g), Np-237 (4.97g), U-238 (4.97g) and 6.42 g of $NdCl_3$. Each drum contained ~ 5.3 liters of microbial inoculum that consisted of 1.06 liters of cake brine and sediment mixture (20%), 1.59 liters of muck-pile solution mixture (30%), and 2.65 liters of G-Seep brine from the Salado Formation (50%).

Based on experience established by assessing the impact of phosphates added to samples of brine from both liter-scale and drum-scale tests, it became obvious that phosphate was effective in reducing the concentration of actinides in STTP brine. However, this experience did not extend to drum-scale tests with added chelators. At the beginning of the STTP, phosphate in the form of $NaH_2PO_4 \cdot H_2O$ had been added to DS-10, 11, and 12 at a concentration of 258 g of $NaH_2PO_4 \cdot H_2O$ per drum or about 1.38 gm/liter based on a brine volume of about 49.4 gal/drum. This represented a concentration of 1.87 mole of $NaH_2PO_4 \cdot H_2O$ per drum or 0.0378 mole/liter. The phosphate concentration was about 0.0378 x 0.6882 = 0.0260 molar solution of phosphate. This is about 1.38 x 0.6882 = 0.95 gm of PO_4^{3-} added per liter or 950 mg/liter which is equivalent to 950 ppm. This concentration of phosphate appeared to be very effective for precipitating and reducing the concentration of actinides in DS 10, DS 11, and DS 12 and a decision was made to add phosphate to DS 7, 8, and 9 to establish the effectiveness of reducing actinide concentrations in the brine of these drums with added chelators.

The identity and concentrations of chelators added to DS-7, 8, and 9 given below.

Table 34. Identity and Concentration of Chelators Added to Drum-Scale Tests

Chelator	DS-07	DS-08	DS-09
Oxalic Acid, Na Salt $\cdot H_2O$	217 ppm	217 ppm	217 ppm
Sodium acetate	210 ppm	210 ppm	210 ppm
Trisodium Citrate $\cdot H_2O$	233 ppm	233 ppm	233 ppm
Acetamide	151 ppm	151 ppm	151 ppm
Ammonium thiocyanate	222 ppm	222 ppm	222 ppm

The concentration of phosphate as sodium orthophosphate or sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) added to each of the tests in DS-7, 8, and 9 was 3 gm per liter or ~ 567.75 gm/drum. This would represent 4.11 mole of $NaH_2PO_4 \cdot H_2O$ or 2.83 mole of phosphate per drum or a solution that is 0.0217 molar in phosphate . Addition of 3 gm of $NaH_2PO_4 \cdot H_2O$ per liter will give a concentration of ~ 2060 mg/liter or 2060 ppm of phosphate. After addition of the phosphate solution, each drum was rotated to mix the phosphate into the brine in the drum.

Effectiveness of the addition of phosphate to the drums with chelators is given below for DS-7, 8, and 9.

Table 35. Reduction in Nd and Actinide Concentrations, DS-07

Element	Average Conc. Before Adding Phosphate (ppb)	Lowest Conc. After Adding Phosphate (ppb)	Reduction Factor	% Reduction
Nd	3,807	40.0	95.6	99.0
Th	10,986	368	29,9	96.7
Np	19,100	1,050	18.2	94.5
U	18,162	721	25.2	96.0
Pu	1,546	32.0	48.3	97.9
Am	7	0.4	17.5	94.3

Table 36. Reduction in Nd and Actinide Concentrations, DS-08

Element	Average Concentration		Reduction Factor	% Reduction
	Before Adding Phosphate (ppb)	After Adding Phosphate (ppb)		
Nd	4,493	206	21.8	95.4
Th	13,338	5,488	2.44	59.2
Np	14,547	2,988	4.87	79.5
U	13,188	894	14.8	93.2
Pu	3,019	506	5.97	83.2
Am	34.9	2.77	12.6	92.1

Table 37. Reduction in Nd and Actinide Concentrations, DS-09

Element	Average Concentration		Reduction Factor	% Reduction
	Before Adding Phosphate (ppb)	After Adding Phosphate (ppb)		
Nd	3,520	388	10.4	90.4
Th	7,880	865.5	9.10	89.0
Np	16,900	1,841	9.20	89.1
U	16,300	826.5	19.7	94.9
Pu	2,180	371.5	5.86	82.9
Am	16.53	2.7	6.12	83.7

The stability constants of the added chelators to the STTP drum-scale tests DS07, 08, and 09 are dependent on the pcH and ionic strength of the solutions. The pcH of the brine solutions before and after addition of phosphate is given in the following data.

