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Spent Crystalline Silicotitanate Storage Study—Post AP-105DF Processing

July 2021

SK Fiskum
AM Westesen
RA Peterson

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Richland, Washington 99354

Change History

Revision	Date Issued	Description of Change
0	January 2021	Initial Issue.
1	July 2021	Added Appendix A describing the condition of the post-processed CST media beds after aging nearly one year at ambient temperature.

Summary

A Tank-Side Cesium Removal (TSCR) system is under development by Washington River Protection Solutions to support initial production of immobilized low-activity waste (LAW) by feeding Hanford tank supernate from tank farms to the Hanford Waste Treatment and Immobilization Plant (WTP) LAW Facility. Tank waste supernate will be filtered to remove suspended solids and then Cs will be removed by processing it through crystalline silicotitanate (CST) ion exchange media manufactured by Honeywell UOP, LLC. The Cs-loaded CST columns will be stored indefinitely, with a goal of eventual CST removal and treatment. Thus, the spent CST needs to be recoverable after undetermined storage time.

Previous testing with AP-105 simulant showed that rinsing the CST bed with 3 bed volumes (1.4 apparatus volumes [AVs]) of 0.1 M NaOH resulted in a dried bed that maintained flow characteristics indicative of ease of recovery.[1] This study explored the intermediate conditions (between feed dried in place and the 1.4 AVs of 0.1 M NaOH rinse) to evaluate CST bed properties after:

1) stoppage with feed in place;
2) stoppage after draining feed;
3) stoppage after 0.7 AV of 0.1 M NaOH rinse through column;
4) stoppage after 1.5 AVs of 0.1 M NaOH rinse through column.

Post processing, each column was heated at 50 °C for 19 days under pseudo-storage conditions to simulate the expected dried and stored CST bed conditions. Testing was conducted at the small scale (12-mL bed volume); actual, Cs-depleted, AP-105 tank waste was used as the feed. Post-dried CST bed physical properties (angle of repose and penetration depth) were measured to evaluate how CST moved and flowed. All process stop-conditions resulted in a solidified CST bed except for the final condition, 1.5 AVs of 0.1 M NaOH rinse. At this small scale, the three CST beds presented an issue for retrievability after the short storage period (19 days at 50 °C). The latter case confirmed the results from simulant testing.

The testing was intended to provide a preliminary assessment of issues that may arise from desiccation of CST during storage with the indicated salt solutions in place. Since these were small-scale tests, the processing system did not scale to full-scale conditions exactly; however, the tests did provide insight into the impact on the dried and stored CST bed after stopping processing at an earlier step (upset condition) than normal. These results indicate that if an upset condition occurs at TSCR, a dilute hydroxide rinse should be considered before the CST dries from internal heating.

[1] Fiskum SK and RA Peterson. 2020. *Spent Crystalline Silicotitanate Storage Study*. PNNL-30174, Rev. 0, RPT-DFTP-018, Rev. 0. Richland, WA: Pacific Northwest National Laboratory.

Acknowledgements

The authors thank the Analytical Support Operations (ASO) for analysis. Jenn Carter conducted analysis by inductively coupled plasma optical emission spectroscopy and Denis Cherkasov conducted the subsequent data review. Andrew Carney conducted the hydroxide analysis and Karl Pool conducted the subsequent technical review. The authors thank Heather Colburn for conducting the technical review of calculation file and this report. The authors also thank Bill Dey for the quality review of the calculation file and this report and Matt Wilburn for his technical editing contribution to this report.

Acronyms and Abbreviations

ASO	Analytical Support Operations
ASR	analytical service request
AV	apparatus volume
BV	bed volume
CST	crystalline silicotitanate
DOE	U.S. Department of Energy
EPMA	emission gun electron probe microanalyzer
FD	feed displacement
IC	ion chromatography
ICP-OES	inductively coupled plasma-optical emission spectrometry
LAW	low-activity waste
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
TSCR	Tank Side Cesium Removal
WAC	Waste Acceptance Criteria (limit)
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The U.S. Department of Energy (DOE) is working to expedite processing of Hanford tank waste supernate at the Hanford Waste Treatment and Immobilization Plant (WTP). To support this goal, Washington River Protection Solutions (WRPS) is designing a Tank Side Cesium Removal (TSCR) system for suspended solids and cesium (Cs/^{137}Cs) removal from Hanford tank waste supernate. The Cs-decontaminated product will be sent to the WTP Low-Activity Waste (LAW) Facility for vitrification. The ion exchange media selected for Cs removal in the TSCR system is crystalline silicotitanate (CST) that is manufactured in a nearly spherical form by Honeywell UOP LLC (UOP; Des Plaines, IL) as product IONSIV™ R9140-B (Na form). The chemical and physical properties have been previously described (Braun et al. 1996, Pease III et al. 2019).

The CST ion exchange system is expected to be composed of three sequential columns (lead, lag, and polish). Once CST ion exchange feed processing is completed, the feed will be displaced with three bed volumes (BVs) of 0.1 M NaOH followed by three BVs water. Residual liquid will then be removed from the ion exchange column system by passing compressed air through the beds. The compressed air dries the CST until the no free liquids criterion is met. The CST/shielded columns will be removed from the system, transferred to a separate location, and stored for an indeterminate time. Ultimately, the CST must be retrievable for further handling/immobilization and disposal. Testing with AP-107 and AW-102 Hanford tank wastes at a small-column configuration (10-mL volumes) showed properly rinsed and dewatered CST can be readily removed from the columns, where CST poured easily shortly after testing was completed (Fiskum et al. 2019a, Rovira et al. 2019). The large-scale processing demonstration conducted on Melton Valley waste was processed following a different paradigm: The rinsed spent CST was transferred as a wet slurry to a vessel and then dried in place for ultimate in situ disposal (Walker Jr. et al. 1998). In this case, retrievability was not relevant for the dried CST form.

Staff at the Hanford Site's 222-S Facility used CST to process AZ-101/102 tank wastes to remove Cs; post tank waste processing rinses were unknown and unreported (Lindberg et al. 2019). The spent CST-loaded columns, exposed to high radiation emanating from loaded ^{137}Cs and hot cell conditions, were stored at cell temperature for ~9 years. During retrieval efforts, staff noted the CST was very difficult to remove from the columns, requiring forceps to physically break up the CST bed. The CST was thought to be cemented in place by cancrinite and a niobium-rich phase formed after feed processing and in conjunction with desiccation and possibly high radiation exposure. Insufficient rinsing following the tank waste processing may have led to the observed solidification of the CST bed. Lindberg's observations triggered concern for CST retrievability after aging in the columns. Further, it was of interest to know the level of rinsing required to avoid formation of a monolithic structure in the event of an upset condition that may stop TSCR processing in place.

