PNNL-28527, Rev. 0
RPT-TCT-001, Rev. 0

Cesium Removal from Tank Waste Simulants Using Crystalline Silicotitanate at 12% and 100% TSCR Bed Heights

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U.S. DEPARTMENT OF ENERGY

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Prepared for
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under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

The Direct Feed Low-Activity Waste flowsheet provides for the early production of immobilized low-activity waste (LAW) by feeding waste directly from Hanford tank farms to the Hanford Tank Waste Treatment and Immobilization Plant (WTP) for vitrification. Prior to the transfer of feed to the WTP LAW Vitrification Facility, tank waste supernatant will be pretreated by the Tank Side Cesium Removal (TSCR) system to meet the WTP LAW waste acceptance criteria (<3.18E-5 Ci ^{137}Cs/mole of Na). This pretreatment will remove cesium from the waste stream using ion exchange (IX). The selected media for IX is crystalline silicotitanate (CST), product number UOP-IONSIV-R9140-B, manufactured by Honeywell UOP LLC (Des Plaines, IL).

Testing was requested by Washington River Protection Solutions to better define IX processing using Low-Activity Waste Pretreatment System (LAWPS) prototypic IX unit operation process steps at full height and medium height. The information is intended to significantly contribute towards establishing accurate process flowsheets for the individual feed campaigns planned for the LAWPS.

Column testing at both the medium (12% of the full bed height) and full height scales was conducted to evaluate process variables and scale up performance of Cs exchange onto the CST, Lot 8056202-999. Nominal process conditions used 5.6 M Na simulant processed at 1.8 bed volumes per hour (BV/h) at 20 °C. Process variables included 1) increased process temperature to 35 °C, 2) increased Na concentration to 6.0 M, 3) added organics to the 5.6 M Na simulant, and 4) flowrate changes. The medium scale tests used single columns containing 44 mL of <25 mesh CST in a 1.44 cm diameter column, 27 cm tall CST bed. The full height columns used lead/lag columns containing 1.15 L unsieved (as-received) CST in 2.54-cm-diameter columns, 226 cm tall CST beds. Two process flowrates were tested at the full height: 1.30 and 1.82 BV/h. IX testing with simulant solutions was conducted using TSCR prototypic IX unit operations: feed processing, feed displacement with 0.1 M NaOH, water rinse, and solution expulsion with compressed air.

Figure ES.1 shows the effect of variable process parameters on the Cs load profile from the medium height column testing. Increased residence time was shown to improve Cs load performance. The Cs loading was sensitive to increased temperature; a 15 °C rise in temperature reduced the effective Cs load capacity at the equilibrium Cs feed condition 31% and dropped the BVs processed to contract limit 30%. Added organics had a marginal effect on the Cs load profile up to the 450 BVs tested with a 15% reduction in BVs processed to the contract limit. Increasing Na concentration to 6.0 M had a marginal adverse effect on the Cs load profile where the percentage of BVs processed to the contract limit was reduced by 15%. Figure ES.2 shows the load profiles for the full height column tests; processing at slower flowrate showed slightly improved exchange performance. Figure ES.3 compares the medium to full height process scales on the Cs load profile. The matched residence times (BV/h) resulted in equivalent load profiles despite the change in the medium to full height test scales and CST mesh sizes, indicating that medium column testing can predict full height test Cs load performance. Table ES.1 summarizes the relevant Cs loading characteristics for both medium and full height column tests.