Table 38. Impact of Phosphate Addition to pcH of DS-07, 08, and 09

Liter-scale	Brine	PcH Before Addition	PcH After Addition
DS-07	Brine A	7.4-7.5	5.0-5.5
DS-08	Brine A	7.2-7.3	6.8-8.1
DS-09	Castile	7.2-7.4	7.4

The chelators added were very successful in solubilizing all actinides and Nd in three tests. Citrate and oxalate were expected to have the greatest effect in solubilizing the actinides as both have stability constants greater than the hydroxide radical in neutral to basic pHs. The concentration of those two chelators was 233 ppm and 217 ppm, respectively. We added phosphate at a concentration that was ~10 times the concentration of the citrate (2060 ppm vs 233 ppm) to try to precipitate the chelated actinides as insoluble phosphates. The reduction of all actinides and Nd averaged about 90% so the phosphate was successful in the metathesis of insoluble actinide phosphates with the soluble chelated species. Interestingly, the Fe, Ca, and Mg were not significantly affected by the addition of phosphate to the Brine A experiments DS-07 and DS-08 but the Fe was significantly reduced in DS-09, the Castile Brine experiment. This data supports the observation that high Mg content increases the ionic strength of Brine A experiments and reduce the effectiveness of chelators in solubilizing actinides in the presence of other chelators with similar stability constants.

Sulfate forms strong complexes in acid solution with tetravalent Pu as demonstrated by potentiometric and spectrophotometric changes. Sulfate does not have high stability constants as phosphate but in the absence of other complexing agents can have a significant effect in stabilizing Pu in the Pu (IV) state. However, the chemistry of Pu and sulfate in a basic media has not been extensively studied. In the absence of other organic and inorganic anions and complexing agents, sulfate has a stabilizing effect for maintaining Pu in the Pu (IV) oxidation state and could have had a major role in allowing Pu (IV) to be oxidized in the sulfate-deficient pertinent liter-scale tests with Direct Oxide Reduction salts.

XXIV. A Comparison of Actinide Concentrations; Rotation vs. Quiescent Mode

The STTP liter-scale and drum-scale tests were all rotated weekly during the 4-5 year test period to assure thorough mixing of the waste with the brine. The process of rotation was integrated into the STTP operation as a compromise that would allow more rapid steady-state conditions for actinides in the comminuted STTP wastes because a test time frame pertinent to the repository would not be practical. The condition in the repository would be more of a quasi-static or quiescent state because movement of brine would be initiated by massive salt creep that would occur relatively slowly compared to the time of the STTP tests. Sampling of STTP tests was conducted about 32 hours after rotation to allow precipitates and large suspensions to settle prior to sampling. On occasion, the needle from the sampling syringe would draw a settled material from the bottom of the test container screen that would eventually be filtered out in the filtering processes. The rotation process for all test containers continued until spring of 1999 (March, April timeframe) and the test containers were allowed to set without rotation for the remainder of the experiments. A comparison was made of the samples taken as part of the final rotation and a sample taken after the test containers set for 1 to 2 years in a quiescent mode after the final rotation had been conducted. The analytical results were compared to determine if there were any test containers that showed unusually large changes in concentration, especially high increases during the quiescent period. Abnormal decreases in activity were also noted to determine whether there was a significant difference between the rotation and quiescent modes of operation. The ICP-MS used for the final analysis of the quiescent mode samples was a newer instrument with greater sensitivity than the analyses made during the rotation mode of operation. It was expected that actinide concentrations would decrease during the quiescent mode because less leaching of the waste would be effected during the quiescent period and small particulate could be adsorbed/absorbed by aged precipitates.

Portland Cement Test Results

The results of the Portland Cement tests were generally a comparison of very low levels of actinide concentrations. The comparison of actinide concentration during rotation and quiescent periods of operation showed in general that there was not a significant increase or decrease in concentration except for pressurized liter-scale test, LS-6 with Castile Brine. For LS-6, U increased during the quiescent mode from 3675 ppb to 7900 ppb and Pu decreased from 319 ppb to 4.2 ppb. The increase in U concentration can be explained because about 60 bar of CO_2 pressure was maintained on this test and U could certainly be solubilized as carbonates during the test period. The greater impact on the Castile Brine test is typical of other STTP test results. The large decrease of Pu from 319 ppb to 4.2 was rather surprising and no explanation is given for this change in concentration.

