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Structural Stability Study of Crystalline Silicotitanate Dispersed in Caustic Solutions for Extended Periods

L. E. Mathurin

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August 2019

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EXECUTIVE SUMMARY

The purpose of this study was to determine if pretreated engineered crystalline silicotitanate (CST) utilized in the Tank Cesium Closure Removal (TCCR) process would aggregate when contacted with sodium hydroxide (NaOH) or simulated tank waste solutions over an extended period. The aggregation of CST could be problematic for the TCCR process as it may lead to increased pressure drops across the columns, due to column plugging. Multiple prior studies have been completed on the agglomeration of CST stored in caustic simulants for prolonged periods showing evidence of clumping especially at elevated temperatures. For this study, pretreated CST was combined with various concentrations of sodium hydroxide and SRS simulant, in both glass and plastic storage containers, and monitored for an extended period. The samples were monitored for signs of agglomeration for a period of 8 months.

After 7 months weak agglomeration was observed in the sample stored in SRS simulant, while no signs of clumping were observed in the samples stored in 2, 3, or 4 M NaOH. This is consistent with previous work where agglomeration of CST was not observed in simple salt solutions, only in simulants containing Al. In addition, the clumping observed for the sample stored in SRS simulant was not replicated in the duplicate sample stored in a plastic (as opposed to glass) vial, indicating leaching of Si from the glass may have contributed. It was also noted during the study that the solution above the CST stored in 4 M NaOH became opaque. The most likely cause of the opaque solution is the presence of micro-CST particles that may have been generated through sample handling, although this has not been confirmed by analysis.

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LIST OF ABBREVIATIONS

CST	Crystalline Silicotitanate
ORNL	Oak Ridge National Laboratory
SCIX	Small Column Ion Exchange
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TCCR	Tank Cesium Closure Remediation
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

Savannah River Remediation (SRR) is deploying an ion exchange process to remove radioactive cesium from tank waste supernate in a process referred to as Tank Closure Cesium Removal (TCCR). This process utilizes crystalline silicotitanate (CST) for the removal of cesium from the liquid waste stream. Prior to feeding tank waste to the ion exchange columns the CST will be pretreated with 3 M NaOH to convert the CST to the sodium form. After pretreatment the columns will remain filled with 3 M NaOH until waste is processed through the column. In addition, between batches, the columns will remain filled with the last waste solution to have been processed. Due to this potential for long term exposure to highly alkaline solutions (either 3 M NaOH or tank waste) studies were undertaken to examine the potential for the CST to agglomerate or clump during storage, which could then result in column plugging or increased pressure drop across the columns during processing. Extensive work with CST by both SRNL and ORNL in the late 1990s resulted in several instances of column plugging.¹ Several causes for these plugging incidents were identified and included solids in the feed (aluminosilicate solids precipitation in feed pumped to column; calcium/aluminosilicate precipitation from feed; CST fines from incomplete backwash; extraction of “proprietary material” from CST precipitated in a different form and fed back to the column), failure to adjust pH between waste solution and water rinse, as well as three instances of unknown cause.¹

ORNL completed several extensive studies of CST clumping in the early 2000s and showed evidence of agglomeration of CST beads when stored in various simulant solutions for prolonged periods and especially at elevated temperatures.^{2,3} In the first set of experiments CST beads, which had been pretreated by recirculating dilute NaOH for 24 hours to reach a pH of ~13, were exposed to four different simulant solutions: SRS Average simulant, a high hydroxide version of the simulant, a high nitrate version of the simulant, and finally a simple salt solution containing only sodium hydroxide and sodium nitrate with a total sodium concentration of 5.6 M (the same as the other more complex simulants).² Samples of engineered CST were contacted with these various solutions at temperatures of 23 °C, 30 °C, 35 °C, 50 °C, and 80 °C. After one month weak agglomeration was seen in all of the complex simulants at temperatures of 30 °C and higher. No agglomeration was seen in any of the samples at 23 °C, nor any of the samples stored in the simple salt solution. After 2 months agglomeration was observed in all samples stored in SRS average, high hydroxide, or high nitrate simulant. No agglomeration was observed at any temperature for the samples stored in the simple salt solution over a period of 12 months. These observations suggest that it is likely the aluminum present in the complex simulants forming aluminosilicates that is leading to the agglomeration observed.

In the later set of experiments performed by Taylor and Mattus, engineered CST that had been pretreated with 3 M NaOH (once through) as well as a batch of material that had been pretreated by UOP to remove leachable material were contacted with SRS Average Simulant for three months.³ Unlike the earlier work, after 1 month only the samples stored at 80 °C showed any signs of agglomeration. After 2 months, weak clumping was observed in the UOP pretreated sample stored at 50 °C. Finally, after 3 months both samples of CST had formed clumps at 35 °C. No clumping was observed in either sample at 23 °C. These results indicate some improvement in preventing agglomeration is obtained with extensive pretreatment of the CST to remove any leachable material.