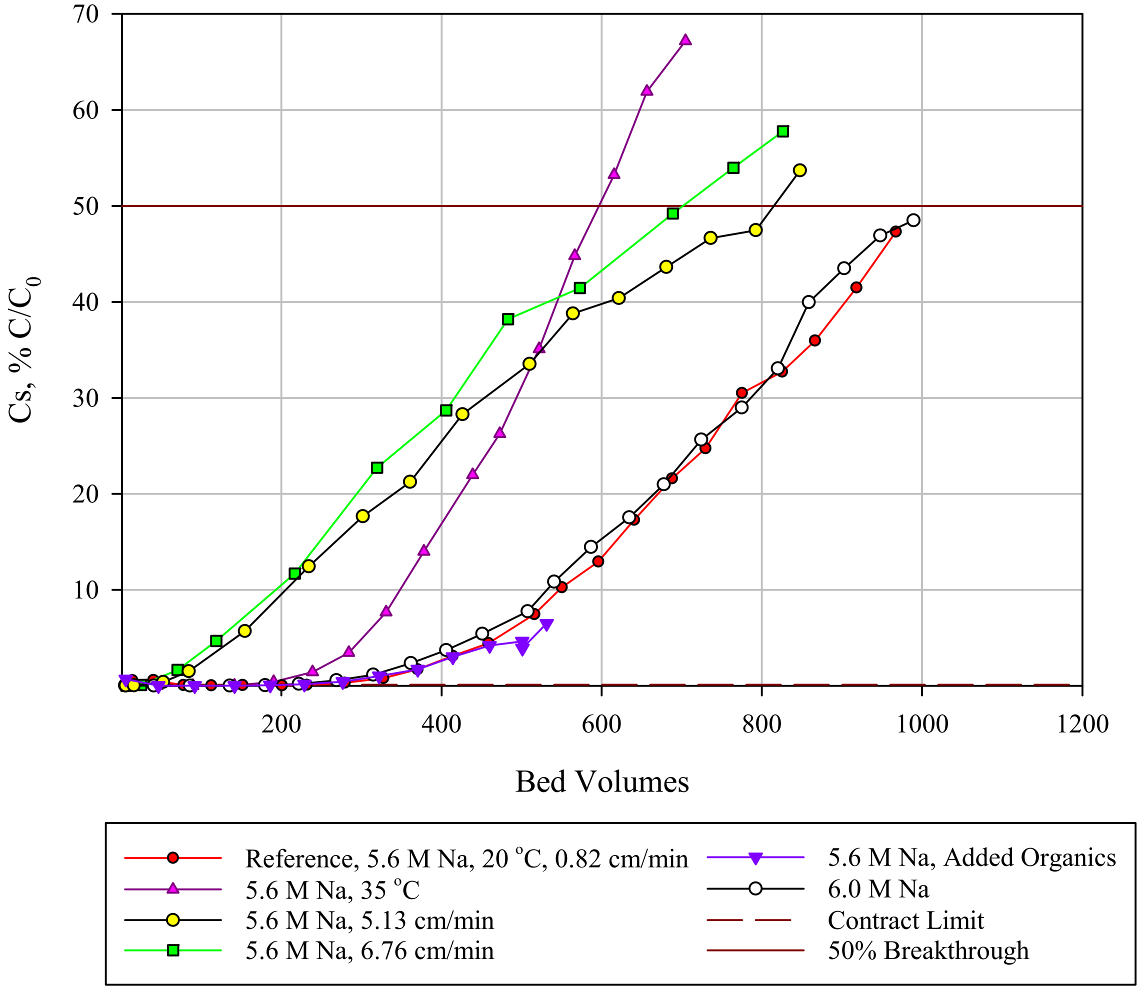

Figure ES.1 Medium Column Variable Testing on Cs Load Performance

Figure note: Except as indicated in the legend, feeds were 5.6 M Na and processed at nominally 20 °C and nominal 0.82 cm/min (1.8 BV/h).