Envirostone Test Results

The actinide concentrations of the Envirostone tests varied more than the Portland Cement tests, especially the U and Pu results. Liter-scale tests LS-16 and LS-18 were examples of large increases in the concentration of Np, U, and Pu. LS-16 was unique in that it was on a definite upward trend of Pu and Np concentrations while U was on a significant downward trend. The increase of concentrations for Np (213 to 1000 ppb), U (182 to1800 ppb) and Pu (1187 to3000 ppb) is considered to be significant for a quiescent mode experiment and no explanation could be established for this difference in concentration. LS-16 was one of the only STTP tests that had a significant upward trend of Pu concentrations at the end of the test period. Likewise, LS-18 showed significant increases in concentration for Th (<0.10 to 7.9 ppb), Np (79 to 560 ppb), U (9519 to 29000 ppb) and Pu (2.7 to 18 ppb). No explanation could be established for the unusual increases in actinide concentrations for this test container. Most other Envirostone tests did not show significant increases in concentration.

Pyrochemical Salt Waste Test Results

The Pyrochemical Salt waste tests contained the highest levels of actinides and were expected to have some of the largest differences in concentrations of actinides between the samples taken during rotation and the samples taken after a lengthy quiescent mode. This expectation was not realized because most of the results did not show significant differences in actinide concentrations. Some of the large differences were noted in the following test containers.

LS-25 Pu increased from 39.8 to 250 ppb.
LS-29 (Pressurized) Pu increased from 6865 to 14000 ppb.
LS-30 U decreased from 2787 to 300 ppb.
LS-34 Pu increased from 13.5 to 87 ppb.
LS-36 Pu decreased from 1439 to 420 ppb.
LS-37 Pu significantly increased from 194 to 5500 ppb.

No explanation for the changes in actinide concentrations was attempted.

Drum-Scale Test Results

The drum-scale tests generally contained very low levels of soluble actinides except for DS-07, 08 and 09, which had added chelators. The levels of activity in these test drums were reduced by addition of sodium dihydrogen phosphate late in the test. The concentrations of actinides in the drum-scale tests conducted during the rotation phase were generally a little higher than the sample analyzed after the quiescent mode, as expected. The examples of tests with significant differences are summarized as follows.

DS-09 All actinides decreased significantly
    Nd (293 to 0.28 ppb)
    Th (794 to 2.0 ppb)
    Np (1615 to 5.4 ppb)
    U (728 to 4.7 ppb)
    Pu (328 to 140 ppb)
    Am (2.4 to 0.5 ppb)

DS-12 All actinides increased significantly
- Nd (<2.0 to 190 ppb)
- Th (<1.2 to 1000 ppb)
- Np (<0.8 to 1200 ppb)
- U (4.6 to 450 ppb)
- Pu (<1.3 to 220 ppb)
- Am (<0.4 to 1.1 ppb)

The differences in the above two test containers are so significant that a confusion of these two samples must be considered. There is no other explanation for the large differences in concentration of the two sets of data.

Overall Assessment of Comparison of Samples with and without Rotation

The environment in the WIPP repository is projected to be fairly static or quiescent for most of the lifetime of the repository. If brine is present in sufficient quantities to immerse the waste, the only perturbation to the brine in the Disposal Room environment would be due to massive salt creep closure movement which is projected to be relatively slow during the 20 to 200 year closure timeframe. A more vigorous brine perturbation could occur on a one-time basis due to human intrusion or geologic upheaval. Given the conditions that are projected for the repository, the concentration of actinides in actual non-comminuted wastes assumed to be immersed in quiescent brine would be at considerably lower levers than found in the STTP tests. For the STTP, the comparison of samples taken during the rotational phase was not significantly different from the sample set taken after one to two years in a quiescent mode.