In order to determine the vulnerability of the TCCR CST to agglomeration over prolonged periods, a bench scale study was developed. This study observed the CST dispersed in various concentrations of caustic solutions over 8 months.

2.0 Experimental Procedure

2.1 Materials

The CST used for this study was UOP IONSIV R9120-B, from lot number 2099000035 and the material was pre-treated using approximately 4.28 bed volumes of 3.75 M NaOH. The details of this pretreatment have been previously documented (Test Pretreatment #1).⁴ Solutions used for contacting the CST included 2, 3, and 4 M NaOH as well as SRS Average Simulant⁵ with the composition shown in Table 2-1.

Table 2-1. SRS Average Simulant Composition

Component	Molarity
Na ⁺	5.60
K ⁺	0.015
Cs ⁺	1.4E-04
OH ⁻	1.91
NO ₃ ⁻	2.14
NO ₂ ⁻	0.52
AlO ₂ ⁻	0.31
CO ₃ ²⁻	0.16
SO ₄ ²⁻	0.15
Cl ⁻	0.025
F ⁻	0.032
PO ₄ ³⁻	0.01
C ₂ O ₄ ²⁻	0.008
SiO ₃ ²⁻	0.004
MoO ₄ ²⁻	0.0002

2.2 Methods

Approximately 1 gram of the pre-treated CST was combined with 2 mL of the specified caustic solution. The details of each sample are summarized in Table 2-2, including CST mass, volume of solution, and storage container type. The CST mobility in the various caustic solutions was of interest and images and videos were obtained of the samples stored in the glass vials. The samples stored in glass vials were visually observed each week for 8 months. Each sample was tilted at an approximately 45-degree angle and rotated to observe if the CST remained free flowing. If the CST did not appear to be free flowing, the vials were gently shaken, and the tilting and rotating process was repeated. The samples stored in plastic vials were considered the blank for the study. These vials were left undisturbed for the majority of the experiment, and only tilted and observed when a comparison was required based on the observations of the glass vials (twice during the 8-month period). All samples were stored at ambient laboratory temperature for the duration of the study.

Table 2-2. Volumes and Weights of CST

	Solution	Container type	CST mass (g)	Solution Volume (mL)
A	2 M NaOH	Glass	1.0030	2.00
B	3 M NaOH	Glass	1.0008	2.00
C	4 M NaOH	Glass	1.0008	2.00
D	SRS Simulant	Glass	1.0011	2.00
E	2 M NaOH	Plastic	1.0021	2.00
F	3 M NaOH	Plastic	1.0025	2.00
G	4 M NaOH	Plastic	1.0073	2.00
H	SRS Simulant	Plastic	1.0138	2.00

2.3 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This work was performed in accordance with the applicable Task Technical and Quality Assurance Plan (TTQAP).⁶

3.0 Results and Discussion

3.1 Initial Results Up to 1 Month of the Study

The CST was monitored periodically for the first month for any clumping or abnormalities in solution. Figure 3-1 contains photographs of the glass vials (A-D) after the CST was initially dispersed in the caustic solutions at the following concentrations: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D) SRS Simulant. The samples were observed and photographed again after 24 hours (2), 1 week (3), and 1 month (4). Over the course of one month, no changes were observed, and the CST remained free flowing.

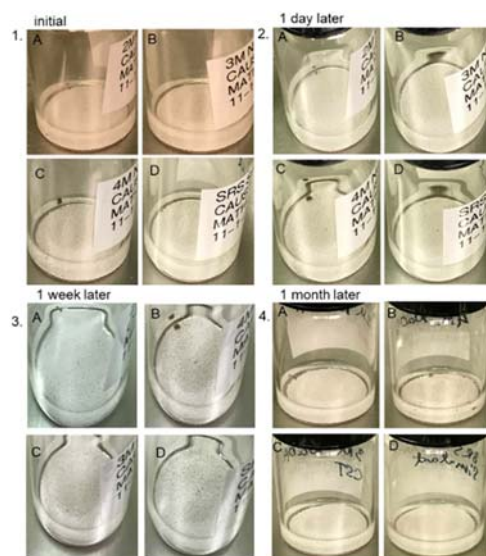


Figure 3-1. Images of CST dispersed in caustic solution. 1. initial, 2. after 1 day, 3. after 1 week 4. after 1 month, at varying concentrations: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, D) SRS Simulant.