A recent study was conducted with AP-105 simulant to evaluate the CST bed condition after stopping processing at key steps in the ion exchange process: 1) feed in place, 2) after 0.1 M NaOH rinse, 3) after water rinse, and 4) after drying under gas flow (Fiskum and Peterson 2020). Testing was conducted at a small scale with 12-mL CST beds in a 2.54 cm diameter column (2.5 cm tall bed). Post-processing, the beds were heated to 70 °C until all columns ceased losing mass (14.9 days) thus drying the contact fluid in place. Selected bed properties (CST angle of repose and penetration) were examined to assess flow properties (expected to be directly related to retrievability). Except for the first condition (feed dried in place), all CST beds flowed easily and indicated minimal challenges to CST retrievability. The CST bed dried with feed in place was immovable when rotated 90° from vertical and not penetrable with a 3/16-inch diameter rod at 650 grams of force.

Modified testing was recommended with the actual AP-105 tank waste to further explore the CST bed conditions when processing was stopped between the feed and the end of the 0.1 M NaOH rinse. This was thought to provide better understanding of the conditions that led to the hardening of the CST bed used to process AZ-101/102 tank wastes.

Testing was conducted in accordance with a test plan approved by WRPS.[1] Testing was conducted at the small scale (12-mL BV); actual AP-105 diluted and Cs-decontaminated tank waste was used as the feed. Following the planned process disruptions, the CST beds were dried in place at 50 °C. Post-dried CST bed physical properties (angle of repose and penetrability) were measured to evaluate how the spent and dried CST flowed. This testing was expected to provide a preliminary assessment of issues that may arise from desiccation of CST under thermal condition with the various salt solutions in place. Since these were small-scale tests, the processing conditions did not match full-scale conditions exactly. The results are intended to provide insight into the impact of CST retrievability for different end state conditions.

[1] Fiskum SK. 2019. TP-DFTP-074, Rev. 1.0. *DFTP Technology Testing and Support: Small Scale Storage Testing of Spent CST*. Pacific Northwest National Laboratory. Richland Washington. Not publicly available.

2.0 Quality Assurance

All research and development (R&D) work at Pacific Northwest National Laboratory (PNNL) is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the PNNL's Washington River Protection Solutions (WRPS) Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2008), and NQA-1a-2009, *Addenda to ASME NQA-1-2008* (ASME 2009), and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research" and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

3.0 Experimental

This section describes the AP-105 diluted and Cs-removed tank waste composition (hereafter called AP-105), CST and its pretreatment, column system and processing, CST bed characterization, and solution analysis. All column work was conducted according to a test instruction.[1]

3.1 AP-105 Composition

The AP-105 metals, anions, and radionuclide compositions were measured following ion exchange processing (Fiskum et al. 2021). Table 3.1 provides the concentrations of selected analytes >0.001 M. The last bulk effluent sample collected from the ion exchange run, and representing the 1023-1091 BV processing interval (660 mL), was selected as the storage study feed. This specific sample was targeted because the ^{137}Cs concentration (0.548 µCi/mL) exceeded the Waste Acceptance Criteria (WAC) limit[2] of 0.155 µCi/mL (based on 5.92 M Na and 122 µCi/mL ^{137}Cs in the ion exchange feed). Further Cs decontamination was required to meet the WAC limit and then the product effluent would be more useful in potential follow-on activities such as vitrification.

Table 3.1. Selected AP-105 Component Concentrations (Fiskum et al. 2021)

ICP-OES	M	IC	M
Al	5.23E-01	Cl^-	1.10E-01
Ca	1.02E-03	$C_2O_4^{2-}$	2.84E-03
Cr	6.56E-03	NO_2^-	1.38E+00
K	1.02E-01	NO_3^-	1.89E+00
Na	6.00E+00	PO_4^{3-}	8.72E-03
P	1.44E-02	SO_4^{2-}	2.44E-02
S	4.65E-02		
Furnace Combustion	M	Titration	M
TOC	2.16E-01	OH^-	1.24E+00
TIC (CO_3^{2-})	4.72E-01		

IC = ion chromatography
ICP-OES = inductively coupled plasma-optical emission spectrometry
TOC = total organic carbon
TIC = total inorganic carbon
Density = 1.285 g/mL

3.2 CST

WRPS purchased the CST from Honeywell LLC, as IONSIV™ R9140-B, Product Number 8056202-999 Lot 2002009604, as an 18 × 50 mesh sieve cut, and provided it to PNNL for use in testing. Fiskum et al. (2019a) provided additional detail associated with receipt and storage of this CST sample.

A 121-g CST aliquot was collected and pretreated by contacting with 250 mL of 0.1 M NaOH. The 0.1 M NaOH rinse solution and colloidal fines from the CST were decanted. Five additional rinses of ~120-mL

[1] Fiskum SK. 2020. TI-DFTP-096. *Condition of CST After Dry Storage Following Upset Process Conditions with Prototypic TSCR Process Solution Flows Using AP-105 Actual Tank Waste*. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available.
[2] From *ICD 30 – Interface Control Document for Direct LAW Feed*, 24590-WTP-ICD-MG-01-030, Rev. 0, 2015, Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

0.1 M NaOH were applied. The final rinse solution was left in contact with the CST for 224 days before CST was collected and placed in the columns.

3.3 Column System

Two duplicate ion exchange systems were constructed and were designated System A and System B. Figure 3.1 provides a schematic of the ion exchange process systems; the two systems were set up similarly to those used for simulant testing (Fiskum and Peterson 2020). Flow through each system was controlled with a Fluid Metering Inc. positive displacement pump. Fluid was pumped past an Ashcroft pressure gage and a Swagelok pressure relief valve with a 10-psi trigger point. The 1/8-inch outside diameter, 1/16-inch inside diameter, polyethylene tubing was purchased from Polyconn (Plymouth, MN). The 1/8-inch outside diameter, 1/16-inch inside diameter, stainless steel tubing was hard plumbed to the manifold structure. Valved quick disconnects were purchased from Cole Parmer (Vernon Hills, IL). Use of the quick disconnects enabled easy column and solution flow realignment. The quick disconnects were color-coded to ease correct alignment.