Analytical Results of Final Sampling of STTP Test Containers in a Quiescent Mode

The analytical data obtained for the final set of samples taken after the liter-scale and drum-scale test containers remained in a static mode for up to 2 years at 30°C is presented. The results were obtained on an ICP-MS that was newer and had a greater sensitivity for actinides than the ICP-MS used for the earlier samples taken during the rotational phase of the STTP. The newer ICP-MS was located in a different laboratory at TA-48 and the final samples were transported to that laboratory for analyses. A comparison follows for the final samples taken during the test phase when the test containers were rotated and analyzed by the ICP-MS in the CMR building and the final samples analyzed at TA-48. The greater sensitivity and lower detection limit of the new TA-48 ICP-MS is most evident in the Am-241 results. The comparison of the two sample sets for Portland Cement, Envirostone, Pyrochemical Salts and Drum-Scale Heterogeneous wastes follows.

Table 39. Final Sampling of STTP Liter-scale Test Containers (Reportable results ppb)

ID	Date	Nd-146	Th-232	Np-237	U-238	Pu-239	Am-241
LS-02	4/10/01	0.10	0.10	0.14	1.3	0.78	<0.0024
LS-03	4/13/01	0.062	0.25	0.22	14	1.7	<0.00063
LS-04	5/11/01	<0.28	3.767	1.4	6500	6.3	0.30
LS-05	5/11/01	<0.057	0.56	0.13	380	1.8	0.07
LS-06	4/21/01	<0.28	1.4	0.51	7900	4.2	0.29
LS-07	4/10/01	<0.057	0.40	130	15	1.0	<0.0011
LS-08	4/10/01	<0.057	<0.14	0.16	0.79	1.3	<0.0024
LS-09	4/27/01	<0.057	0.079	0.24	4.9	0.72	0.057
LS-10	2/7/01	<0.057	0.69	93	13	20	0.24
LS-11	2/7/01	0.10	0.16	0.15	5.1	1.2	<0.0024
LS-12	2/1/01	0.062	0.17	0.11	0.82	<0.78	<0.0024
LS-13	1/25/01	2.9	3.1	2.4	270	5.2	0.14
LS-14	1/19/01	13	2.2	0.95	320	6.8	0.27
LS-15	4/27/01	22	7.8	88	3500	17	0.30
LS-16	12/20/00	170	190	1000	1800	3000	3.9
LS-17	2/15/01	4.7	0.38	50	1000	1.5	0.063
LS-18	1/10/01	<1.1	7.9	560	29000	18	1.4
LS-22	4/10/01	1.1	0.39	2.1	1000	0.88	0.090
LS-23	3/14/01	6.1	0.64	250	770	2.6	0.89
LS-24	4/13/01	0.50	1.4	0.57	330	0.81	0.069
LS-25	4/10/01	<0.28	2.0	120	6.4	250	0.63
LS-26	1/25/01	<4.2	<14	9.1	<6.3	2400	12
LS-28	5/11/01	<52	430	580	410	86000	160
LS-29	6/6/01	30	130	9300	8200	14000	35
LS-30	6/6/01	0.77	29	100	300	710	0.69
LS-33	2/1/01	<0.084	<0.28	11	4.6	140	0.37
LS-34	4/10/01	<0.057	0.51	13	21	87	0.20
LS-35	3/14/01	0.43	36	630	34	83	0.83
LS-36	11/30/00	<0.42	16	4.4	0.85	420	3.4
LS-37	12/6/00	<8.4	0.47	15	0.93	5500	8.6
LS-38	12/20/00	<0.042	0.084	0.22	0.037	15	0.022
LS-39	11/15/00	<0.84	2.5	3.5	31	970	2.7

Table 40. Final Sampling of STTP Drum-Scale Test Containers (Reportable results ppb)

ID	Date	Nd-146	Th-232	Np-237	U-238	Pu-239	Am-241
DS-01	6/6/01	2.4	6.4	32	29	1.2	0.020
DS-02	6/6/01	0.82	2.7	23	180	0.81	0.020
DS-03	6/6/01	0.67	1.4	5.7	110	0.77	0.011
DS-04	6/6/01	0.10	1.2	2.3	13	0.29	0.008
DS-05	6/6/01	0.20	1.3	1.0	15	1.1	0.014
DS-06	6/6/01	0.21	1.3	17	39	1.3	0.015
DS-07	6/6/01	14	290	480	300	19	0.67
DS-08	6/6/01	78	5000	2400	760	210	1.6
DS-09	6/6/01	<0.28	2.0	5.4	4.7	140	0.50
DS-10	6/6/01	0.064	2.3	11	20	0.56	0.016
DS-11	6/6/01	0.091	1.3	6.0	51	0.25	0.026
DS-12	6/6/01	190	1000	1200	450	220	1.1
DS-13	6/6/01	<0.055	3.1	4.2	4.1	1.3	0.020
DS-14	6/6/01	28	1.3	11	6.1	0.84	0.022
DS-15	6/6/01	49	1.6	2.2	2.9	1.1	0.093