3.2 Overview of results from 1 month to 5 months, with a focus on abnormalities

The CST dispersed in various types of caustic solutions were monitored beyond the first month in order to determine if the CST would remain free flowing with prolonged exposure to the caustic solutions. The vials were monitored weekly, during which they were tilted slightly and rotated approximately a quarter turn in order to see the CST particles flowing in solution. The results from the first five months of the study are shown in Figure 3-2 (1) and (2) at the following concentrations A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D) SRS Simulant. No agglomeration was observed in any of the samples in various concentrations of NaOH or SRS Simulant. However, during this period some of the samples began to exhibit an opaque solution. At the 2-month mark, the 4 M NaOH sample in the glass vial solution became opaque, as demonstrated in Figure 3-3. The most likely cause of the alteration in solution transparency is the development of micro CST particles suspended in solution; however the solution was not analyzed to confirm this assumption. Another possible cause for the development of the opaque solution could be leaching, and reprecipitation of components of the binder used to prepare the engineered CST. While the 4 M NaOH sample appeared opaque, the remaining samples remained transparent. This parameter was monitored for all solutions until the end of the experiment. Further characterization would be required in order to definitively determine the composition of the fine suspended particles.

Photographs from the 8 month of the study are shown in Figure 3-2 (3), with the following concentrations: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D) SRS Simulant. Additional images are shown in Figure 3-4, images A to C contain results from CST dispersed in NaOH, while images D to F contain results from CST dispersed in SRS Simulant. In the 7th month of the study, the sample in SRS simulant in a glass vial, demonstrated some agglomeration/clumping, as shown in Figure 3-4, images D to F. This sample had been left undisturbed for ~ 2 months, and upon initial tilting did not demonstrate free flowing CST. The sample was gently shaken, and then vial tilting was repeated. The gentle shaking was enough to break apart the weakly agglomerated CST and it returned to a free flowing state. An opaque solution was also observed, as shown in Figure 3-4 images D & E. In order to determine if the agglomeration was a reoccurring phenomenon the process was repeated a week later, as demonstrated in Figure 3-4, image F. The clumping was not observed to have reoccurred within one week of storage. The SRS Simulant sample was the only vial to demonstrate clumping. This observation is consistent with the earlier work by Taylor and Mattus where they did not observe clumping or agglomeration in the simple salt solution, only in simulants containing Al.^{2,3} The CST stored in NaOH can be seen in Figure 3-4, images A - C. None of the samples demonstrated agglomeration, however, the 4 M NaOH sample did appear as an opaque solution as noted earlier. The opaqueness of the solution is likely due to the formation of smaller CST particles.

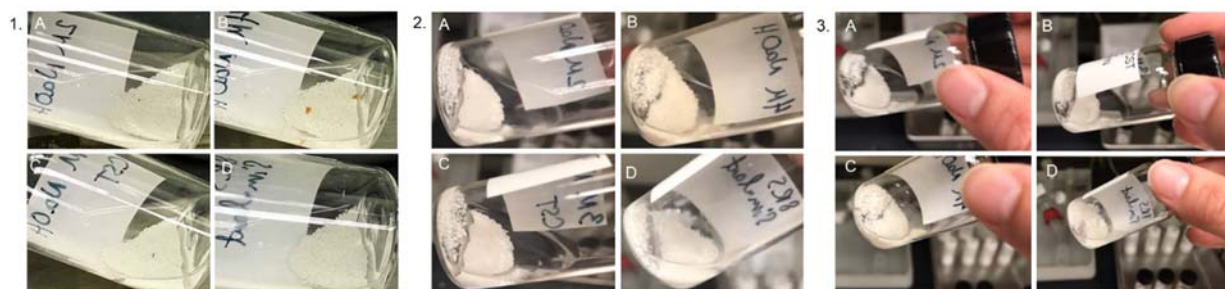


Figure 3-2. Free-flowing CST over prolonged periods 1) 1 month, 2) ~5 months, and 3) 8 months. The solutions are as follows: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, D) SRS Simulant.

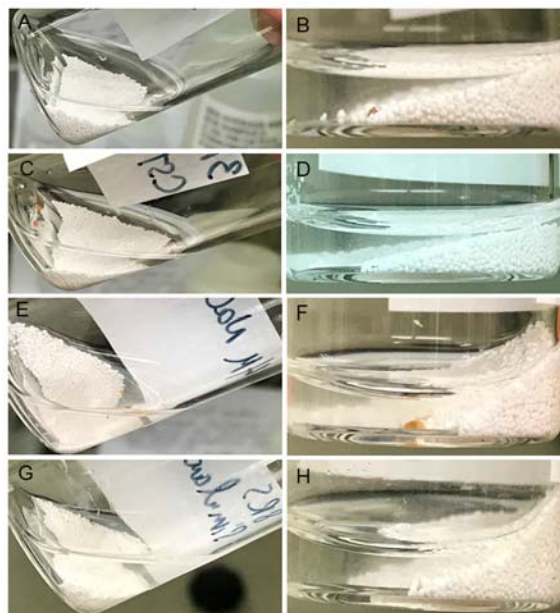


Figure 3-3. Images of the CST in caustic solutions after two months, at which point the transparency of the solution began to change. A & B) are 2 M NaOH, C & D) are 3 M NaOH, E & F) are 4 M NaOH, G & H) are SRS Simulant.