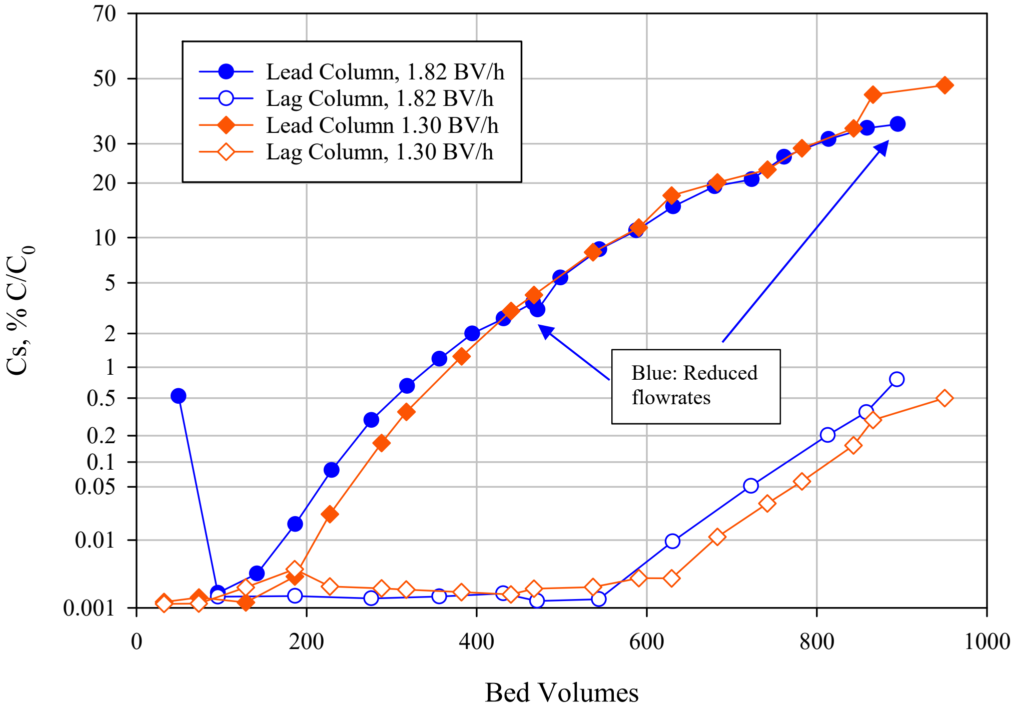

Figure ES.2. Full-Height Test Cs Breakthrough Profiles from the Lead and Lag Columns

