Solids Formation on Filtrate Neutralization

by

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INTER-OFFICE MEMORANDUM

SAVANNAH RIVER PLANT

F B-Line
Filtrate
Neutralization
Solids

DPSP-88-272-61

May 26, 1988

TO: M. TOMAS, 246-F

FROM: H. P. HOLCOMB, 772-F *HPH*SOLIDS FORMATION ON FILTRATE NEUTRALIZATIONINTRODUCTION AND SUMMARY

You requested the Separations Technology Laboratory to study what happens when a filtrate solution, which will be a F B-Line product, is neutralized with sodium hydroxide. You were primarily concerned about the formation of solids that could cause damage in pump seals, resulting in their failure.

We prepared, according to the recipe furnished us, a synthetic filtrate solution containing nitric acid, hydroxylamine nitrate, hydroxylamine sulfate, hydrofluoric acid, and ascorbic acid. The solution was studied in two ways. For the first test, the solution was titrated with 50% NaOH, scheduled to be the process neutralizing agent. pH changes during the titration were monitored. As requested, a 25 volume percent excess of caustic was also slowly added to the solution once pH 7 was obtained. No solids had formed after the neutralized solution had stood for 3 days. This information was reported to you in my memorandum of May 2.

However, after 5 days of standing, white needlelike solids appeared in the mother liquor. These solids were determined to be approximately 90% sodium oxalate and 10% sodium fluoride. Although oxalate ion was not present in the original chemicals used to prepare the synthetic solution, it was formed, substoichiometrically, from the reaction between nitric acid (1.8M) and ascorbic acid (0.4M) in the synthetic solution. According to R. M. Wallace, SRL Research Fellow, oxalate can be one of the reaction products in the oxidation-reduction reaction between these two.

The second test more closely approximated process conditions and used the same quantities of solutions employed for the first test. For this test, caustic was added rapidly to the stirred filtrate solution. The entire quantity of caustic, 25 volume percent excess included, was added over a period of 10-15 seconds. The temperature

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rise was from 30°C to 83°C, and no solids were immediately noted. After one hour, some solids were observed on the bottom of the reaction vessel. After 24 hours, about the same quantity was noted. The solids were granular and appeared to be crystalline. Analysis by x-ray diffraction indicated the solids to be almost entirely sodium fluoride, NaF.

The clear, solids-free supernate from each test was stored in the laboratory. Over a 3-week period, white solids slowly formed and settled to the bottom of both flasks. The solids appeared similar to each other. Samples were submitted for x-ray diffraction analysis. Both solids were identified as being comparable in composition to the solids initially formed following the rapid addition of caustic to the synthetic filtrate. Those were mostly sodium oxalate with some sodium fluoride. Therefore, slow post-precipitation of these solids might prove a problem if such neutralized filtrate solutions were stored for some length of time.

Other parametric studies were made. These include scanning electron microscopy (SEM) of the solids as well as cationic and anionic analyses of their water solutions. SEM was also employed to ascertain the particle size range of the two solids. Details of these studies appear in the body of this report.

In summary, the results of our experiments indicate that under process conditions, granular, crystalline sodium fluoride will be produced by rapid neutralization of the filtrate solution with 50% NaOH plus a 25 volume percent excess. Postprecipitation of sodium oxalate-sodium fluoride and its accumulation can occur over a three-week storage period of the neutralized filtrate. Such solids could pose operational problems from pump seal abrasion and potential failure caused by them.

EXPERIMENTAL

Synthetic Filtrate Solution

The composition of the filtrate solution to be tested was furnished as:

1.8M HNO₃
0.1M (NH₂OH)₂·H₂SO₄ (HAS)
0.1M NH₂OH·H₂SO₄ (HAN)
0.8M HF
0.4M C₆H₈O₆ (Ascorbic Acid).

Each test solution was prepared in the same manner. To approximately 150 mL of water was added 3.3 g of solid hydroxylamine sulfate, 11.1 mL of 1.8M hydroxylamine nitrate, 14 g of ascorbic acid, and 5.8 mL of 27.6M HF. Following dissolution of the solids

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via magnetic stirring, 23 mL of 15.7M HNO_3 was slowly added to the stirred solution. The solution was finally diluted to 200 mL with deionized water.

As nitric acid was being added during preparation of both test solutions, there was a small quantity of NO_x released, indicating a reaction between the nitric acid and one of the solution components. The reaction was neither vigorous nor rapid. Nitric acid was interacting with ascorbic acid to a slight extent, resulting in the small quantity of brown fumes.

50% (19M) NaOH, to be used as the process neutralizing agent, was prepared by dissolving reagent-grade NaOH in deionized water. The solution was allowed to cool to room temperature prior to use.

Test #1 - Titration of Synthetic Filtrate with 50% NaOH

This test was described in my May 2 memorandum to you. I shall repeat our procedure and latest findings since solids did not form in the neutralized solution for the first 3 days, but were present after 5. My previous memo reported only the results after 70 hours of standing. The solids formed later.