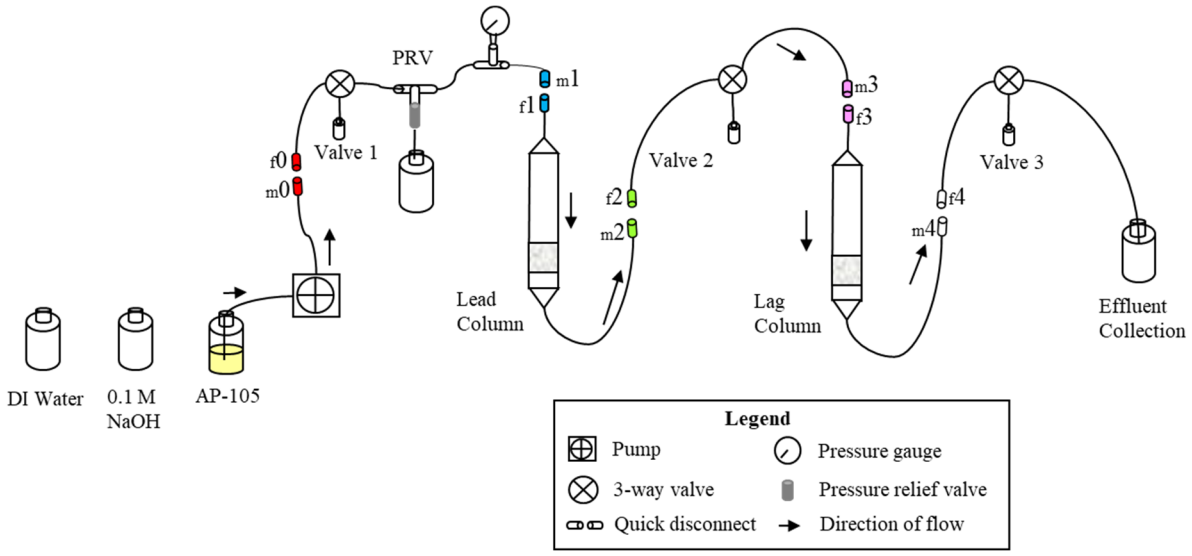


Figure 3.1. Ion Exchange System Schematic

Chromaflex® column assemblies, 2.54 cm inner diameter and 15 cm tall, were used (Kimble Chase, www.kimble-chase.com). Each column assembly included the column plus the standard top and bottom end fittings. Each column was made of borosilicate glass; column fittings and tubing connectors were composed of polytetrafluoroethylene. The vendor-provided 20 µm pore size high density polyethylene bed support was removed from each fitting to mitigate chances for plugging. The CST was instead supported by an in-house constructed support consisting of a 200-mesh stainless steel screen tack welded onto a stainless-steel O-ring. With a rubber O-ring, the fitting was snug-fitted into place in the column as previously described by Fiskum et al. (2018). The small cavity under of each bed support was filled to the extent possible with 4-mm-diameter glass beads to minimize the mixing volume below the CST bed. An adhesive centimeter scale with 1-mm divisions (Oregon Rule Co. Oregon City, OR) was affixed to the column with the 0-point coincident with the top of the support screen. The tare masses of the columns with fittings were measured before CST was added.

Three Swagelok valves were installed in the valve manifold. Valve 1 was used to isolate the columns from the pump (when in the closed position) and purge the tubing from the inlet to valve 1 (when placed

in the sampling position). The AP-105 and 0.1 M NaOH feed displacement (FD) solution were collected from the final line to the effluent collection.

The system was filled with water and then slightly pressurized to confirm system leak tightness. The pressure relief valve was confirmed to trigger at the manufacturer set point (10 psig). Water was removed from the columns and replaced with 0.1 M NaOH. Four 12-mL aliquots of CST were measured using a 25-mL graduated cylinder and quantitatively transferred to each of four columns. The CST was allowed to settle through the 0.1 M NaOH solution, thus mitigating gas bubble entrainment. The columns were tapped with a rubber bung until the CST height no longer changed. Figure 3.2 provides a closeup image of the System B lead column just after processing was completed; it shows the CST bed, the fluid headspace, and the CST bed support.

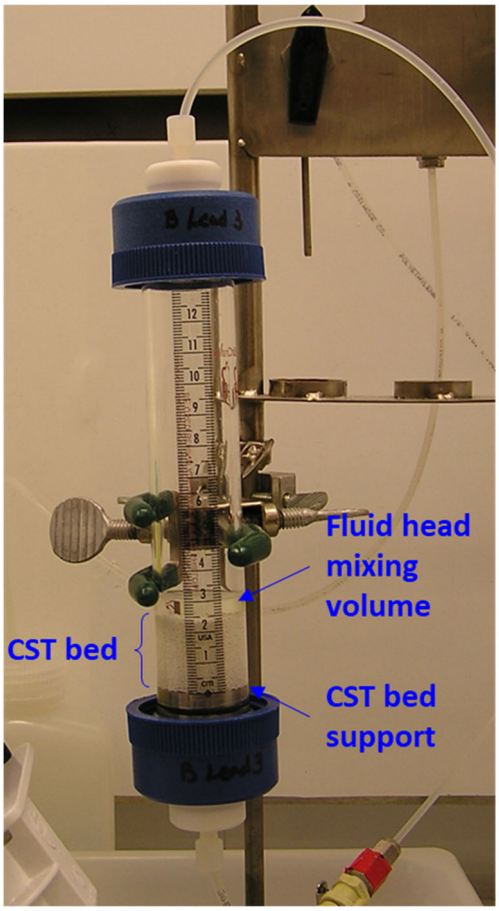


Figure 3.2. Closeup of Loaded System B Column 3

The CST BV corresponded to the settled CST media volume as measured in the graduated cylinder prior to transferring the media into the ion exchange column. The reference CST BV was 12.0 mL. The settled CST bed heights in the columns were 2.5 cm. With a column inner diameter of 2.54 cm, this corresponded to a length/diameter ratio of 0.98.

The entire fluid-filled volume of the assembly was ~46 mL, inclusive of fluid in the lines, valves, quick disconnects, and CST beds. Fluid headspace was kept as low as practical at 2.5 to 5.6 mL, as was the fluid mixing volume below each CST bed at ~3.5 mL. The bed void volume was 67.6% (Fiskum et al. 2019b); therefore, each CST bed held 8.1 mL of fluid. About 53% of the total fluid holdup volume was associated with the CST beds and fluid head of the two columns in series; this represents the fluid fraction that

would dry in the two system CST beds. About 47% of the fluid volume was associated with the tubing, valve, connectors, and fluid below the CST bed support. These fluid mixing volume fractions are not likely to be representative of plant-scale operations. All column attributes matched those of the AP-105 simulant test as closely as practical (Fiskum and Peterson 2020).

3.4 Process Conditions

Table 3.2 delineates the target stopping conditions as they applied to selected columns. The lead and lag columns were assembled in series for Systems A and B. Table 3.3 through Table 3.6 specify the implemented process parameters, including process volumes, flowrates, CST contact times for each column, and sampling points. All processing was conducted at ambient temperature conditions, nominally 20 °C. Flow was stopped at the end of the normal workday and restarted the next morning; thus, a 30.6 h loading duration spanned three operational days.

Table 3.2. Feed Stoppage Conditions

Stop-Feed Condition	Column Identification
AP-105 feed in place	System A, lead column 1
AP-105 feed drained	System A, lag column 2
3 BVs (1.4 AVs) 0.1 M NaOH[(a)]	System B, lead column 3
3 BVs (0.7 AVs) 0.1 M NaOH[(a)]	System B, lag column 4
(a) Fluid left in place.	

