Summary of Tests to Determine Effectiveness of Gelatin Strike on SS&C Dissolver Solutions

by

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May 26, 1998

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Executive Summary

The solutions from the dissolution of sand, slag, and crucible (SS&C) material are sufficiently different from previous solutions processed via the F-Canyon Purex process that the effectiveness of individual process steps needed to be ascertained. In this study, the effectiveness of gelatin strike was tested under a variety of conditions. Specifically, several concentrations of silica, fluoride, nitric acid (HNO_3), boric acid (H_3BO_3), and aluminum nitrate nonahydrate (ANN) were studied. The disengagement times of surrogate and plant SS&C dissolver solutions from plant solvent also were measured. The results of the tests indicate that gelatin strike does not coagulate the silica at the low concentrations of silica (~30 ppm) expected in the SS&C dissolver solutions because the silicon is complexed with fluoride ions (e.g., SiF_6^{2-}). The silicon fluoride complex is expected to remain with the aqueous phase during solvent extraction and not interfere with solvent extraction. The disengagement times of the dissolver solutions from plant solvent were not affected by the presence of low concentrations of silica and no third phase formation was observed in the disengagement tests with the low silica concentrations. Tests on surrogate SS&C dissolver solutions with higher concentrations of silica (>150 ppm) did show that gelatin strike followed by centrifugation resulted in good phase disengagement of the surrogate SS&C dissolver solution from the plant dissolver solution. At the higher silica concentrations, there is not sufficient fluoride to complex with the silica, and the silica must be entrained by the gelatin and removed from the dissolver solution prior to solvent extraction.

1.0. Introduction

Experiments were done to evaluate the effectiveness of gelatin strike on solutions from the dissolution of the sand, slag, and crucible (SS&C) material. Gelatin strike is done to remove silica prior to solvent extraction. The presence of undissolved silica in dissolver solutions leads to the stabilization of a detrimental emulsive third phase in solvent extraction.

These tests were done because the solutions from the dissolution of the SS&C material are different from the previous dissolver solutions that were subjected to gelatin strike. The previous solutions were from the dissolution of metal, and as a result, the final solution had a relatively low acid concentration (~1 Molar) compared to that expected for the SS&C solutions (~7-8 Molar). The SS&C solutions also will have higher fluoride concentrations because fluoride is added to the initial solution to help promote the dissolution of plutonium oxide, and any dissolved slag (calcium fluoride) also will contribute to the fluoride concentration. Another difference between the previous solutions and the SS&C solutions is the presence of boric acid (H_3BO_3) which is added as a neutron absorber. These experiments involved solutions with high acid and/or high fluoride concentrations and with or without H_3BO_3 . Several experiments were done with surrogate SS&C dissolver solutions, i.e., solutions that had been compounded to resemble the SS&C dissolver solution.

2.0. Background

Gelatin strike was implemented to remove silica from the F-Canyon solutions after the dissolution of the depleted uranium or natural uranium metal cores from target or fuel slugs. Silica impurities in the feed metal may be present in the dissolver solution as suspended material and/or as dissolved material. The silica can be detrimental to the subsequent solvent extraction because silica stabilizes emulsions (i.e., a third phase in the solvent extraction) and causes solids to collect in the solvent extraction equipment. Gelatin effectively coagulates the silica and the gelatin/silica coagulant can be removed from the dissolver solution via centrifugation.

There are concerns that silica contamination may arise in the solution from the dissolution of SS&C material because of silica impurities in the crucible that are estimated to be as high as 1 weight%. The solution resulting from the dissolution of metal material and that from the dissolution of SS&C material have important differences with respect to acid concentration, fluoride concentration, and H_3BO_3 concentration. Furthermore, aluminum nitrate nonahydrate (ANN) will be added to the SS&C dissolver solution prior to gelatin strike to complex the fluoride ions; such a step was not required for the dissolution of metal.

The differences between the two solutions are sufficient to require assurance that any deleterious effect of silica impurities can be mitigated by gelatin strike or that those impurities are complexed and soluble and do not pose a problem for solvent extraction. This study was done to understand how the dissolved silica will behave in the SS&C solution with respect to gelatin strike and to test the effect of the silica on the disengagement of the organic and aqueous phases of solvent extraction on the SS&C surrogate solutions with and without gelatin strike.

3.0 Hydrofluorosilic Acid Tests

A series of tests was done using hydrofluorosilic acid (H_2SiF_6) as the source of silicon. This silicon source was considered reasonable as the SiF_6^{-2} anion is a likely silicon species in the presence of relatively high fluoride concentrations (~0.2 Molar) that are expected for the SS&C dissolution solutions.

3.1 Experimental Details and Observations

A range of nitric acid (HNO_3) solutions (8 Molar, 4 Molar, and 1 Molar) were tested with the H_2SiF_6 to determine the effectiveness of the gelatin strike. The solutions had about 200 ppm silicon. No coagulation was observed immediately after the addition of 0.1 ml of a 1 weight% gelatin solution. The solutions were heated in a water bath for one hour at 50-60°C and no coagulation was observed.