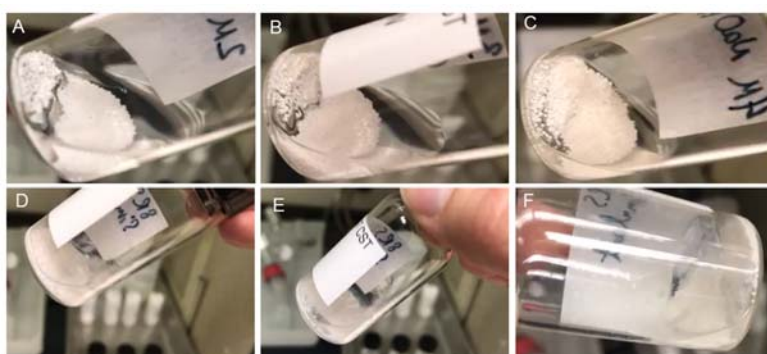


Figure 3-4. Images of CST samples that had been left undisturbed for ~2 months. A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D – F) is SRS simulant.

3.3 Evaluation of Samples Stored in Plastic Vials and Legacy Sample

In order to determine if the abnormalities in the study were unique to the glass vials, the samples stored in plastic vials were observed, during the 7th month. These samples had only been observed twice during this experiment. The images were collected after the second tilting, and the results can be seen in Figure 3-5, images E to H. Each of these samples demonstrated free flowing CST in their respective solutions. The solutions in these vials remained transparent and no agglomeration was observed. This suggests that the type of storage vial as well of handling of the samples may have influenced the results observed. Leaching of Si from the glass vials could have contributed to the clumping observed in the CST stored in SRS Simulant in the glass vial as corresponding clumping was not observed for the sample stored in plastic. Additionally, the formation of micro-CST particles leading to the observed opaqueness in the glass vial

samples could be attributed to the repeated handling and movement of those samples causing the generation of fine particles.

Additionally, a legacy sample from 2010 was located during this study. This sample contained ground CST from the Small Column Ion Exchange (SCIX) program and had been stored in salt batch supernate simulant.⁷ The bottle was shaken, and the CST in the top layer was easily dispersed into the solution, indicating that it had not strongly agglomerated. A photograph of this sample is provided in Figure 3-6.

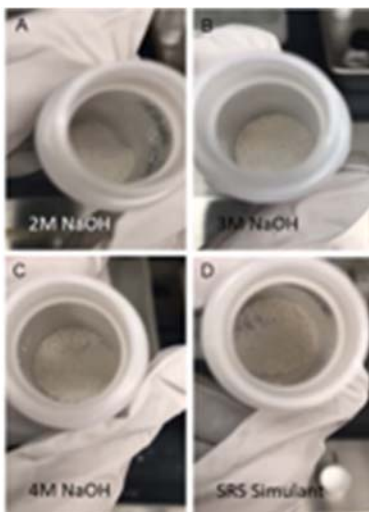


Figure 3-5. Images of the CST dispersed in NaOH stored in plastic vials. The concentration of the samples are as follows: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D) SRS Simulant.

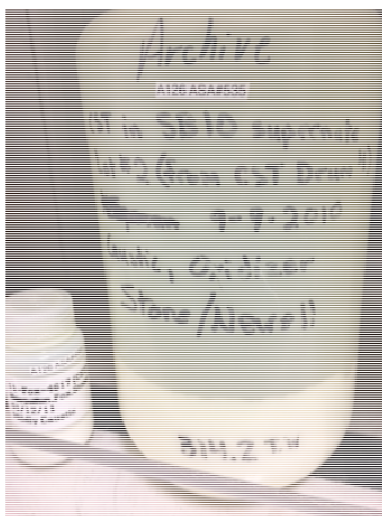


Figure 3-6. Photograph of archived ground CST stored in Salt Batch 10 Simulant from 2010.

4.0 Conclusions

Ultimately no substantial and lasting clumping was seen throughout the 8-month study. The sample stored in SRS simulant, in a glass vial, did show some weak agglomeration during month 7 of the study; however, the agglomeration was easily broken up by gentle shaking, returning the beads to a free-flowing state. This observation was consistent with earlier work where agglomeration was only seen in simulants containing Al, and not in simple salt solutions. The agglomeration was not observed in the duplicate samples stored in SRS simulant in a plastic vial, which indicated leaching of Si from the glass may have also impacted the results. Additionally, a legacy sample of ground CST stored in salt supernate simulant appeared to remain dispersible after 9 years of storage.