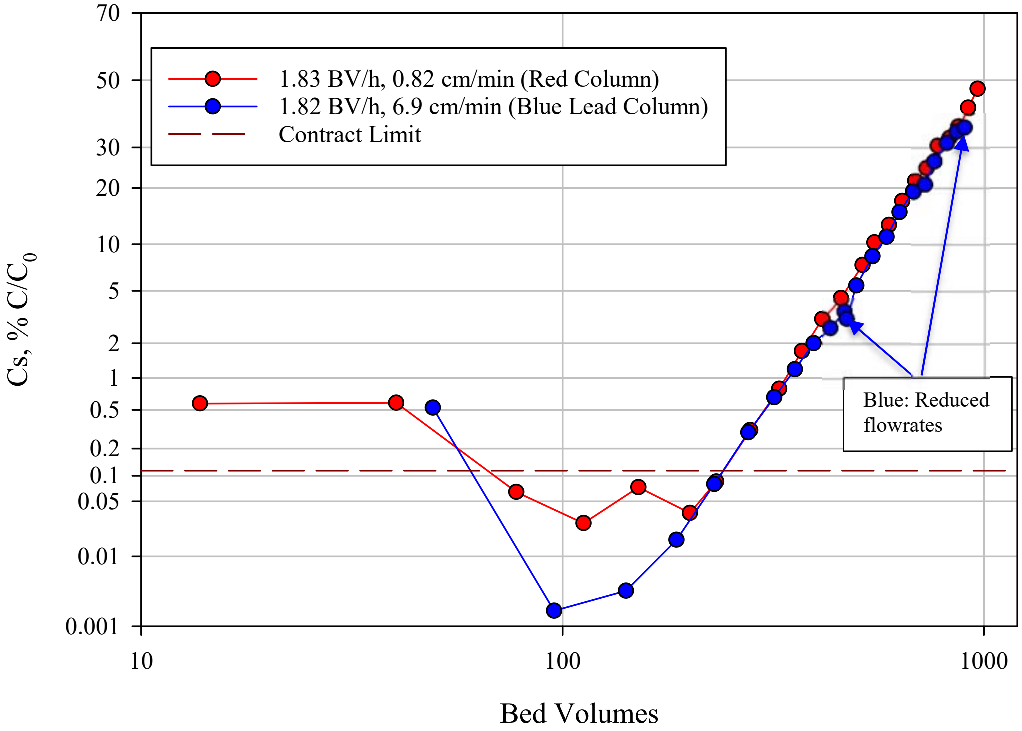

Figure ES.3. Medium and Full Height Column Scale Comparison

Table ES.1. Column Performance Summary

Column Test Color Code	Flowrate, BV/h	50% Cs Breakthrough, BV	Cs Loading, mg/g(a)	Contract Limit(b) Cs Breakthrough, BV
Medium Columns				
Red (5.6 M Na)	1.83	~1000(c)	6.95	240
Yellow (5.6 M Na)	11.4	800	4.99	27
Green (5.6 M Na)	15.0	700	4.80	29
Pink (5.6 M Na), 35 °C	1.93	600	4.77	162
Purple (5.6 M Na) (with added organics)	1.86	na	4.26	210
White (6.0 M Na)	1.88	~1000(c)	6.89	200
Full Height Columns				
Orange (5.6 M Na)	1.30	~960(c)	6.77	280
Blue (5.6 M Na)	1.82	~1050(c)	6.60	240

(a) The Cs loading was calculated based on the achieved Cs breakthrough—not necessarily the 50% Cs breakthrough. This value is close to the effective capacity for Cs at the equilibrium feed conditions.

(b) The contract limit was defined to be 0.114 % C/C_0, congruent with tank waste at 5.6 M Na and 156 µCi/mL ^{137}Cs. This corresponded to a decontamination factor of 877.

(c) Extrapolated value to 50% Cs breakthrough.

The kinetics of Cs exchange were also examined for each of the variable simulant test matrices. Cs exchange as functions of time were not statistically different within the uncertainty of the method. Although most Cs exchanged within the first 45 h, an excess of 123 h is likely required to reach equilibrium Cs concentration under the implemented process conditions. The Cs load was 6.67 µg Cs per gram CST ±3.7% from an initial ~40 µg/mL Cs simulant and a liquid volume to solids ratio of 200 at the 123-h contact time.

Acknowledgments

The authors thank the Analytical Support Operations staff Sam Morison and Garret Brown for the simulant feed sample ^{133}Cs, Na, and K analyses and Carolyne Burns for the crystalline silicotitanate particle density and particle size distribution. The authors thank Renee Russell for reviewing the ion exchange calculation files, test data packages, and this technical report, Bill Dey for reviews to ensure compliance with strict quality assurance standards, and Matt Wilburn for technical editing of this report.

Acronyms and Abbreviations

AV	apparatus volume
BSE	backscattered electron (microscopy)
BV	bed volume
CST	crystalline silicotitanate
DF	decontamination factor
DI	deionized (water)
EDS	energy dispersive spectroscopy
FIO	for information only
FMI	Fluid Metering, Inc
GEA	gamma energy analysis
ID	identification (number) or inner diameter, see context
IX	ion exchange
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
PTFE	polytetrafluoroethylene
QA	quality assurance
R&D	research and development
SEI	secondary electron imaging
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TSCR	Tank Side Cesium Removal
VF	void fraction
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The U.S. Department of Energy is tasked with the disposal of low-level radioactive waste stored at the Hanford Site. The supernatant waste, currently stored in underground tanks, will be vitrified following specific pretreatment processing including filtration and ^{137}Cs removal. The ^{137}Cs removal from the supernatant is important to meet the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste Facility contract specification and ultimately for creating a contact-handled waste form. The final ^{137}Cs concentration in the low-activity glass is targeted to be at or below 3.18E-5 Ci ^{137}Cs/mole of Na contract limit[1] (generally a Cs decontamination factor [DF] of ~1000). Although the underlying technology is well established, ion exchange for Cs removal from low-level waste at the Hanford Site poses many challenges. The ion exchange material must withstand high alkalinity, high salt, and high radiation fields, while at the same time using selectivity for parts per million Cs in the presence of molar concentrations of chemically similar ions such as sodium and potassium.