A series of solutions with a range of silicon concentrations, in the form of SiF_6^{-2} , was made up at 1 Molar HNO_3 . Specifically the silicon concentrations in four solutions were: 200 ppm, 1000 ppm, 2000 ppm, and 4100 ppm. None of those solutions showed coagulation when 0.1 ml of 1 weight% gelatin solution were added. The

addition of 0.3 ml of the 1 weight% gelatin solution to a fifth solution with 1500 ppm silicon did not show any coagulation either. The five solutions were heated in a water bath for one hour at 50-60° C and no coagulation was observed.

3.2 Conclusions regarding Gelatin Strike

If the silicon is present as SiF_6^{-2} up to concentrations of 4100 ppm at 1 Molar HNO_3 , then the gelatin strike is ineffective in coagulating the silicon. Gelatin strike is also ineffective at low concentrations of SiF_6^{-2} over a range of HNO_3 concentrations. As a dissolved species, the SiF_6^{-2} is not expected to stabilize an emulsive third phase in the solvent extraction step and should remain with the aqueous phase.

4.0 Silica Sol Tests

The silicon may also be present as silica from a dissolved silica species to a colloidal or polymerized silica. Silica sols were used as the silicon source for several tests on the effectiveness of gelatin strike as a function of fluoride concentration, H_3BO_3 concentration, and ANN concentration. Most of the tests were done at 1 Molar HNO_3 . The silica sols were made up per a procedure given in "The Chemistry of Silica".¹ A 0.1 Molar solution of sodium metasilicate nonahydrate was made up. That solution was basic. The solution was warmed to about 35-40°C. Nitric acid was added slowly while the warm solution was stirred. The pH of the solution was checked very closely (i.e., after every addition of HNO_3) because the sol forms in a limited pH range: 8-9. If the solution becomes too acid, then a silica gel forms. Once the correct pH range was reached, the sol solution was allowed to cool and was used in subsequent experiments. Typically, new sol solutions were made every day.

4.1 Tests on Solutions with ~80 ppm Silica

The dissolution of the silica impurities in the magnesium oxide crucibles in the SS&C material is expected to yield dissolver solutions with up to 100 ppm silica. A series of tests was done on solutions which had about 80 ppm to examine the effect of fluoride concentration, H_3BO_3 concentration and ANN on the effectiveness of gelatin strike. After the gelatin was added, the solutions were heated for one hour at 50-60°C.

4.1.1 Effect of Fluoride Concentration

The effect of a small amount of fluoride on the effectiveness of gelatin strike was studied in solutions with 1 Molar HNO_3 . A 1 Molar potassium fluoride (KF) solution was used to make up the test solutions to 0.06 Molar fluoride concentration. Solutions without fluoride additions were studied as a control. The observations are given in Table 1. Those tests indicate that even the presence of a small amount of fluoride is sufficient to complex with the 80 ppm silica and prevent the gelatin from coagulating the silica.

4.1.2 Effect of Fluoride Concentration on H_3BO_3 Solutions

The F-Canyon dissolver solutions use boron as a neutron absorber. Those solutions are made up as 0.23 Molar H_3BO_3 . A series of tests was done to determine the effectiveness of gelatin strike as a function of fluoride in H_3BO_3 solutions. There were two concentrations of H_3BO_3 studied (0.16 Molar and 0.27 Molar) and five concentrations of fluoride from 0.06 Molar to 0.45 Molar. Potassium fluoride solutions provided the fluoride ions. All of the tests were done in 1 Molar HNO_3 . The results and observations are in Table 2. The presence of fluoride seemed to inhibit the effectiveness of the gelatin in coagulating the silicon.

¹ Iler, Ralph K., The Chemistry of Silica, Wiley-Interscience Publication, New York, 1979.

Table 1. Solutions with 0.06 Molar Fluoride/1 Molar HNO₃/80 ppm Silica

Identification	Fluoride Molarity	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silicon Ratio
A (03/09/98)	None	White coagulation	White coagulation	After 16 hours: white coagulation	0
A' (03/09/98)	None	White coagulation	White coagulation	After 16 hours: white coagulation	0
B (03/09/98)	0.06 M	Solution remained clear and colorless	Solution remained clear and colorless		20:1
B' (03/09/98)	0.06 M	Solution remained clear and colorless	Solution remained clear and colorless		20:1
B' (03/10/98)	0.06 M	Solution remained clear and colorless	Solution remained clear and colorless	After 20 hours: solution remained clear and colorless	20:1
B'' (03/10/98)	0.06 M	Solution remained clear and colorless	Solution remained clear and colorless	After 15 hours: solution remained clear and colorless	20:1
B'' (03/11/98)	0.06 M	Solution remained clear and colorless	Solution remained clear and colorless	After 16 hours: solution remained clear and colorless	20:1

A clear, colorless, crystalline phase was observed in solutions with high fluoride concentrations, i.e., T, T', U, U''(03/13/98), U''' (03/16/98), U''', and V''. Each of those solutions was filtered, the weight of the crystals was determined, and the crystals were submitted for analysis via x-ray diffraction. The amounts of the crystalline phase seemed to be related to the fluoride concentration, i.e., the highest weight came from the solution with the highest fluoride concentration. Those weights are given in Table 3. The solutions were about 17 milliliters.