While no significant agglomeration was observed in the CST samples stored in NaOH solutions, an opaque solution was observed for the sample stored in 4 M NaOH. The most likely cause of the opaque solution is the generation of micro CST particles that became suspended in solution, although the composition has not been confirmed analytically.

5.0 Recommendations

It is recommended that the studies continue with less frequent periodic monitoring. Weekly observations (with sample movement) may have prevented clumping as evidenced by the agglomeration observed in the SRS simulant sample after sitting undisturbed for approximately 2 months. The clumping that was observed appeared weak and was easily broken by gentle movement. The frequent handling may also have contributed to the generation of micro CST particles which are assumed to be the cause of the opaque solution observed in some samples. The samples were not monitored for solution evaporation, but it was assumed that there was no evaporation based on the experiment being run at 25 °C, but ambient field (35 °C to 38 °C) conditions could be considered for future study. It is recommended that the supernate from the experiments is analyzed to confirm the composition of the particulates causing the opaque solution, through ICPMS, TEM, XPS, and EDX mapping. If the study is to be repeated in the future it is recommended that plastic vials are used to mitigate the potential leaching of Si from glass vials. It is also recommended that several vials are prepared for each condition so that some can be left undisturbed for longer periods as the frequent handling and observations may have prevented CST from clumping and may also have led to the generation of micro CST particles.

6.0 Reference

- ¹ D. D. Walker, “Crystalline Silicotitanate Column Plugging Incidents”, SRT-LWP-2000-00136, August 22, 2000.
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- ³ P. A. Taylor and C. H. Mattus, “Thermal and Chemical Stability of Baseline and Improved Crystalline Silicotitanate”, ORNL/TM-2001/165, December 2001.
- ⁴ K. M. L. Taylor-Pashow, T. B. Edwards, C. A. Nash, “Pretreatment of Crystalline Silicotitanate (CST) and Development of a Digestion Standard to Support Tank Closure Cesium Removal (TCCR)”, SRNL-STI-2019-00045, Rev. 0, March 2019.
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- ⁶ W. D. King, “Task Technical and Quality Assurance Plan for Batch Contact Sorption and Desorption Testing to Support Tank Closure Cesium Removal Operations”, SRNL-RP-2017-00536, Rev. 2, October 2018.
- ⁷ D. C. Koopman, “SCIX Impact on DWPF CPC”, SRNL-STI-2011-00075, Rev. 0, June 2011.