Table 41. Portland Cement Test Results
Actinide Concentrations after Final Rotation
vs.
Brine Quiescent State for 1-2 Years
(all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
LS-02	12/14/98	<2.0	<1.2	<0.9	1.2	<1.3	<0.4	10.3
	4/10/01	0.10	0.10	0.14	14	0.78	<0.0024	
LS-03	2/22/99	<2.0	<1.2	<0.9	9.6	0.60	<0.4	12.9
	4/13/01	0.06	0.25	0.22	14	1.7	<0.00063	
LS-04	9/21/98	<0.5	6.3	15.9	8507.0	255	0.70	7.3
	5/11/01	<0.28	3.8	1.4	6500	6.3	0.30	
LS-05	9/21/98	<0.5	0.6	1.7	479.0	13.9	<0.1	7.4
	5/11/01	<0.06	0.56	0.13	380	1.8	0.07	
LS-06	9/21/98	2.7	3.0	11.4	3675.0	319.0	0.90	7.6
	4/21/01	<0.28	1.4	0.51	7900	4.2	0.29	
LS-07	3/15/91	5.6	1.5	254.0	12.7	4.1	0.80	8.8
	4/10/01	<0.06	0.04	130	15	1.0	<0.0011	
LS-08	3/15/91	4.8	0.90	0.90	1.4	11.3	1.0	9.3
	4/10/01	<0.06	<0.14	0.16	0.79	1.3	<0.0024	
LS-09	3/15/99	4.3	0.90	0.80	3.2	3.6	1.0	13.0
	4/27/01	<0.06	0.80	0.24	4.9	0.72	0.057	
LS-10	3/15/99	5.9	3.2	32.5	11.9	21.5	1.9	8.7
	2/7/01	<0.06	0.69	93	13	20	0.24	
LS-11	3/15/99	3.9	1.0	0.60	1.1	6.4	0.7	9.7
	2/7/01	0.10	0.16	0.15	5.1	1.2	<0.0024	
LS-12	3/15/99	3.3	0.70	0.60	0.80	3.1	0.7	13.0
	2/1/01	0.06	0.17	0.11	0.82	<0.78	<0.0024	

* The first date for each test container is the final sample taken during the test phase with rotation. Analysis completed in the CMR building.
The second date is the sample taken after the quiescent mode. Analysis completed at TA-48 with newer ICP-MS.

Table 42. Envirostone Results
Actinide Concentrations after Final Rotation
vs.
Brine Quiescent State for 1-2 Years
(all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
LS-13	3/1/99	<2.0	<1.2	<0.9	1295.0	26.0	<0.4	7.1
	1/25/01	2.9	3.1	2.4	270	5.2	0.14	
LS-14	4/5/99	16.5	19.2	3.6	1651.0	62.0	1.4	7.1
	1/19/01	13	2.2	0.95	320	6.8	0.27	
LS-15	4/5/99	22.1	6.4	59.8	1052.0	22	1.3	7.6
	4/27/01	22	7.8	88	3500	17	0.30	
LS-16	2/22/99	51.2	282.0	213.0	182.0	1187.0	3.0	7.5
	12/20/01	170	190	1000	1800	3000	3.9	
LS-17	2/22/99	<2.0	<1.2	1.6	269.0	1.5	0.4	7.8
	2/15/01	4.7	0.38	50	1000	1.5	0.063	
LS-18	3/8/99	1.4	<0.10	79.0	9519.0	2.7	0.3	7.8
	1/10/01	<1.1	7.9	560	29000	18	1.4	
LS-22	2/22/99	2.5	<1.2	<0.9	619.0	2.4	<0.4	7.2
	4/10/01	1.1	0.39	2.1	1000	0.88	0.090	
LS-23	3/01/99	<2.0	<1.2	<0.9	261.0	8.2	<0.4	7.5
	3/14/01	6.1	0.64	250	77	2.6	0.89	
LS-24	2/22/99	<2.0	<1.2	3.5	267.0	2.0	<0.4	7.8
	4/13/01	0.50	1.4	0.57	330	0.81	0.069	