Two compounds were identified in the crystalline phase: avogadrite (KBF₄) and hieratite (K₂SiF₆). Both compounds precipitated from Solutions T and U. Those solutions each had a H₃BO₃ concentration of 0.16 Molar; Solution T was 0.23 Molar with respect to the fluoride concentration and Solution U had a 0.35 Molar fluoride concentrations. Both compounds also precipitated from Solution V'' (0.27 Molar H₃BO₃ and 0.45 Molar fluoride). The KBF₄ compound was the predominant species. The remaining four solutions only showed KBF₄ in the precipitate. The presence of the K₂SiF₆ species substantiates the earlier assumption that if the fluoride:silicon ratio is large, then it is reasonable to expect that silicon will be complexed with the fluoride as SiF₆²⁻, for example.

4.1.3 Effect of ANN

Prior to the gelatin strike, it is anticipated that ANN will be added to the F-Canyon dissolver solution to assure that all of the fluoride ions are complexed. Free fluoride ions will have a deleterious effect on the solvent extraction step by competing with the nitrate ions for complexation with plutonium. Furthermore, free fluoride ions in the acid solutions will have corrosive effects on the stainless-steel equipment.

A series of tests was done using a ratio of ANN:fluoride of 0.5:1. This ratio was recommended for this study by Chemical Technology personnel that have been examining solvent extraction for solutions from the dissolution of SS&C material. The solutions were made up to the molarities designated for fluoride, H₃BO₃, HNO₃, and silicon. Then, if required, the ANN was added as a solid. No attempt was made to correct the molarities for the volume change caused by the ANN dissolution but the volume change is not expected to be more than 5%. Table 4 contains the observations of these tests. Again, the presence of fluoride seemed to inhibit the effectiveness of gelatin to coagulate the silicon. However, the ANN was successful in complexing the fluoride and preventing the precipitation of the KBF₄ and K₂SiF₆ compounds even at high fluoride concentrations.

Table 2. Solutions with up to 0.45 Molar Fluoride at 0.16 Molar and 0.27 Molar H_3BO_3 in 1 Molar HNO_3

Identification	Fluoride Molarity	H_3BO_3 Molarity	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silica Ratio
Q (03/12/98)	None	0.16 M	Milky cloudiness spreading through solution	Fine, white sediment settling to bottom	After 17 hours: fine white sediment settled to bottom	0
Q'' (03/13/98)	None	0.27 M	Milky cloudiness spreading through solution	Fine, white sediment settling to bottom	After 2 hours: fine white sediment settling to bottom	0
R (03/12/98)	0.06 M	0.16 M	Milky cloudiness spreading through solution	Milky cloudiness disappeared; solution clear and colorless	After 17 hours: clear and colorless solution - no sediment	20:1
R'' (03/16/98)	0.06 M	0.27 M	Solution became opaque	Opacity disappeared; solution clear and colorless	After 2 hours: clear and colorless solution - no sediment	20:1
S (03/12/98)	0.11 M	0.16 M	Solution remained clear and colorless	Solution remained clear and colorless	After 17 hours: solution remained clear and colorless	40:1
S'' (03/16/98)	0.11 M	0.27 M	Solution remained clear and colorless	Solution remained clear and colorless	After 2 hours: solution remained clear and colorless	40:1
T (03/12/98)	0.23 M	0.16 M	Solution remained clear and colorless	Solution remained clear and colorless	After 17 hours: solution remained clear and colorless; after 4 days a clear crystalline phase was observed	80:1
T'' (03/16/98)	0.23 M	0.27 M	Solution remained clear and colorless	Solution remained clear and colorless	After 2 hours: solution remained clear and colorless; after 2 days a clear crystalline phase was observed	80:1
U (03/12/98)	0.35 M	0.16 M	Solution remained clear and colorless	Solution remained clear and colorless	After 17 hours: solution remained clear and colorless but a clear, crystalline phase was observed	120:1
U'' (03/13/98)	0.35 M	0.27 M	Solution became opaque	Opacity disappeared; solution clear and colorless	Solution remained clear and colorless but clear, crystalline phase was observed	120:1
U''' (03/16/98)	0.35 M	0.27 M	Solution remained clear and colorless	Solution remained clear and colorless	After 4 hours: solution remained clear and colorless but there was clear, crystalline phase observed	120:1
U'''' (03/16/98)	0.35 M	0.27 M	Solution remained clear and colorless	Solution remained clear and colorless	After 2 hours: solution remained clear and colorless but there was clear, crystalline phase observed	120:1
V'' (03/16/98)	0.45 M	0.27 M	Solution remained clear and colorless	Solution remained clear and colorless	Solution remained clear and colorless but clear, crystalline phase was observed	160:1

Table 3. Weights of Sediments in Solutions with 0.23 Molar, 0.35 Molar, and 0.45 Molar Fluoride.