Table 3.3. Experimental Conditions for System A Lead Column 1, August 10-12, 2020

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(AV)	(mL)	(BV/h)	(mL/min)	(h)
Lead → Lag							
Loading	AP-105	28.0	17.4	336	1.93	0.385	30.6
BV = bed volume (12.0 mL as measured in graduated cylinder) AV = apparatus volume; through Column 1, ~28 mL							

Table 3.4. Experimental Conditions for System A Lag Column 2, August 10-12, 2020

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(AV)	(mL)	(BV/h)	(mL/min)	(h)
Lead → Lag							
Loading	AP-105	28.0	10.5	336	1.93	0.385	30.6
Drain	AP-105	--	--	--	--	--	--
BV = bed volume (12.0 mL as measured in graduated cylinder) AV = apparatus volume; through Columns 1 and 2 combined, ~46 mL							

Table 3.5. Experimental Conditions for System B Lead Column 3, August 10-12, 2020

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(AV)	(mL)	(BV/h)	(mL/min)	(h)
Lead → Lag							
Loading column	AP-105	26.2	11	314	1.78	0.352	30.8
Feed displacement	0.1 M NaOH	3.57	1.4	42.8	3.45	0.691	1.15

BV = bed volume (12.0 mL as measured in graduated cylinder)
AV = apparatus volume; through Column 3, ~30 mL

Table 3.6. Experimental Conditions for System B Lag Column 4, August 10-12, 2020

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(AV)	(mL)	(BV/h)	(mL/min)	(h)
Lead → Lag							
Loading column	AP-105	26.2	6.6	314	1.78	0.352	30.8
Feed displacement	0.1 M NaOH	3.57	0.69	42.8	3.45	0.691	1.15

BV = bed volume (12.0 mL as measured in graduated cylinder)
AV = apparatus volume; through Columns 3 and 4 combined, ~47 mL

System A column effluent was only collected from the valve following Column 2 (lag column); the effluent composition was assumed to be equivalent to that from Column 1 (lead column). Once a stop-feed condition was neared for System B columns, the last 10-mL of process volume was collected as a sample from the valve immediately following Column 4 and was representative of the Column 4 fluid. The Column 3 fluid sample was collected from the quick disconnect below the column. This sampling paradigm differed from the simulant test (Fiskum and Peterson 2020) where the corresponding sample was collected at the valve and was subject to a larger in-line fluid volume. Thus, Column 3 fluid sampling resulted in a relatively more accurate assessment of the fluid condition in the column.

3.5 Column Drying

The columns were removed from the manifold system by unhooking the quick disconnects above and below the column. The columns were carefully removed from the manifold system so as not to disturb the CST bed. The column contents included the fluid headspace, interstitial fluid, CST, and fluid below the support screen. The columns were placed onto a stand supporting the columns in a 2×2 array as previously described (Fiskum and Peterson 2020).

A blank male quick disconnect fitting was installed at the top column female quick disconnect to allow for air displacement. The top column fittings were removed to allow water to evaporate. The bottom fittings were maintained in place such that fluid would not drain. Heat tape was wrapped around the columns and insulation was wrapped around the assembly. The initial 24-h heating period incorporated a stepwise ramp from room temperature to 35, 40, 45, and 50 °C. The temperature was maintained at 50 °C for the next 19 days with one interruption for mass measurement. Gross column mass measurements were collected on day 16 and day 19 to confirm that steady state mass was obtained. The system was checked periodically during the drying period to confirm the temperature and visually assess system integrity (e.g., signs of leakage).

3.6 Post Processing Analysis

The angle of repose for CST was measured for each column after rotating the columns 90° onto their sides and allowing the CST beads to spread naturally. Images were collected such that the angle of repose could be calculated as shown in Figure 3.3. In this case, a right triangle was superimposed over the image to match the shape of the slumped CST. The length (a) and height (b) of the right triangle were measured and the angle, θ, was calculated according to standard geometric functions. The furthest longitudinal distance a CST particle traveled was also noted. After testing, the columns were gently turned upright.

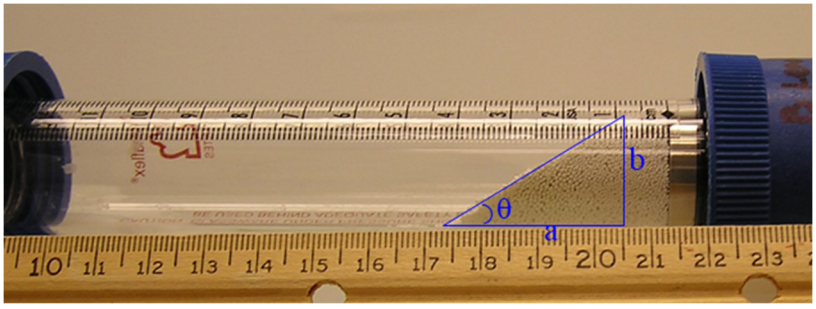


Figure 3.3. Column 3 Angle of Repose Measure

A 3/16-inch (0.476-cm) diameter rod was mated to the foot of an AMS pocket penetrometer (AMS Inc. American Falls, ID) using a union prepared in-house. The penetrometer was calibrated using a balance to measure compressive force per penetrometer increment (Figure 3.4). Because of the nearly 6-month interval between the non-radiological and radiological tests, the December 2019 calibration was confirmed in August 2020.

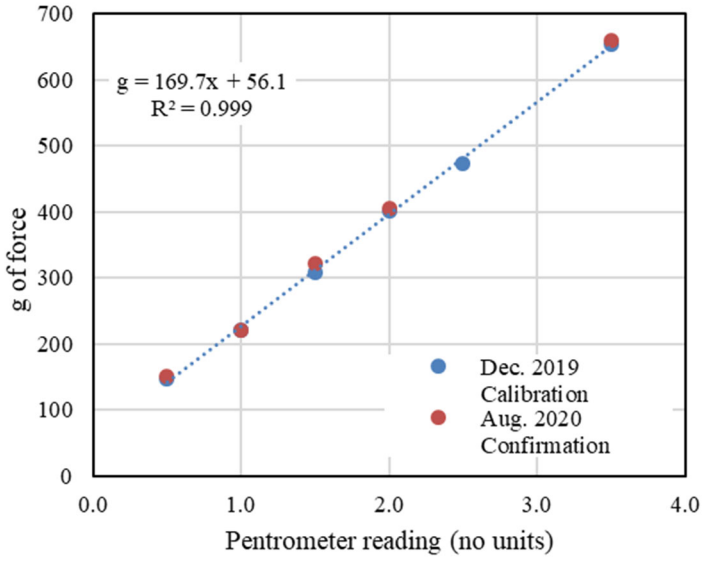


Figure 3.4. Penetrometer Calibration Curve, g of Force vs. Penetrometer Reading

The penetration test consisted of pushing the rod extension of the penetrometer into each CST bed by hand and measuring the penetrometer compressive force required to reach the bottom of the bed. Using the calibration curve, the g of force was determined.