Table 43. Pyrochemical Salt Test Results Actinide Concentrations after Final Rotation vs. Brine Quiescent State for 1-2 Years (all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
LS-25	10/18/99	4.4	2.4	154	5.1	39.8	0.5	8.1
	4/10/01	<0.28	2.0	120	6.4	250	0.63	
LS-26	10/18/99	2.6	0.5	1.7	0.8	3287.0	9.9	8.1
	1/25/01	<4.2	<14	9.1	<6.3	2400	12	
LS-28	5/17/99	49.3	519.0	744.0	668.0	188463	347	5.1
	5/11/01	<52	430	580	410	86000	160	
LS-29	9/21/98	6.9	377	8179.0	9513.0	6865.0	36.6	4.7
	6/6/01	30	130	9300	8200	14000	35	
LS-30	9/21/98	6.0	32.9	135.0	2787.0	1011.0	2.8	6.6
	6/6/01	0.77	29	100	300	7.0	0.69	
LS-33	3/8/99	1.5	0.4	5.5	0.7	135.0	0.8	9.6
	2/1/01	<0.08	<0.28	11	4.6	140	0.37	
LS-34	3/8/99	1.6	11.1	152.0	74.0	13.5	0.60	8.8
	4/10/01	<0.06	0.51	13	21	87	0.20	
LS-35	3/8/99	1.0	62.0	1260.0	53.0	86.0	0.90	8.3
	3/14/01	0.43	36	630	34	83	0.83	
LS-36	3/8/99	1.4	53.0	16.5	4.4	1439.0	6.7	11.4
	11/30/01	<0.42	16	4.4	0.85	420	3.4	
LS-37	3/15/99	3.2	0.6	0.6	0.5	194.0	1.2	7.8
	12/6/01	<8.4	0.47	15	0.93	5500	8.6	
LS-38	3/15/99	4.2	0.6	0.9	0.9	16.8	0.8	8.0
	12/20/01	<0.04	0.08	0.22	0.04	15	0.022	
LS-39	3/15/99	4.1	0.8	5.9	31.1	1994.0	17.6	9.5
	11/15/01	<0.84	2.5	3.5	31	970	2.7	

Table 44. Drum-Scale Test Results
Actinide Concentrations after Final Rotation
vs.
Brine Quiescent State for 1-2 Years
(all results are in ppb)

Test Container	Date	Nd	Th	Np	U	Pu	Am	pcH
DS-01	2/1/99	6.5	10.6	44.0	45.0	1.8	0.6	7.7
	6/6/01	2.4	6.4	32	29	1.2	0.020	
DS-02	2/1/99	5.4	16.7	51.0	227.0	2.6	0.7	7.7
	6/6/01	0.82	2.7	23	180	0.81	0.020	
DS-03	2/1/99	1.5	0.8	0.9	142.0	0.6	0.5	6.9
	6/6/01	0.67	1.4	5.7	110	0.77	0.011	
DS-04	2/1/99	0.5	0.5	0.6	20.2	1.0	0.3	7.4
	6/6/01	0.10	1.2	2.3	13	0.29	0.008	
DS-05	2/1/99	<0.4	0.5	1.1	32.2	1.1	0.3	7.2
	6/6/01	0.20	1.3	1.0	15	1.1	0.014	
DS-06	2/1/99	<0.4	0.2	1.6	11.5	0.3	0.4	7.2
	6/6/01	0.21	1.3	17	39	1.3	0.015	
DS-07	10/1/99	39.8	368.0	1052.0	721.0	32.0	0.4	5.0
	6/6/01	14	290	480	300	19	0.67	
DS-08	10/18/99	197.0	6400.0	3508.0	980.0	538.0	2.6	6.8
	6/6/01	78	5000	2400	760	210	1.6	
DS-09	10/18/99	293.0	794.0	1615.0	728.0	328.0	2.4	7.4
	6/6/01	0.28	2.0	5.4	4.7	140	0.50	
DS-10	2/8/99	<2.0	23.7	312.0	131.0	24.9	<0.4	7.5
	6/6/01	0.06	2.3	11	20	0.56	0.016	
DS-11	2/8/99	<2.0	<1.2	1.6	25.2	1.2	<0.4	7.4
	6/6/01	0.091	1.3	6.0	51	0.25	0.026	
DS-12	2/8/99	<2.0	<1.2	<0.8	4.6	<1.3	<0.4	6.3
	6/6/01	190	1000	1200	450	220	1.1	
DS-13	2/8/99	55	<1.2	0.7	1.1	1.6	<0.3	6.0
	6/6/01	<0.06	3.1	4.2	4.1	1.3	0.02	
DS-14	2/8/99	18	<1.2	25.3	375.0	<1.3	<0.3	6.7
	6/6/01	28	1.3	11	6.1	0.84	0.022	
DS-15	2/8/99	<2.0	<1.3	44.7	404	<1.3	<0.4	7.7
	6/6/01	49	1.6	2.2	2.9	1.1	0.093	