Identification	Fluoride Molarity	H ₃ BO ₃ Molarity	Weight of Crystalline Phase
T (03/12/98)	0.23 M	0.16 M	0.038 grams
T'' (03/16/98)	0.23 M	0.27 M	0.036 grams
U (03/12/98)	0.35 M	0.16 M	0.138 grams
U'' (03/13/98)	0.35 M	0.27 M	0.125 grams
U''' (03/16/98)	0.35 M	0.27 M	0.128 grams
U'''' (03/16/98)	0.35 M	0.27 M	0.125 grams
V'' (03/16/98)	0.45 M	0.27 M	0.205 grams

Table 4. Solutions with up to 0.35 Molar Fluoride at 0.27 Molar H₃BO₃ and 1 Molar HNO₃ with ANN added in the ratio 0.5 ANN:1 Fluoride

Identification	Fluoride Molarity	ANN	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silica Ratio
AA (03/17/98)	0.06 M	0.19 grams	Milky cloudiness spreading through solution	Opacity disappeared; solution clear and colorless; no sediment	After 15 hours: solution clear and colorless; no sediment	20:1
BB (03/18/98)	0.12 M	0.38 grams	Milky cloudiness spreading through solution	Opacity disappeared; solution clear and colorless; no sediment	After 15 hours: solution clear and colorless; no sediment	40:1
CC (03/18/98)	0.23 M	0.75 grams	Less milky cloudiness spreading through solution	Opacity disappeared; solution clear and colorless; no sediment	After 15 hours: solution clear and colorless; no sediment	80:1
DD (03/18/98)	0.35 M	1.13 grams	Solution clear and colorless	Solution remained clear and colorless	After 15 hours: solution clear and colorless; no sediment	120:1

4.1.5 Conclusions

Gelatin is ineffective at coagulating low concentrations of silica if fluoride ions are present at ratios of at least 20:1 fluoride:silicon. At high concentrations of KF, K₂SiF₆ precipitates at 1 Molar HNO₃. That precipitate indicates that silicon may be present as the SiF₆⁻² species if there is sufficient fluoride present for complexation. In addition, KBF₄ precipitates at high concentrations of KF in 1 Molar HNO₃. The addition of ANN inhibits the precipitation of the two potassium salts. It is possible that other silicon fluoride species may form in the dissolver solution, e.g., SiF₄ which is volatile.

4.2 Tests on Solutions with >200 ppm Silica

A series of tests was done on solutions in which the silicon concentrations were much higher, typically about 800 ppm. Those tests were done to determine how gelatin strike would perform if the fluoride:silicon ratios were sufficiently low that silicon could not be completely complexed by the fluoride ions.

4.2.1 Effect of Fluoride Concentration

The effect of fluoride on the effectiveness of gelatin strike was studied in solutions with 1 Molar HNO₃. The ratio of fluoride:silicon ranged from 2:1 to 16:1. A 1 Molar KF solution was used to provide the fluoride ions. Solutions without fluoride additions were studied as a control. The observations are given in Table 5.

Table 5. Solutions with up to 0.45 Molar Fluoride at 1 Molar HNO₃ with about 800 ppm Silica