Appendix A: Figures

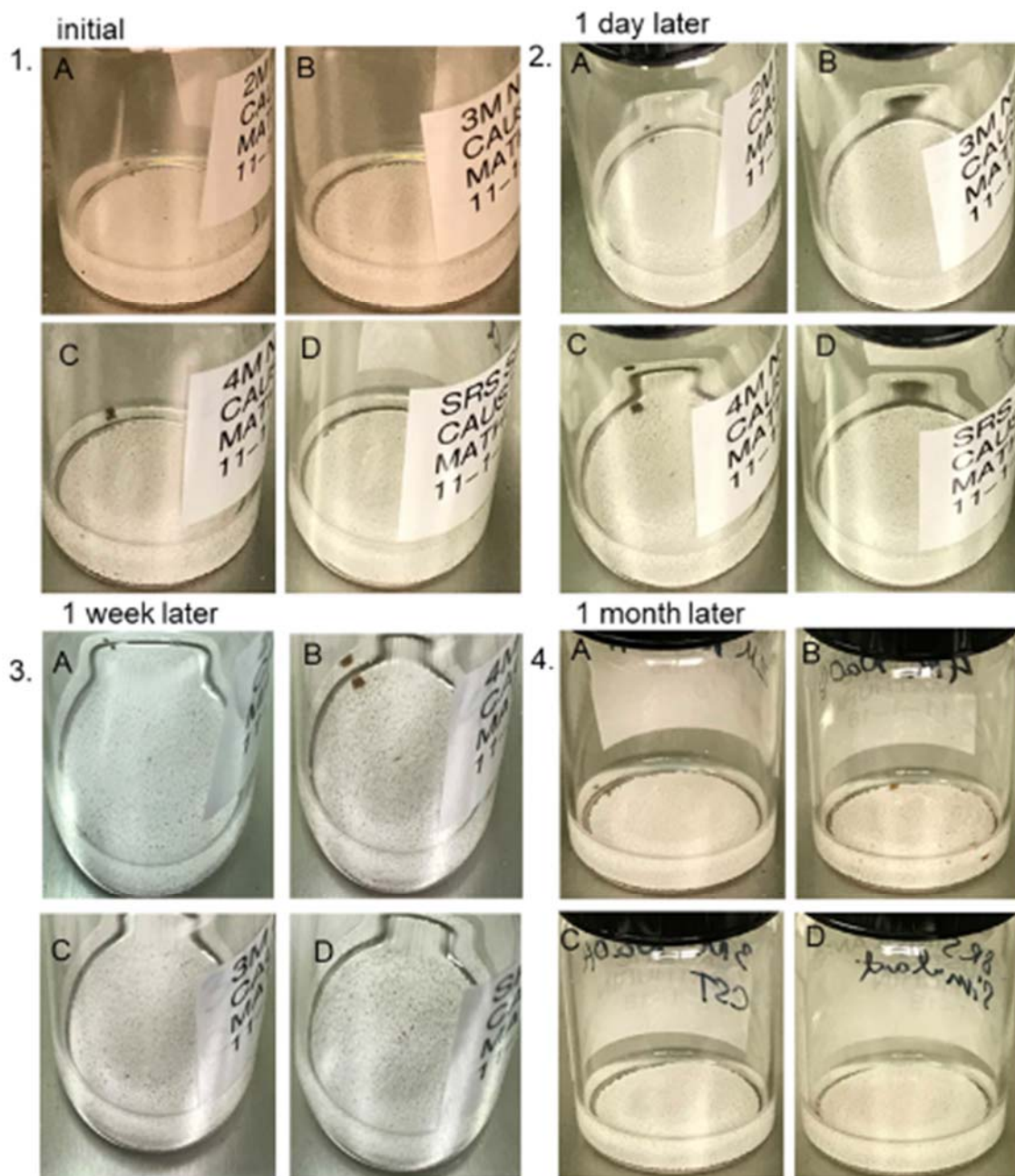


Figure A-1. Images of CST dispersed in caustic solution. 1. initial, 2. after 1 day, 3. after 1 week 4. after 1 month, at varying concentrations: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, D) SRS Simulant.