The aqueous samples were measured for hydroxide, Al, K, and Na concentrations by Analytical Support Operations (ASO) according to Analytical Service Request (ASR) 1110 (see Table 3.7). Hydroxide was measured using potentiometric acid titration. Al, K, and Na concentrations were measured by inductively coupled plasma optical emission spectroscopy.

Table 3.7. Aqueous Sample Descriptions (ASR 1110)

Sample ID	ASO ID	System	Associated Column	Description
TI096-EFF-AA	20-1804	A	2	Last 10 mL of AP-105 collected from the lag column
TI096-FD-BLA	20-1805	B	3	Last 10 mL of the FD processed through the lead column only
TI096-FD-BPA	20-1806	B	4	Last 10 mL of the FD processed through the combined lead/lag columns

4.0 Results

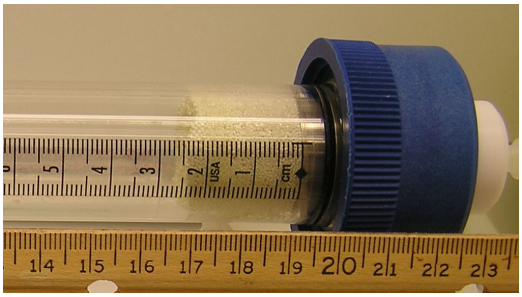
This section describes the dried CST physical features as they relate to CST movement. It also summarizes the solution analysis from the samples collected from the columns just before removal from the manifold system.

4.1 Physical Properties

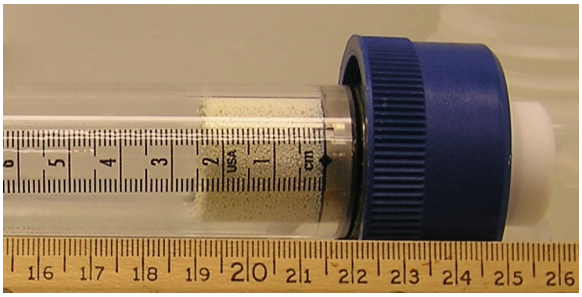
The dried CST beds associated with disruptions at various process steps during TSCR operations were evaluated. Only one CST bed (Column 3) flowed readily with no evidence of agglomeration and the bed could be penetrated to the support screen with no measurable force. All other CST beds were "cemented" in place with the dried salts (see Figure 4.1). A 400 – 560 g, compressive force applied to Columns 1, 2, and 4 resulted in no bed penetration.

The behaviors of the two pairs of CST beds processed with simulant AP-105 (Columns 5 and 6, Fiskum and Peterson 2020) and actual AP-105 tank waste (Columns 1 and 3) under similar conditions were compared. Column 1 and Column 5 were dried with feed in place. Both CST beds were immovable and impenetrable with up to ~600 g force. Column 3 and 6 were rinsed with 1.4 AVs 0.1 M NaOH. The angles of repose for Column 3, 31°, agreed with that of Column 6 angle. Like Column 6, Column 3 could be easily penetrated to the support screen with no resistance measured by the penetrometer.

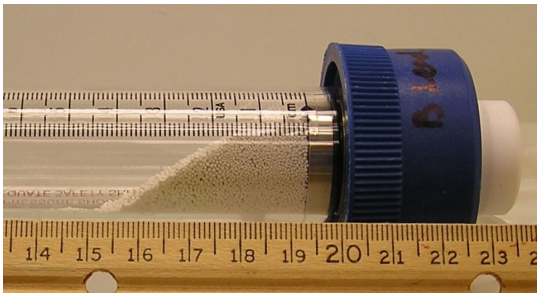
These results again indicated that the residual salts from actual tank waste in the CST bed, following processing of 1.4 AVs of FD solution, may not lead to a catastrophic CST bed recovery and that the simulant accurately emulated the angle of repose and bed penetration properties.



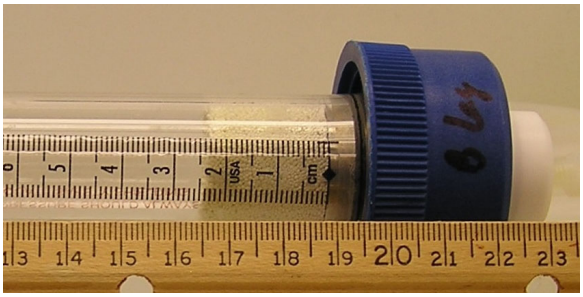
Column 1



Column 2



Column 3



Column 4

Figure 4.1. Angle of Repose, All Tests

Previous attempts to remove CST particles from solidified columns were met with difficulty (Fiskum and Peterson 2020). Scraping the "cemented" solids caused the CTS particles to pulverize. CST is easily friable and a small gram force caused the CST to crush into powder. Therefore, attempts to further evaluate the CST with microscopy were abandoned.

It was unclear whether any of the tested processing conditions emulated the conditions that resulted after processing AZ-101/102 tank wastes (Lindberg et al. 2019). Lindberg et al. reported that the CST was essentially cemented near the top of the 20-cm bed and had to be chiseled out, similar to the conditions previously reported by Fiskum and Peterson (2020). Lindberg et al. further reported that the lower CST bed portion was extracted with forceps. The cohesion that was found with the AZ-101/102 test was attributed to cancrinite and a Nb-rich phase. The role of radiation exposure in cohesion was not clear. The suite of anion content measured in the CST water leachate for the current study was similar to the anion suite present in AZ-101/102 tank wastes. Thus, residual tank waste in the CST bed was likely, and inadequate CST bed rinsing post tank waste processing could easily have resulted in the observed particle cohesion along with cancrinite production.

4.2 Solution Analysis

The last ~10-mL aliquot processed through each column was collected and analyzed for hydroxide, Al, K, and Na, as described in Table 3.7. The analysis provided a sense of the actual salt solution composition remaining in contact with the CST before the column was removed for drying. It is noted that the 10-mL sample salt concentrations (Na, Al, K, and hydroxide) may be biased higher than the actual salt solution concentrations in contact with the CST; this is attributed to the mixing volumes and fluid volume in the lines between the CST bed and the sampling point. Table 4.1 provides the cross reference of sample identifications (IDs), column processing configurations, and codes (for use in figures).

Table 4.1. Analytical Samples

Column Configuration	Column Identification	Sample ID	Analysis Sample	Figure Code
None	None	TI082-Comp-Eff[a]	AP-105 feed solution	Feed
System A lead/lag	2	TI096-EFF-A	Drained feed from lag column	Free-drained
System B lead/lag	4	TI096-FD-BPA	Last 10 mL sample from lag column, FD (3.57 BVs, 0.65 AV, 43 mL)	0.65 AV FD (normal off lag)
System B lead	3	TI096-FD-BLA	Last 10 mL sample from lead column, FD (3.57 BVs, 1.4 AVs, 43 mL)	1.4 AV FD (normal off lead)

BV = bed volume, 12.0 mL
FD = feed displacement
AV = fluid filled apparatus volume
(a) Fiskum et al. 2021.