Identification	Fluoride Molarity	Silica ppm	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silica Ratio
C' (03/10/98)	None	810 ppm	Milky cloudiness spreading through solution	Fine, white sediment settling to bottom	After 20 hours: fine white sediment settled to bottom	0
C'' (03/10/98)	None	810 ppm	Milky cloudiness spreading through solution	Fine, white sediment settling to bottom	After 15 hours: fine white sediment settling to bottom	0
D' (03/10/98)	0.06 M	810 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom of solution	After 20 hours: clear and colorless solution and fluffy white sediment	2:1
D'' (03/10/98)	0.06 M	810 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom of solution	After 15 hours: clear and colorless solution and fluffy white sediment	2:1
D'' (03/11/98)	0.06 M	810 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom of solution	After 16 hours: clear and colorless solution and fluffy white sediment	2:1
E' (03/10/98)	0.12 M	990 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom of solution	After 20 hours: clear and colorless solution and fluffy white sediment	4:1
E'' (03/10/98)	0.12 M	820 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom of solution	After 15 hours: clear and colorless solution and fluffy white sediment	4:1
F' (03/10/98)*	0.25 M	560 ppm	Solution opaque before gelatin added; no change when gelatin added	Opacity disappeared; solution clear and colorless	After 20 hours: solution remained clear and colorless; but when shaken gel-like material left on walls of vial	8:1
F'' (03/10/98)*	0.25M	910 ppm	Solution opaque before gelatin added; no change when gelatin added	Opacity disappeared; solution clear and colorless	After 15 hours: solution remained clear and colorless; but when shaken gel-like material left on walls of vial	8:1
F'' (03/11/98)*	0.23M	810 ppm	Solution opaque before gelatin added; no change when gelatin added	Two phases with aqueous phase about 95% of volume; denser phase about 5% of volume	After 16 hours: very thin, fluid, dense second phase; aqueous phase clear and colorless	8:1
G'' (03/11/98)	0.35M	810 ppm	Solution opaque before gelatin added; no change when gelatin added	Two phases with aqueous phase about 95% of volume; denser phase about 5% of volume	After 16 hours: very thin, fluid, dense second phase; aqueous phase clear and colorless; after several days second phase had gelled to solid	12:1
H'' (03/11/98)	0.47 M	810 ppm	Solution opaque before gelatin added; no change when gelatin added	Two phases with aqueous phase about 95% of volume; denser phase about 5% of volume	After 16 hours: very thin, fluid, dense second phase; aqueous phase clear and colorless; after several days second phase had gelled to solid	16:1

*Solutions F' and F''(03/10/98) were only four milliliters. Therefore, observation of the second phase would have been difficult compared to the observation in Solution F'' (03/11/98) because Solution F'' (03/11/98) was 20 milliliters.

The gelatin strike was effective for those solutions with KF concentrations up to 0.12 Molar. However, in solutions with higher KF concentrations, a dense second phase formed (Solutions F''[03/11/98], G'' and H''). The addition of gelatin did not have any visible effect on those three solutions. The fluoride:silicon ratio in the solutions with the dense second phase were 8:1, 12:1, and 16:1. Those three solutions were filtered and the solids were washed with water. The solids appeared crystalline and were identified as K_2SiF_6 .

4.2.2 Effect of Fluoride Concentration on H_3BO_3 Solutions

As mentioned previously, the F-Canyon dissolver solutions use boron as a neutron absorber. Those solutions are made up as 0.23 Molar H_3BO_3 . A series of tests was done to determine the effectiveness of gelatin strike as a function of fluoride in 0.27 Molar H_3BO_3 solutions. There were six concentrations of fluoride from 0.06 to 0.45 Molar. All of the tests were done in 1 Molar HNO_3 . The results and observations are in Table 6.

Gelatin strike does seem effective at coagulating silica at fluoride:silicon ratios of at least 8:1. At higher fluoride:silicon ratios, a clear, colorless, crystalline phase precipitated from solution and the addition of gelatin did not have any observable effect on the solutions. Solutions X and X'' were filtered and the crystalline phases were submitted for analysis. The x-ray diffraction pattern of the crystalline phase from Solution X showed both KBF_4 and K_2SiF_6 while the x-ray diffraction pattern of the crystalline phase from Solution X'' only showed KBF_4 . However, there was no silica added to Solution X'' so the absence of K_2SiF_6 was expected.

4.2.3 Effect of ANN

As discussed in Section 4.1.3, ANN will be added to the SS&C dissolver solution prior to the gelatin strike. The ANN addition is done to assure that all of the fluoride ions are complexed. Free fluoride ions will have a deleterious effect on the solvent extraction step by competing with the nitrate ions for complexation with plutonium. Furthermore, free fluoride ions in the acid solutions will have corrosive effects on the stainless steel equipment.

A series of tests was done using a ratio of ANN:fluoride of 0.5:1 similar to the tests described in Section 4.1.3. The silica concentration in these tests was about 810 ppm. Table 7 contains the observations of the tests. The addition of ANN did not seem to affect the effectiveness of gelatin strike. The addition of gelatin to solutions with 0.06, 0.12, and 0.23 Molar fluoride resulted in the formation of a white mass with and without the presence of ANN.

4.2.4 Conclusions

At higher concentrations of silica (200-1000 ppm) in 1 Molar HNO_3 and at KF concentrations up to 0.12 Molar, gelatin strike successfully coagulates at least some, if not most, of the silica; silicon fluoride complexes also may be forming in those solutions. At higher concentrations of KF (0.25, 0.35, and 0.47 Molar), a dense second phase forms which is not visibly affected by the addition of gelatin. That phase was identified as K_2SiF_6 . The presence of H_3BO_3 prevents the formation of K_2SiF_6 at KF concentrations up to 0.35 Molar. The boron probably is complexed with the fluoride. In the ≤ 0.35 Molar fluoride solutions, a white sediment forms with the addition of gelatin. At 0.45 Molar KF and 0.27 Molar H_3BO_3 , gelatin strike is not effective. Two potassium salts (KBF_4 and K_2SiF_6) precipitate at that concentration of KF prior to the addition of gelatin. The addition of ANN did not affect the effectiveness of gelatin strike for the 0.06, 0.12, and 0.23 Molar fluoride solutions that were studied. A white mass formed in all three of those solutions with the addition of gelatin with and without the presence of ANN.