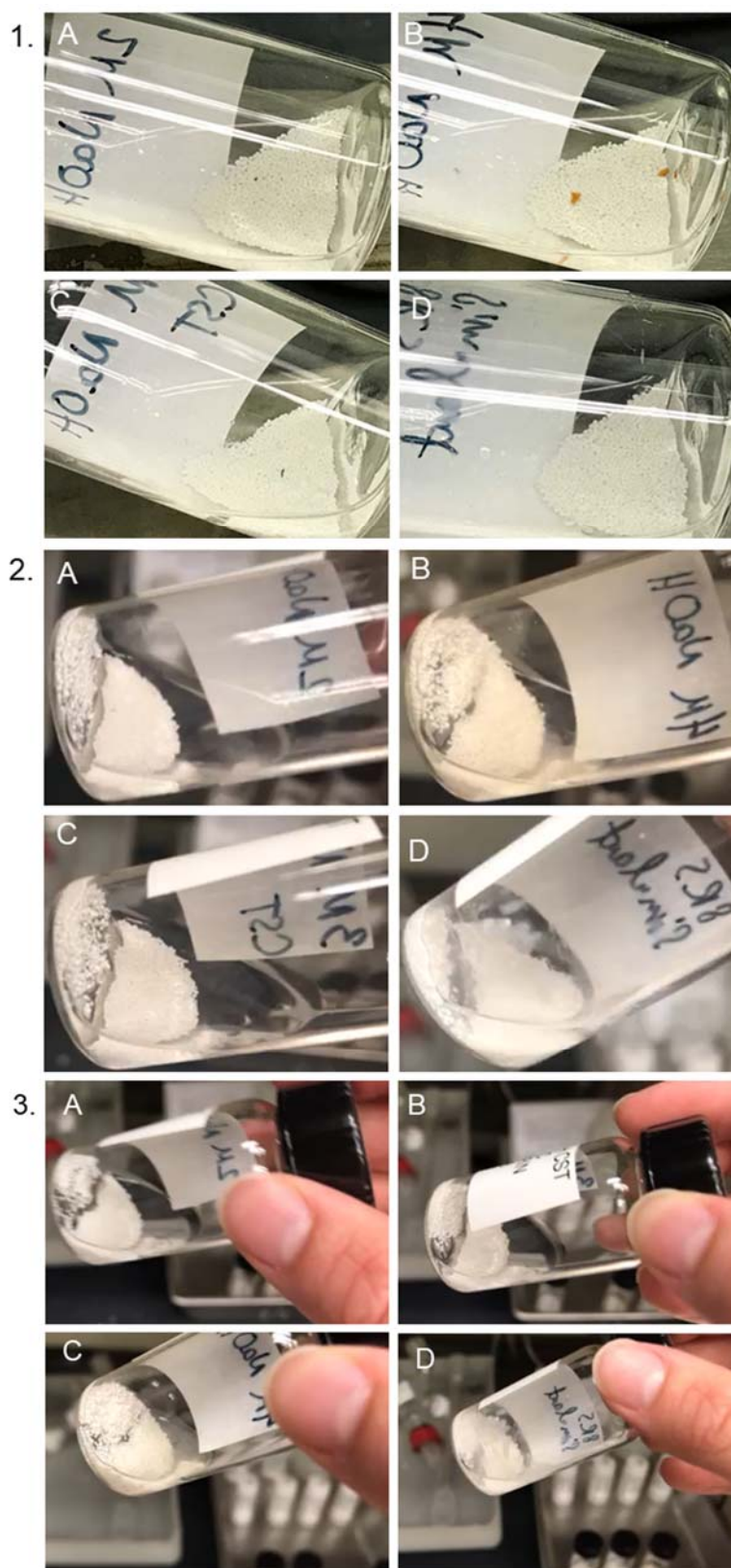


Figure A-2. Free-flowing CST over prolonged periods 1) 1 month, 2) ~5 months, and 3) 8 months. The solutions are as follows: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, D) SRS Simulant.

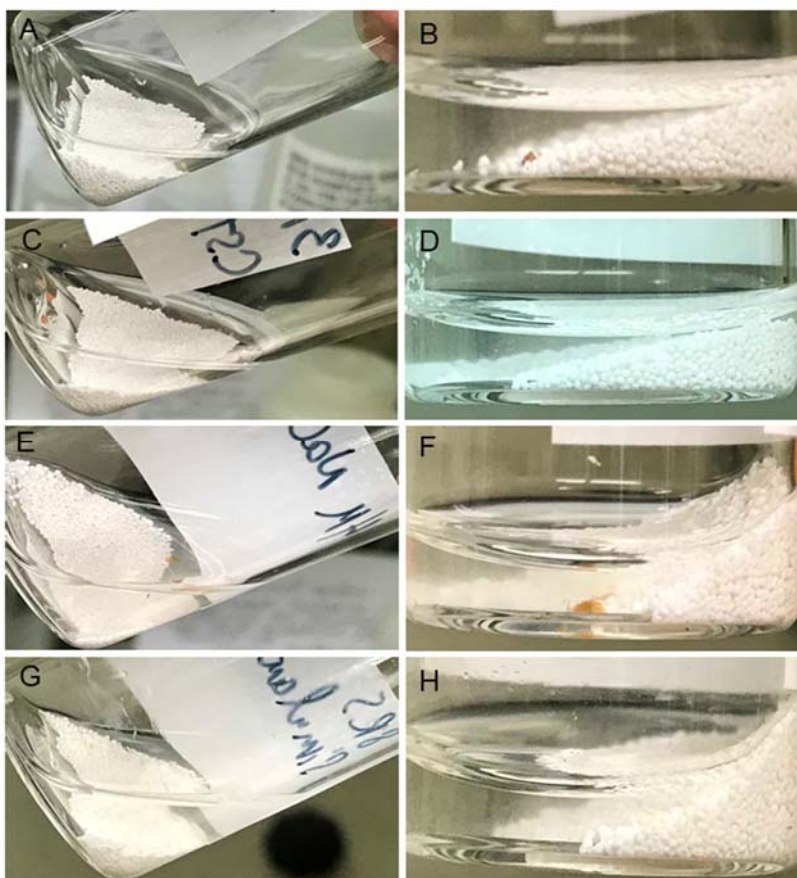


Figure A-3. Images of the CST in caustic solutions after two months, at which point the transparency of the solution began to change. A & B) are 2 M NaOH, C & D) are 3 M NaOH, E & F) are 4 M NaOH, G & H) are SRS Simulant.