200 mL of the synthetic filtrate was placed in a 400-mL beaker with a magnetic stirring bar. A 50-mL burette was filled with the 50% NaOH solution. The caustic was added very slowly, almost dropwise, to the stirred filtrate. pH changes in the solution were monitored with an immersed pH electrode and digital pH meter standardized with pH 7 buffer. The standardization was checked at least twice during the neutralization. Initial pH of the solution prior to any caustic addition was 1.6.

After 53.9 mL of 50% NaOH had been added to the original synthetic filtrate, the pH of the solution was 7.06; thus, it had been neutralized. No solids were noted at this point. Then, for the 25 volume percent excess of caustic, 13.5 mL was slowly added from the burette. After this addition, the pH of the solution was 11.8, and its temperature was 50°C. Total volume was 275 mL. No solids were noted.

The neutralized solution was covered with a watch glass and allowed to stand in the laboratory. Some 70 hours following neutralization, the pH was 12.8, and solution volume was 268 mL. No solids were noted. At this point, the results of this test were reported to you in my May 2 memo.

However, after standing 5 days, a small quantity, estimated to be 1 to 2 mL, of white, somewhat needlelike solids, was noted in the neutralized filtrate. These were allowed to remain in the mother liquor until Test #2 was completed.

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A note concerning pH readings should also be made again. The initial solution was very acidic, and the pH reading should have been less than the indicated 1.6. Likewise, the neutralized solution with the 25% excess caustic was calculated to be 0.93M in NaOH and should have had a pH reading quite close to 14. The pH electrode being used was an ORION Combination Electrode, Model 91-56. Contact with the ORION Technical personnel yielded the information that was reported to you in my memo of May 2. Due to liquid junction potential, this particular electrode is not rapid in its response to solution pHs below 2 or above 12. However, it is quite capable of rapid pH measurement within that range. So, the neutralization curve obtained with its use should be accurate.

Test #2 - Rapid Neutralization of Filtrate

Following reporting the results of Test #1 to you, you requested us to conduct a similar experiment in which all the 50% NaOH, excess included, was to be rapidly added to the stirred synthetic filtrate, instead of the slow titration conditions of Test #1.

On conducting Test #2, the temperature rise was from 30°C to 83°C. No solids were noted immediately following the caustic addition. However, after one hour, some solids were seen on the bottom of the beaker. The solution temperature at this point was 43°C. After 3 hours of standing, there appeared to be a few more granular-appearing solids. Their color was difficult to discern due to the dark red-amber color of the solution. Its temperature was now 29°C.

Some 24 hours following the caustic addition, there was approximately 5 mL of granular solids on the beaker bottom. After 48 hours, conditions were the same.

Washing of Solids and Preparation for Sampling

The solids-containing solutions from both tests were allowed to stand undisturbed so that most of the mother liquor could be removed via decantation. A small amount of each reddish-amber mother liquor was used to transfer the solids to 30-mL graduated centrifuge cones. The slurry was then centrifuged. A photo of the centrifuged solids is shown as Figure 1 (all Figures are in the Appendix). Some 5 mL of granular, reddish solids resulted from the "rapid" caustic addition; about 1.5 mL of white solids resulted from the "slow" caustic addition after the neutralized solution had stood for 5 days. The color of the "rapid" solids is believed due to occlusion or sorption of the neutralized, colored products produced by ascorbic acid degradation. Since the "slow" solids crystallized from solution over a longer period, they were not highly contaminated with these products.

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The solids, assumed to be sodium salts, would therefore be soluble in water, so aqueous washing was out of the question. The solids in each tube were washed with four 20-mL portions of absolute ethyl alcohol in order to remove as much of the mother liquor as possible. Washing was by vortex mixing, followed by centrifugation, and then, decantation of the wash liquid. The solids were rather insoluble in the alcohol since about as many remained following washing as were present before.

The solids, still in the centrifuge cones, were placed in a drying oven that was at ambient temperature. The temperature inside the oven was slowly brought to 60°C and allowed to remain there for 4 hours. Following the drying operation, the solids were free and mobile.

For ICP (Inductively Coupled Plasma) cation analysis and IC (Ion Chromatography) anion analysis, 0.100 g of each solid was dissolved in deionized water giving a final volume of 5 mL. The sample for ICP was sent to SRL; the IC, to 772-F Labs.

Three sets of samples of the solids were prepared and given to ADD, SRL, for examination by scanning electron microscopy (SEM), for x-ray diffraction analysis, and for particle size analysis. However, SRL is not equipped to do the latter, nor can Labs do particle size on aqueous-soluble solids. Particle size analysis on such can be done off-site, but that can take from 4-6 weeks.

The decanted, solids-free supernates from each test were allowed to stand in the laboratory for 3 weeks. At the end of this time, both solutions contained white, crystalline solids that had postprecipitated from solution during this additional standing period. These solids were washed like those formed initially. Samples of the postprecipitates were submitted only for x-ray diffraction analysis for identification.

RESULTS AND DISCUSSION

X-Ray Diffraction

Figures 2 and 3 are spectral patterns produced by the x-ray diffraction analysis of the two solids. Figures 4 and 5 are the diffraction patterns obtained from the solids postprecipitated during the 3-week standing period.