4.3 Tests with Surrogate SS&C Dissolver Solutions

A series of tests was done to examine the effectiveness of gelatin strike on surrogate SS&C dissolver solutions. One surrogate solution was made up to simulate the solution from the dissolution of SS&C material. Another surrogate solution was made up except that the acid concentration was kept low. The compositions of the two surrogate dissolver solutions are described in Table 8 and the concentrations are given in Table 9.

Table 6. Solutions with up to 0.45 Molar Fluoride at 0.27 Molar H_3BO_3 in 1 Molar HNO_3

Identification	Fluoride Molarity	Silica ppm	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silica Ratio
I" (03/12/98)* (no H_3BO_3)	None	810 ppm	Milky cloudiness spreading through solution	Translucent mass floating in solution	After 20 hours: diffuse white mass floating in clear, colorless solution	0
I''' (03/13/98) (no H_3BO_3)	None	810 ppm	Milky cloudiness spreading through solution	White sediment settling to bottom	After 2 hours: white sediment settled to bottom of clear, colorless solution	0
J" (03/12/98)*	None	810 ppm	Milky cloudiness spreading through solution	Translucent mass floating in solution	After 20 hours: diffuse white mass floating in clear, colorless solution	0
J''' (03/13/98)	None	800 ppm	Milky cloudiness spreading through solution	White sediment settling to bottom	After 2 hours: white sediment at bottom of clear colorless solution	0
K" (03/12/98)*	0.06 M	810 ppm	Milky cloudiness spreading through solution	Translucent mass floating in solution	After 20 hours: diffuse white mass floating in clear, colorless solution	2:1
K''' (03/13/98)	0.06 M	810 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom	After 2 hours: fluffy white sediment settled to bottom of solution	2:1
L" (03/12/98)*	0.12 M	810 ppm	Milky cloudiness spreading through solution	Translucent mass floating in solution	After 20 hours: diffuse white mass floating in clear, colorless solution	4:1
L''' (03/13/98)	0.12 M	810 ppm	Milky cloudiness spreading through solution	Fluffy white sediment settling to bottom	After 2 hours: fluffy white sediment settled to bottom of solution	4:1
M" (03/12/98)*	0.23 M	280 ppm	Milky cloudiness spreading through solution	Translucent mass floating in solution; much less than II" - LL"	After 20 hours: diffuse white mass floating in clear, colorless solution; much less than II" - LL"	22:1
M''' (03/12/98)	0.23 M	810 ppm	Milky cloudiness spreading through solution	White fluffy mass settling to bottom of solution	After 17 hours: white fluffy sediment at bottom of clear, colorless solution	8:1
M''' (03/13/98)	0.23 M	810 ppm	Milky cloudiness spreading through solution	White fluffy mass settling to bottom of solution	After 2 hours: white fluffy sediment settled to bottom of solution	8:1
N" (03/12/98)	0.23 M	810 ppm	Milky cloudiness spreading through solution	White fluffy mass settling to bottom of solution	After 17 hours: white fluffy sediment at bottom of clear, colorless solution	8:1
W (03/16/98)	0.35 M	810 ppm	Two phases formed before gelatin added; after gelatin added solution was milky	White fluffy mass settling to bottom of solution	After 16 hours: white fluffy sediment settled to bottom of solution	12:1
X (03/16/98)	0.45 M	810 ppm	Two phases formed before gelatin added; after gelatin added no effect observed	Second phase observed but not white, fluffy sediment as observed before	After 16 hours: clear, colorless, crystalline sediment at bottom of clear, colorless solution	16:1
X" (03/16/98)	none	810 ppm	Two phases formed before gelatin added; after gelatin added no effect observed	Second phase observed but not white, fluffy sediment as observed before	After 16 hours: clear, colorless, crystalline sediment at bottom of clear, colorless solution	not applicable

*The silica sol used for these solutions was over 23 hours old and that age probably accounts for the different physical appearance of the coagulated silica.