Analytical results are summarized in Table 4.2. The best marker to evaluate displacement of feed from the column is the Al concentration (FD is composed of 0.1 M NaOH and some K uptake was possible). The analytical uncertainty was reported to be up to ±15% by the lab (ASO) that performed the chemical analyses. The AP-105 feed solution was analyzed separately from the other samples. It appeared that a high ICP-OES bias was realized with the suite of three samples analyzed under ASR 1110 because the Al and K concentrations were upwards of 20% higher in TI096-EFF-A and TI096-FD- BLA than found in

the feed. The operations described herein would not have physically resulted in higher effluent analyte concentration relative to the feed.

Table 4.2. Sample Results

Sample ID	Al (M)	K (M)	Na (M)	Free OH^- (M)
TI082-Comp-Eff[a]	0.523	0.102	6.00	1.36
TI096-EFF-A	0.580	0.121	6.11	1.36
TI096-FD- BPA	0.040	0.004	0.338	1.31
TI096-FD- BLA	0.567	0.120	6.13	0.31

(a) Fiskum et al. 2021.

Very little feed removal was realized at the lag column following the FD step (Column 4, 0.65 AV), whereas significant feed reduction was observed for the lead column (Column 3, 1.4 AVs). The data set was reevaluated for fraction of analyte remaining in the CST bed and is summarized in Figure 4.2. The ~90% reduction of the interstitial AP-105 feed content following the 1.4 AVs of FD (Column 3) allowed easy movement of CST post-drying. Note that the 1.4 AVs FD rinse following the AP-105 simulant test showed a lower (60%) removed fraction; in that test the sample was collected at the valve, which incorporated another ~5 mL downstream from the bed and therefore likely contained more tank waste simulant associated with the larger holdup volume. Processing 0.65 AV of FD was insufficient to measurably decrease the solution in contact with the CST below the nominal feed composition. The free-drained CST apparently contained enough interstitial tank waste to create salt bridging between CST particles upon drying.

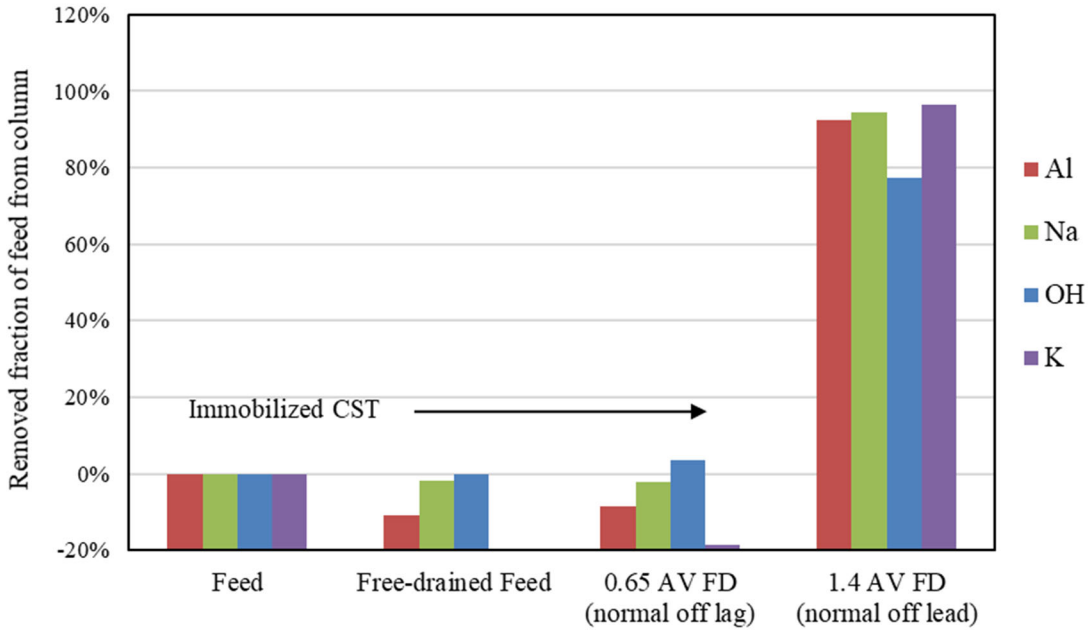


Figure 4.2. Fraction of Feed Removed from Column System during Key Process Steps

The AP-105 feed contained 0.554 μCi ^{137}Cs/mL. The AP-105 effluents were combined and measured for ^{137}Cs by gamma energy analysis. The effluent composite measured 2.51×10^{-4} μCi ^{137}Cs/mL, which corresponded to a Cs decontamination factor of 2207. The Cs decontamination was sufficient to bring the AP-105 effluent ^{137}Cs concentration below the WAC limit of 0.155 μCi ^{137}Cs/mL.

4.3 Extended Storage Post Processing

The following three columns were forwarded to the planned 1-year storage period post-processing evaluation;

1) Column 2, free-drained CST following AP-105 tank waste processing (this study)
2) Column 3, 1.4 SV FD rinsed CST following AP-105 tank waste processing (this study)
3) Column 6, 1.4 SV FD rinsed CST from the AP-105 simulant testing (Fiskum and Peterson 2020).

Column 2 would act as a benchmark, mirroring the most likely scenario that was applied to the AZ-101/102 testing (the results of the AZ-101/102 CST condition triggered this study, Lindberg et al. 2019). Column 3 and column 6 are analogs between actual waste and simulant processing; they stand at the processing cusp resulting in cemented CST and free-flowing CST post-drying.

5.0 Summary

CST removal from the TSCR system columns is anticipated for eventual processing. However, little experience is available with stored CST after contact with tank waste. One evidence-based process showed CST retrievability to be difficult, but post loading rinsing processes were not reported (Lindberg et al. 2019). Recent testing with AP-105 simulant showed that rinsing with 1.4 AVs FD and beyond (water rinse, flushing dry) indicated no issues with CST mobilization (Fiskum and Peterson 2020). The current testing evaluated various stop-flow (upset) processing conditions in the same small-column format (12 mL CST in 1-inch diameter column) with actual AP-105 tank waste (diluted and largely Cs removed). Four stop flow scenarios were evaluated:

1) High salt AP-105 feed in place with CST bed
2) Free-drained AP-105 from the CST bed
3) FD solution in place in CST bed after 3 BVs processed (0.65 AV)
4) FD solution in place in CST bed after 3 BVs processed (1.4 AVs)

After processing, the columns were removed from the manifold and entrained solutions were dried in place at 50 °C for 19 days to emulate CST conditions after a lengthy storage period. The CST retrievability was assessed with two tests: 1) angle of repose at 90° column rotation, and 2) penetration with a 3/16-inch diameter rod. The results were used to provide an indication of how easily CST might be mobilized for retrieval from a column following the upset condition (where processing had to be stopped, liquid left in place, and columns stored for indeterminate time).