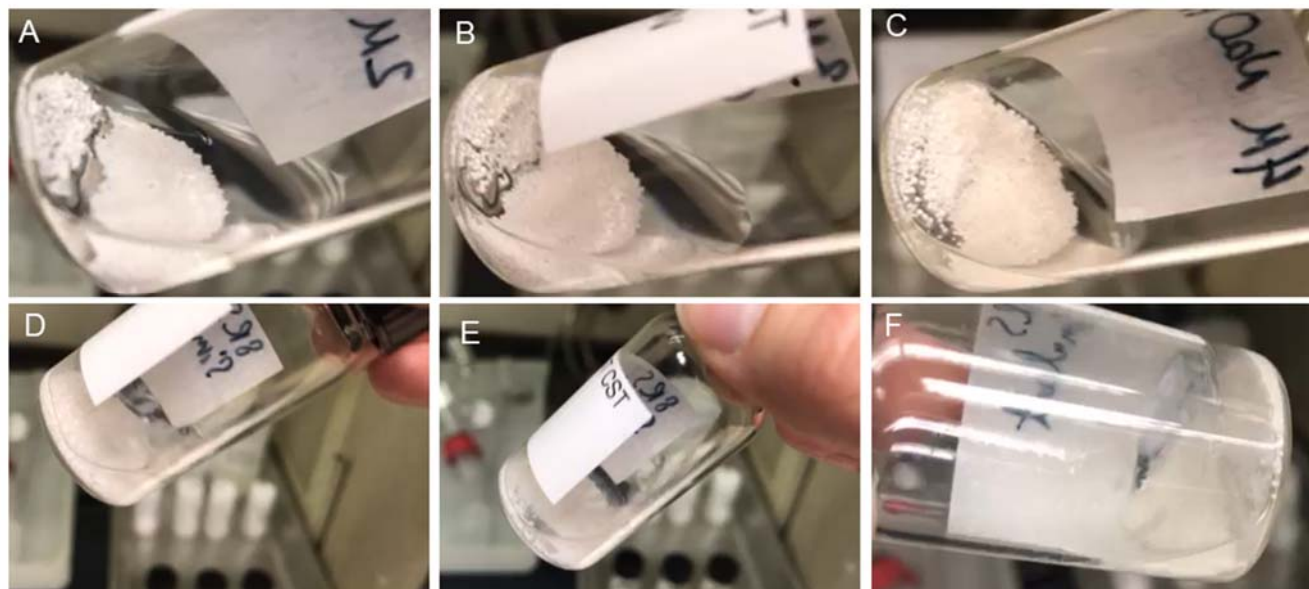


Figure A-4. Images of CST samples that had been left undisturbed for ~2 months. A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D – F) is SRS simulant.

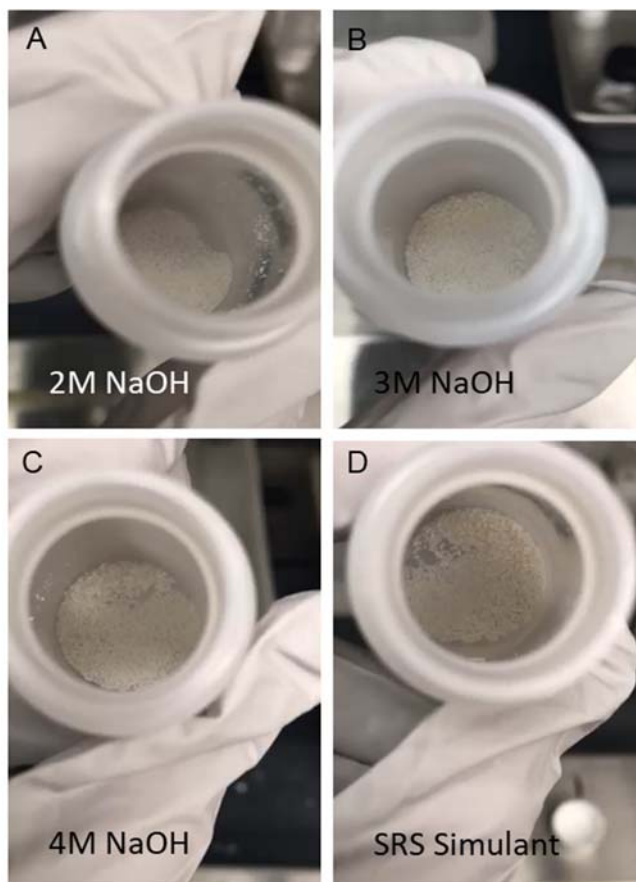


Figure A-5. Images of the CST dispersed in NaOH stored in plastic vials. The concentration of the samples are as follows: A) 2 M NaOH, B) 3 M NaOH, C) 4 M NaOH, and D) SRS Simulant.

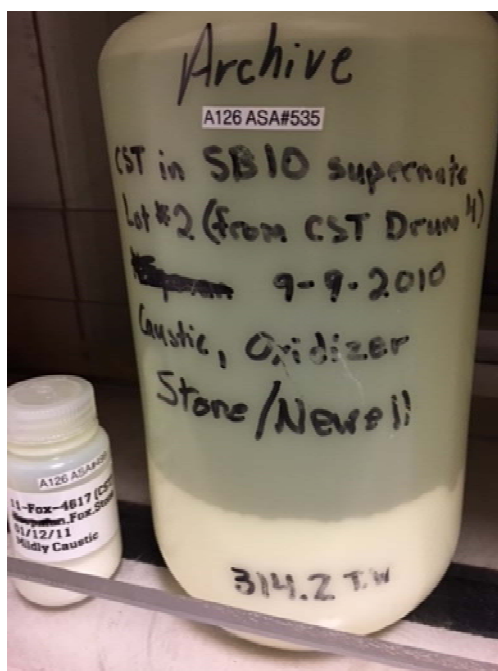


Figure A-6. Photograph of archived ground CST stored in Salt Batch 10 Simulant from 2010.

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