Table 7. Solutions with up to 0.45 Molar Fluoride at 0.27 Molar H_3BO_3 and 1 Molar HNO_3 with ANN added in the ratio 0.5 ANN:1 Fluoride and 810 ppm Silica

Identification	Fluoride Molarity	ANN	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silica Ratio
EE (03/17/98)	0.06 M	0.19 grams	Milky cloudiness spreading through solution	White, translucent mass settling to bottom of solution	After 15 hours: white, billowy mass at bottom of clear, colorless solution	2:1
FF (03/18/98)	0.12 M	0.38 grams	Milky cloudiness spreading through solution	White, translucent mass settling to bottom of solution	After 15 hours: white, billowy mass at bottom of clear, colorless solution	4:1
GG (03/18/98)	0.23 M	0.75 grams	Milky cloudiness spreading through solution	Fluffy white mass settling to bottom	After 15 hours: white, billowy mass at bottom of clear, colorless solution	8:1

Table 8. Composition of Dilute and Concentrated Surrogate SS&C Dissolver Solutions

Solution	Conc. H_3NO_3	H_3BO_3	Conc. HF	KF	CaF_2	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	H_2O	Total Volume
Dilute Acid Surrogate	50 ml	17 grams	14 ml	none	none	none	22 grams	1,130 ml	1,203 ml
Conc. Acid Surrogate	700 ml	17 grams	none	none	18 grams	none	22 grams	480 ml	1,189 ml

Table 9. Concentrations of Dilute and Concentrated Surrogate SS&C Dissolver Solutions

Solution	Conc. H_3NO_3	H_3BO_3	Conc. HF	KF	CaF_2	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Dilute Acid Surrogate	0.66 M	0.23 M	0.34 M	none	none	none	0.045 M
Conc. Acid Surrogate	9.3 M	0.23 M	none	none	0.19 M	none	0.046 M

4.3.1 Tests with ~80 ppm Silica

Four test solutions were made up using the surrogate SS&C dissolver solutions to test the effectiveness of gelatin strike at about 80 ppm silicon. Two dilute surrogate SS&C dissolver solutions were tested with 80 ppm silica added; ANN was added to one solution and not to the other solution. A similar pair of solutions was made up with the concentrated surrogate SS&C dissolver solution. The ANN was added at a ratio of aluminum: fluoride moles of 0.5:1. Although there was some observable milky after gelatin was added to the dilute surrogate SS&C dissolver solution without ANN (Solution II), after digestion at 50-60°C for one hour all four of the solutions were clear with no sign of any coagulation or sediment. No precipitation of a crystalline compound from the dilute surrogate solution without ANN (Solution II) was expected as KF was not used as the fluoride ion source. The observations of those four tests are in Table 10.

Table 10. Solutions with up with Dilute and Concentrated Surrogate Dissolver Solutions

Identification	Surrogate Solution	ANN	Observations after Gelatin Added	Observations after Digestion for 1 Hour	Observations after Cooling	Fluoride: Silica Ratio
II (03/18/98)	Dilute	none	Milky cloudiness spreading through solution	Opaqueness disappeared; solution clear and colorless; no sediment	After 24 hours: solution clear and colorless; no sediment	120:1
JJ (03/18/98)	Dilute	1.26 grams	Solution clear and colorless	Solution remained clear and colorless	After 24 hours: solution clear and colorless; no sediment	120:1
KK (03/18/98)	Concentrated	none	Solution clear and colorless	Solution remained clear and colorless	After 24 hours: solution clear and colorless; no sediment	120:1
LL (03/18/98)	Concentrated	1.46 grams	Solution clear and colorless	Solution remained clear and colorless	After 24 hours: solution clear and colorless; no sediment	120:1

4.3.2 Tests over a Range of Silica Concentrations

These tests were done with the concentrated surrogate SS&C dissolver solution. Aluminum nitrate nonahydrate was added to the solutions at a ratio of aluminum moles:fluoride moles of 1:1. Table 11 contains the information regarding solution composition and the observations. At the silica concentrations of ≥ 160 ppm, a translucent mass formed with the addition of gelatin and subsequent digestion at 50-60°C.

Table 11. Solutions with Silica Concentrations of 80 ppm -500 ppm in a Surrogate SS&C Dissolver Solution with ANN added at an Aluminum:Fluoride Mole Ratio of 1:1

Identification	Silica ppm	Fluoride Molarity	ANN	Observations after Gelatin Added	Observations after 1-Hour Digestion	Observations after Cooling	Fluoride: Silica Ratio
MM (03/26/98)	80	0.38 M	2.46 grams	Clear yellow solution	Clear yellow solution	After 10 days: clear yellow solution	130:1
NN (03/26/98)	160	0.37 M	2.36 grams	Clear yellow solution	Translucent mass floating in solution - need flashlight to detect	After 10 days: clear yellow solution with translucent mass floating in solution	65:1
OO (03/26/98)	240	0.35 M	2.31 grams	Clear yellow solution	Translucent mass floating in solution - need flashlight to detect	After 10 days: clear yellow solution with translucent mass floating in solution	40:1
RR (03/26/98)	490	0.32 M	2.06 grams	Some coagulation observed	Substantial translucent mass floating in solution	After 10 days: clear yellow solution with translucent mass floating in solution	18:1

4.3.3 Conclusions

At low concentrations of silicon (i.e., <100 ppm), gelatin strike is ineffective for both the concentrated and dilute surrogate SS&C solutions whether ANN is present or not present. At higher concentrations of silica (≥ 160 ppm), gelatin strike appears to be effective. Tests were done with the concentrated surrogate SS&C solutions with ANN added a ratio of aluminum moles:fluoride moles of 1:1; a translucent mass did form upon the addition of gelatin and subsequent digestion at 50-60°C.