All CST from the first three test conditions had cemented in place with enough strength to resist ~560 grams of force with the penetrometer rod. The fourth test condition resulted in free-flowing CST with a 31° angle of repose and bed penetration through the bed to the support screen with no measurable force. Approximately 90% of feed solution was removed from this CST bed. These results were consistent with previously reported results with AP-105 simulant (Fiskum and Peterson 2020).

The following conclusions were drawn:

1) The AP-105 simulant provided a reasonable replica to the actual AP-105 tank waste for the CST/solution physio-chemical interaction despite the more complex nature of the actual tank waste.

2) Simple free draining of tank waste from a CST bed followed by storage to dryness results in a hardened bed.

3) Processing 1.4 AVs of 0.1 M NaOH was sufficient to remove tank waste salts and allow for free movement of CST after drying at 50 °C for at least 19 days.

6.0 References

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Appendix A – Post-Processing CST Evaluation after Extended Storage

This appendix describes the crystalline silicotitanate (CST) samples that were generated from various column processing operations, post-processed CST storage conditions, and selected CST physical properties after approximately 1 year in storage. Washington River Protection Solutions (WRPS) staff identified three CST sample beds to submit to the storage test; however, since the incremental effort required to test the remaining five CST samples was minimal, PNNL tested all eight CST samples in parallel.

A.1 Test Sample Generation Overview

The planned nominal processing progression at the Tank Side Cesium Removal (TSCR) system following tank waste feed processing is to sequentially process 3 bed volumes (BVs) of 0.1 M NaOH to effect feed displacement, 3 BVs of water rinse, and then displace the water using compressed gas. Lindberg et al. (2019) observed difficulty in CST retrievability from small columns after processing tank waste and storage for ~9 years at the Hanford 222-S laboratory. However, Lindberg et al. did not report what post-processing rinse steps were applied to the CST beds. Thus, there was some concern about CST retrievability after extended storage in an ion exchange column. In testing at Pacific Northwest National Laboratory (PNNL), various upset conditions were investigated, with respect to CST retrievability, to simulate disruptions that may occur at any of the TSCR processing steps. In the process, it was hoped to replicate the CST bed rinse conditions applied to the 222-S laboratory test to better understand what happened to limit CST retrievability.

Bench-scale testing was conducted following the TSCR processing approach, applying process-disruption scenarios during TSCR operations. Four columns, each containing 12 mL (12.0 g) of CST, were processed with simulated AP-105 tank waste and underwent various rinses followed by a stop-flow condition (Fiskum and Peterson 2020). An additional four columns were similarly processed with actual AP-105 tank waste[1] and underwent an alternate suite of rinses/stop-flow conditions. In each case, a process stream was stopped and dried in place. The resultant CST physical properties were assessed, as they relate to CST retrievability from columns. Table A.1 summarizes the applied process conditions for each column test, along with the associated report where more detail is given.

[1] The AP-105 tank waste was processed in the fume hood after it was initially processed in the hot cell to remove Cs as previously described (Fiskum et al. 2021).

Table A.1. CST Column Rinse Summary

Stop-Flow Condition	Column Identification	Associated Report
1 BV AP-105 tank waste[a]	Column 1	This report, main body.
AP-105 tank waste gravity-drained	Column 2	
3 BVs (1.4 AVs) 0.1 M NaOH[a,b]	Column 3	
3 BVs (0.7 AVs) 0.1 M NaOH[a,b]	Column 4	
1 BV AP-105 simulant[a]	Column 5	Fiskum and Peterson 2020
2.9 BVs (1.4 AVs) 0.1 M NaOH[a]	Column 6	
3.2 BVs (0.83 AVs) 0.1 M NaOH followed by 3 BVs (0.80 AVs) water rinse, then Ar gas flush	Column 7	
3.2 BVs (0.83 AVs) 0.1 M NaOH followed by 3 BVs (0.80 AVs) water rinse[a] (no Ar gas flush)	Column 8	

(a) Fluid left in place at onset of drying.
(b) Columns 3 and 4 were in lead-lag positions, respectively; thus, column 3 experienced more effective feed displacement as represented by the higher AVs processed.
AV = apparatus volume
BV = bed volume

A.2 Storage Conditions

The glass columns 6, 7, and 8 cracked from excessive heat used in the drying process (70 °C), therefore, these CST beds, which were apparently free flowing, were transferred to 50-mL plastic digestion tubes with similar internal diameter to the columns. All other CST beds were stored in the columns used for processing. The CST beds that processed simulant (Columns 1-4) were stored for 1.3 years (February 25, 2020 to June 9, 2021); the CST beds that processed actual tank waste (Columns 5-8) were stored for 0.77 year (August 31, 2020 to June 9, 2021). The CST beds were stored at room temperature with very mild temperature fluctuation, averaging 20.9 °C with a range of 16.8 to 24.9 °C (Figure A.1 shows the temperature log for the logged portion of the storage period; COVID-19 pandemic-related constraints limited early temperature logging setup). The CST beds were not disturbed during storage.

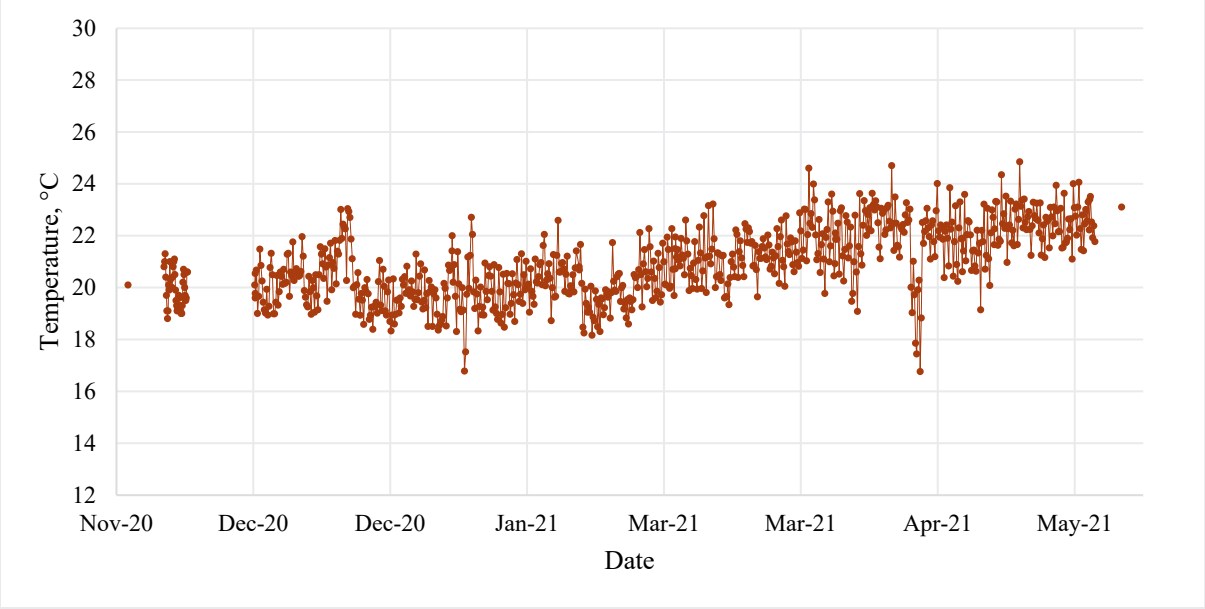
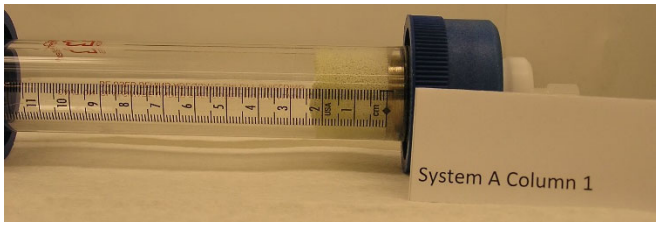