XXV. Oxidation-Reduction (Eh) of STTP Samples

The measurement of the Eh or oxidation-reduction potential in STTP brines was accomplished by observing the response of a Pt electrode/Ag/AgCl reference electrode that had been calibrated in the high ionic strength brine solutions. Each measurement was completed after allowing the redox electrodes to achieve equilibrium in the solution as evidenced by an electrode readout drift of ≤ 1 mV/min. A measurement that resulted in a readout that failed to attain the ≤ 1 mV/min stability within 10 minutes was considered to not be in equilibrium. The measurement system was checked against a Fe^{2+}/Fe^{3+} ammonium sulfate solution in 1M H_2SO_4. The goal of the measurement of Eh is to establish the oxidation-reduction potential in a very complex and high ionic strength brine solution that actually expresses the thermodynamic red-ox state of the solution. To accomplish this measurement in the STTP solutions required a recognition that a large number of factors could yield results that are not representative of the thermodynamic properties of the solution such as variable exchange currents, non-electroactive redox couples in actual samples, mixed potentials, electrode poisoning, non-equilibrium of couples in non-ideal solutions, different gas compositions in the headspace of samples, and establishing Eh measurements in samples with a host of different cations, anions, and radiolytic levels. It would be presumptuous to assert that a comparison of the redox conditions in different test containers can be made. With some degree of confidence, one could say that a specific test container is changing in time from measurement to measurement in a specific direction. To establish whether a specific test container has established a specific oxidation-reduction environment requires that an arbitrary Eh value be selected to indicate whether a solution is oxidizing or reducing and to what extent the solution exhibits these properties.

An assessment of all the Eh measurements made of STTP samples resulted in a conclusion that only one test showed significant oxidizing Eh values, liter-scale No. 26. Interestingly, LS-26 was the test container that had the highest and most persistent concentration of Pu (VI). A graphic display of the Eh measurements made on select test containers and LS-26 is shown as follows.

Table 45. Select STTP Eh Results

Container ID	Content	Description	Most Recent Eh (mV)	Date	Redox
LS-03	Portland cement		-30.6	02-Jul-98	Reducing
LS-05	Portland cement	CO_2 pressure	-38.8	07-Aug-97	Reducing
LS-12	Portland cement	^{241}Am added	7.5	22-Jul-98	Reducing
LS-14	Envirostone	Organic added	11.2	09-Jul-98	Reducing
LS-15	Envirostone	Organic added	-10.9	09-Jul-98	Reducing
LS-26	Pyrochem. salt	DOR	441.4	09-Jul-98	Oxidizing
LS-27	Pyrochem. salt	DOR	220.6	09-Jul-98	Neutral
LS-36	Pyrochem. salt	DOR	190.7	15-Jul-98	Neutral
DS-04	Drum scale	Combustible	46.2	28-Jul-98	Reducing
DS-14	Drum scale	Metal	-89.8	17-Jun-98	Reducing