5.0 Disengagement Tests

Tests were done to determine the behavior of silica on the disengagement time of surrogate and plant SS&C dissolver solutions from plant solvent. In previous studies², the presence of uncoagulated silica showed a profound effect of the disengagement time. All of the tests used organic solvent obtained from F-Canyon Operations.

5.1 Tests with Plant Solvent and Surrogate SS&C Solution

A surrogate SS&C dissolver solution was made up as follows: 8.3 Molar HNO_3 , 0.33 Molar fluoride, 0.23 Molar H_3BO_3 , 0.27 Molar calcium nitrate, 0.16 Molar ferric nitrate, and 0.07 Molar magnesium nitrate. The silica concentration was >150 ppm; a freshly-prepared silica sol was the source of silica. A 50:50 surrogate dissolver solution:organic solvent mixture was shaken in a 100-milliliter graduated cylinder. The separation of the two phases was timed.

Three 50-milliliter surrogate dissolver solutions were tested. In the first test no silica sol was added to the surrogate dissolver solution prior to mixing with the organic phase. Silica sol was added to the surrogate dissolver solution in the second test but no gelatin was added prior to mixing with the organic solvent. For the third test, silica sol was added to the surrogate dissolver solution and then gelatin was added. The coagulant was removed by filtration prior to mixing with the organic solvent. The disengagement times of the two phases were measured. The disengagement time of the first solution from the organic solvent was 30 seconds. The second solution had a disengagement time of 65 seconds whereas the third solution had a disengagement time of 30 seconds.

5.2 Tests with Plant SS&C Dissolver Solution and Surrogate SS&C Solutions with Plant Solvent

About 40 milliliters of SS&C dissolver solution was obtained from F-Canyon Operations. Analysis of the solution found 8.6 Molar HNO_3 , 0.77 grams/liter plutonium, 0.095 Molar iron (III), 0.23 Molar boron, 0.000233 Molar aluminum, 0.0046 Molar chromium (III), 0.0022 Molar nickel (II), 0.086 Molar magnesium, and 28.9 ppm silicon. The plant solvent was treated as follows prior to the phase disengagement tests. The plant solvent was washed two times with each of the following solutions: 0.2 Molar sodium carbonate, water, and 0.25 Molar HNO_3 . The washed plant solvent was then contacted twice with fresh portions of the surrogate SS&C solution.

For the first set of these phase disengagement test, the surrogate SS&C solution was prepared to the same concentrations of HNO_3 , iron(III), boron, aluminum, and magnesium with a fluoride concentration of 0.2 Molar. The plutonium, chromium (III), nickel (II), and silicon were omitted. An equal volume of the treated plant solvent was contacted with an equal volume of plant SS&C dissolver solution or with an equal volume of the surrogate SS&C dissolver solution. The disengagement time from the plant SS&C dissolver solution was 41 seconds and from the surrogate SS&C solution was 40 seconds. The times are an average of three measurements. The mixed phases separated with clean interfaces.

A second set of phase disengagement tests was done to determine the effect of ANN on the phase disengagement. For these tests, the surrogate SS&C solution was prepared to the same concentrations of HNO_3 , iron(III), boron, aluminum, magnesium, and silica as were found for the plant SS&C dissolver solution and the fluoride concentration was 0.2 Molar. Plutonium, chromium (III), and nickel (II) were omitted from the solution. Two portions of the surrogate SS&C dissolver solution were treated with different amounts of ANN. Aluminum nitrate nonahydrate was added to one of the surrogate SS&C dissolver solution portions at an aluminum:fluoride

² Graham, F., private communication, March 19, 1998.

ratio of 0.1:1, and ANN was added to the other surrogate SS&C dissolver solution portions at an aluminum:fluoride ratio of 1:1. Each of those two solutions was contacted with the plant dissolver solution and the disengagement times were measured. The volume ratio of organic phase to aqueous phase was 30 milliliters:50 milliliters. The disengagement times were 34 and 37 seconds for the solutions with 0.1:1 and 1:1 aluminum:fluoride ratios, respectively.

5.3 Conclusions

These tests indicate that the low concentrations of silica in the SS&C dissolver solutions (~30 ppm) did not affect the disengagement times of the dissolver solution from plant solvent. Addition of ANN did not cause an increase in the disengagement time of the surrogate SS&C dissolver solution from plant solvent. Higher concentrations of silica (>150 ppm) did affect the disengagement times of a dissolver solution from plant solvent. Gelatin strike followed by the removal of the coagulant from the dissolver solution, was effective in recovering the good disengagement time of the dissolver solution from plant solvent.