Figure 2 identifies the solid produced in the NaOH titration test to be mostly (>90%) sodium oxalate with a minor quantity of sodium fluoride and a trace of sodium nitrate.

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Figure 3 likewise identifies the solid produced in the NaOH rapid addition test to be fairly pure sodium fluoride.

Figures 4 and 5 are quite similar to the pattern of Figure 2, so the postprecipitated solids from both tests were primarily sodium oxalate with some sodium fluoride present.

These tests are quite definitive as to the composition of the solids to be expected from filtrate neutralization.

Ion Chromatography

Water solutions of each solid were prepared and submitted to Laboratories for anion analysis to assist in ascertaining the solids' composition as well as to identify other anions present as impurities.

For the sodium oxalate-sodium fluoride solid, a small quantity of both nitrate and sulfate were identified as impurities. The $\text{SO}_4^{2-}/\text{NO}_3^-$ weight ratio was about 7. The sodium fluoride solid also contained the same anionic impurities, but the sulfate/nitrate weight ratio in it was about 17.

ICP Analysis

Results of the ICP cation analysis showed sodium ion to be the predominant cation present in the water solution of each solid. Silicon was present as a trace element. However, this is to be expected since all the experimental work was conducted in Pyrex® glass containers. Caustic is known to slowly attack glasses, so silicon is suspected to come from the containers' SiO_2 .

Scanning Electron Microscopy

A foreword of caution is necessary regarding interpreting the results of this analysis. The solids submitted for SEM scans were alcohol-washed by vortex mixing. This mixing action would yield particulates that were not the same size or shape as those originally present in the aqueous solution in which the solids formed. Also, agglomeration characteristics would be changed by going from an aqueous to an alcohol medium. However, we can get some relative differences between the solids as well as get an approximation as to what they were initially like.

Figures 6-9 show photomicrographs of the solids that resulted from the process of caustic neutralization by slow titration. These particulates vary in size from large, porous-appearing agglomerates, approximately 250 μm unidimensionally, down to individual crystals some 5-10 μm . The scale is at the bottom of each photo and is denoted as the length of the white line.

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Figures 10-13 are photomicrographs of the particulates that formed shortly after the rapid neutralization of the synthetic filtrate solution with caustic. These photos show particles and agglomerates of various sizes, but ones especially of interest would be the octahedra single crystals that are evident, especially in Figures 10 and 11. These are some 40 μm , unidimensionally, and are probably unchanged from the alcohol washing. Some of the smaller (10 μm or less), more rounded particles, shown in a different field of view in Figures 12 and 13, are assumed to be the result of the abrading wash action on the single crystals. A part of one of the larger octahedral crystals can be seen in the upper left corner of Figure 12. If these octahedra form during neutralization, they could be very damaging to pump seals, especially if the latter are easily abraded.

CONCLUSIONS

The neutralization of the synthetic filtrate solution by the rapid addition of 50% caustic, plus a 25 volume percent excess, does result in solids formation within a period of one hour following neutralization. The solids are primarily sodium fluoride.

If the filtrate solution is allowed to stand for a period of more than 3 weeks, additional solids postprecipitate from solution. The composition of these solids are primarily sodium oxalate (about 90%) with sodium fluoride constituting most of the remainder.

The granular, crystalline nature of these solids could pose a definite processing problem if solutions containing them are moved with pumps containing internal seals.

ACKNOWLEDGMENTS

ADD, SRL, is recognized for providing excellent cooperation and analytical services that allowed us to characterize the solids. P. Kent Smith gave us rapid service in identifying the solids via x-ray diffraction. D. F. Steedly did the SEM work and provided the photomicrographs that constitute part of this report.

P. B. Berry of Laboratories Department oversaw the IC analysis.

R. M. Wallace of DWPFT, SRL, is acknowledged for the information he provided concerning the chemistry of the interaction between ascorbic acid and nitric acid.

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(Original photomicrographs with MT copy only.)

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FIGURE 1

Original Solids - Left, Rapid NaOH Addition; Right, Titration

FIGURE 2

X-Ray Diffraction Pattern - NaOH Titrated
Initial Solids

FIGURE 3

X-Ray Diffraction Pattern - NaOH Added Rapidly
Initial Solids

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FIGURE 4

X-Ray Diffraction Pattern - NaOH Titrated
Postprecipitated Solids

FIGURE 5

X-Ray Diffraction Pattern - NaOH Added Rapidly
Postprecipitated Solids

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FIGURE 6

Initial Solids -
NaOH Titrated

39X

FIGURE 7

Initial Solids -
NaOH Titrated

250X

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FIGURE 8

Initial Solids -
NaOH Titrated

1000X

FIGURE 9

Initial Solids -
NaOH Titrated

2000X

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FIGURE 10

Initial Solids -
NaOH Added Rapidly

500X

FIGURE 11

Initial Solids -
NaOH Added Rapidly

1000X

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FIGURE 12

Initial Solids -
NaOH Added Rapidly

1000X

FIGURE 13

Initial Solids -
NaOH Added Rapidly

2000X