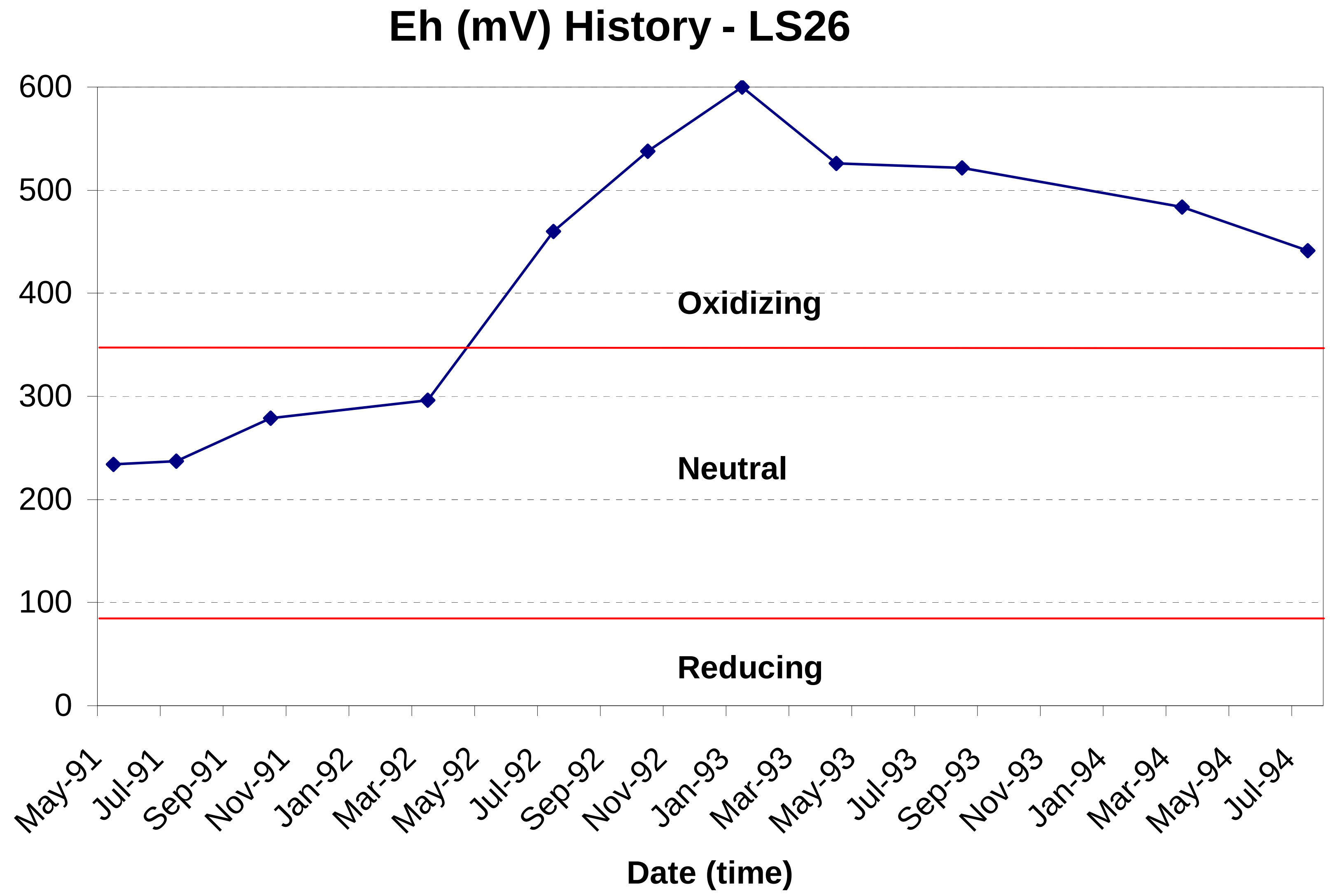
Eh: vs Ag/AgCl reference electrode
Red/Ox criteria:
Reducing is arbitrarily selected to be within 250 mV of the lowest measured value, -164.3 mV
Oxidizing is arbitrarily selected to be within 250 mV of the highest value, 600 mV

Table 46. LS-26 Eh History

Date	Eh (mV)
05-May-95	234.2 (Neutral)
13-Jul-95	237.2 (Neutral)
25-Oct-95	278.9 (Neutral)
14-Mar-96	296.3 (Neutral)
02-Jul-96	460 (Oxidizing)
02-Oct-96	538 (Oxidizing)
29-Jan-97	600 (Oxidizing)
30-Apr-97	525.8 (Oxidizing)
20-Aug-97	521.6 (Oxidizing)
01-Apr-98	483.3 (Oxidizing)
09-Jul-98	441.4 (Oxidizing)

Liter-scale test container L-26 had Pu (VI) and LS-27 and L-36 had Pu (V).

Figure 12.


Eh (mV) History - LS26
600
500
400
300
200
100
0
Eh (mV)
Oxidizing
Neutral
Reducing
May-91
Jul-91
Sep-91
Nov-91
Jan-92
Mar-92
May-92
Jul-92
Sep-92
Nov-92
Jan-93
Mar-93
May-93
Jul-93
Sep-93
Nov-93
Jan-94
Mar-94
May-94
Jul-94
Date (time)