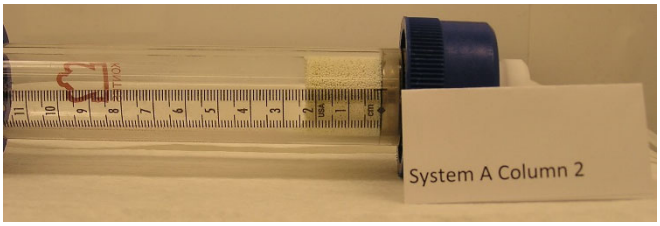
Figure A.1. Recorded Storage Temperature Profile; November 3, 2020 to June 9, 2021

A.3 Physical Property Tests and Results

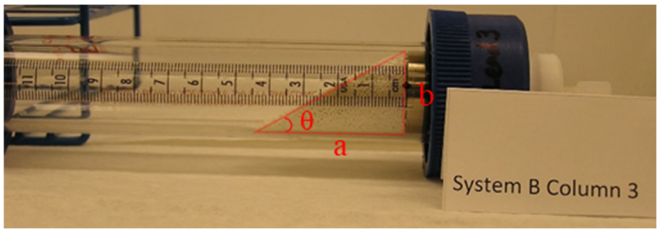
The physical property testing conducted on the aged CST beds was identical to that conducted on the initial dried beds: 1) measure of angle of repose and 2) measure depth of bed penetration using a pocket penetrometer with a 3/16-inch-diameter rod. Figure A.2 shows all CST beds as they were laid at 90° from vertical after the aging period; the scale affixed to each column/container is a centimeter scale showing millimeter graduation. The system B, column 3 image shows the relative positions of length (a) and height (b) of the right triangle where the angle of repose, θ, was calculated according to standard geometric functions. It was assumed that the plastic digestion tubes (for columns 6, 7, and 8) would not affect the angle of repose. Also shown parenthetically for reference is the angle of repose initially measured on the CST beds before the storage study began. Columns 6 and 7 showed slight reduction in the angle of repose. This is possibly an artifact of the modified container or an indication that the CST may have become slightly more cohesive.



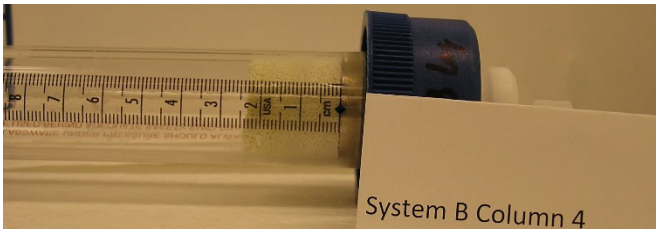
Column 1, θ = 0° (same as before aging)



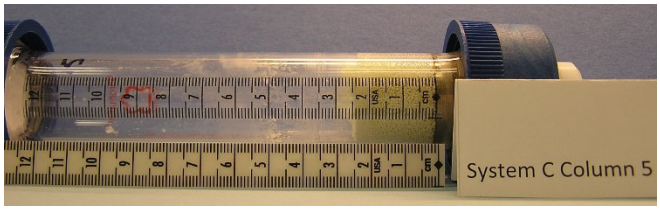
Column 2, θ = 0° (same as before aging)



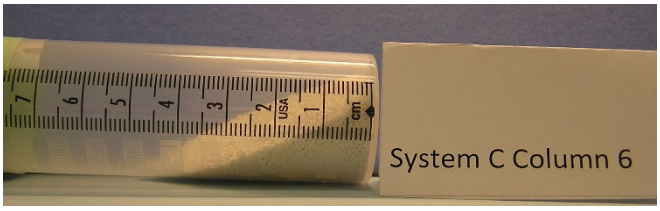
Column 3, θ = 30° (31° before aging)



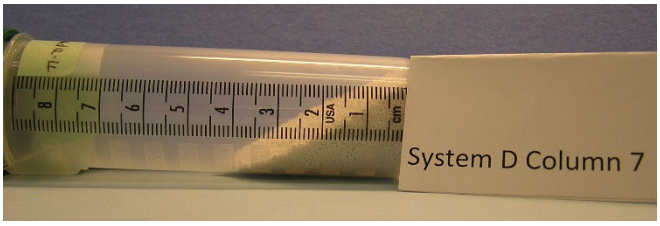
Column 4, θ = 0° (same as before aging)



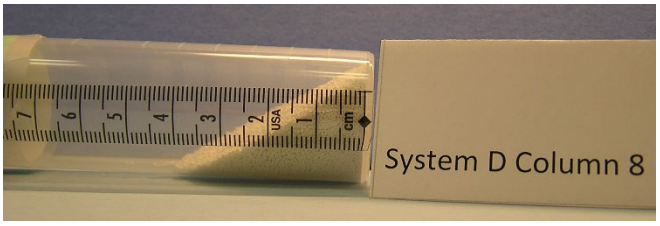
Column 5, θ = 0° (same as before aging)



Column 6, θ = 26° (31° before aging)



Column 7, θ = 29° (32° before aging)



Column 8, θ = 29° (28° before aging)

Figure A.2. Angle of Repose, θ, for Aged Columns, All Tests

The penetrometer testing showed no difference from the results reported for non-aged spent CST. For all beds that showed an angle of repose, the penetrometer rod reached the bottom of the bed easily with no measurable resistance. Where the CST showed no movement to the angle of incline measurement, maximum downward penetrometer force did not dent the CST bed; the dried salts remained solidly in place.

A.4 Summary and Conclusions

Lindberg et al. (2019) were able to remove spent CST from long-stored columns with some difficulty associated with the top layer of the bed. In no case were these observations reproduced for the CST samples inspected and reported here. Given the potential scenarios for failure during TSCR processing, it is clear that at least 1.4 apparatus volumes of rinse solution (0.1 M NaOH feed displacement plus water) must pass through the bed to expect the CST to be retrievable from the spent column. Full processing anticipated at TSCR and as manifested by column 7 appears to support complete CST retrievability as measured by the angle of repose and bed penetrability.

A.5 References

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