Augmented pretreatment is planned near the Hanford waste tanks in skid-mounted platforms termed Tank Side Cesium Removal (TSCR). A promising Cs ion exchange material, crystalline silicotitanate (CST) made by Honeywell UOP LLC (Des Plaines, IL) in an engineered bead form (R9140-B), is under investigation to support the TSCR pretreatment flow sheet for Cs removal from the tank waste supernate. The Cs is not easily removed from the CST; thus, the CST is described as non-elutable and will need to be managed with high ^{135}Cs and ^{137}Cs activity post processing. Extensive work has been conducted on CST in the powdered and engineered (generally spherical bead) forms, demonstrating applicability of the CST to caustic tank waste supernates (Pease et al. 2018). Pacific Northwest National Laboratory (PNNL) evaluated a recent production batch of the engineered CST for removal of Cs from Hanford tank waste using a simplified simulant (Fiskum et al. 2018a) and later with actual AP-107 tank waste supernate (Rovira et al. 2018) in small, lead/lag column formats (10-mL CST bed volumes [BVs], 6 cm tall). In all cases, effective Cs removal from the tank waste simulant and actual Hanford waste AP-107 was demonstrated. Simulant testing showed 475 BVs of simulant feed could be processed at 1.99 BV/h before reaching the contract limit from the lag column (Fiskum et al. 2018a). Hanford tank waste testing with AP-107 supernate showed that 410 BVs could be processed at 2.2 BV/h before reaching the contract limit (Rovira et al. 2018).

The work presented in this report summarizes the testing of a different production batch of CST (IONSIV^{TM} R9140-B, material number 2002009604, lot number 8056202-999) in a medium column height (one 44-mL bed, 27 cm tall)[2] and at full height (1.15-L bed, 226 cm tall per column) in a lead/lag column format. Parametric testing was conducted with the medium columns varying feed composition, process temperature, and flowrates. Two process flowrates were tested in the tall column format. Batch contact testing was conducted to evaluate the kinetics of Cs exchange as functions of different feed compositions, complementing the medium column testing. The full height column tests evaluated the Cs load performance of a 5.6 M Na simulant at two different superficial velocities.

These studies were intended to provide results and experience using the CST in a full height column format and assess impacts of multiple process variabilities. Washington River Protection Solutions

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[1] 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.
[2] The 27-cm-tall column is 12% of the full-height column.

(WRPS) will use these results to anticipate and manage problems that may occur during actual waste processing. Results from these tests will significantly contribute towards WRPS establishing accurate process flowsheets for the individual feed campaigns planned for TSCR.

2.0 Quality Assurance

The work described in this report was conducted with funding from WRPS contract 36437/259, *TSCR Technology Testing and Support*. This contract was managed under PNNL Project 72885. All research and development (R&D) work at 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 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). These are implemented through 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 Test Conditions

This section describes the CST media, various simulants tested, batch contact ion exchange test conditions, and column ion exchange test conditions. All testing was conducted in accordance with a test plan prepared by PNNL and approved by WRPS.[1]

3.1 CST Media

WRPS purchased ten 5-gallon buckets (149 kg total) of IONSIV™ R9140-B[2], material number 2002009604, lot number 8056202-999 from Honeywell UOP LLC (Des Plaines, IL). This CST production batch was screened by the manufacturer to achieve an 18 x 50 mesh size product. The media was delivered to WRPS in a series of 5-gallon buckets (as opposed to a 50-gallon drum) to aid in material distribution, handling, and sampling at PNNL. The CST was transferred from WRPS to PNNL on September 20, 2018, under chain of custody. Once received, the CST was maintained at PNNL in environmentally controlled spaces. One of the 5-gallon buckets of CST was delivered to the PNNL Radiochemical Processing Laboratory and used for the testing described herein. The CST subsampling, sieving, pretreatment, and physical properties are described in the following subsections. The CST processing activities were conducted according to a test instruction (internally prepared and reviewed).[3]

3.1.1 CST Subsampling

It was important to collect representative subsamples of the CST without crushing it in the sampling process. Fiskum et al. (2018a) described how easily the CST can be crushed with minimal force. Thus, the use of the cone penetrometer for subsample collection was not preferred because the compressive forces associated with use of the penetrometer could crush CST particles. Use of a riffle type splitter was considered to have the least detrimental impact on the CST particle integrity. The entire 5-gallon bucket of CST was serially split using a Humboldt riffle-type sample splitter into a multitude of aliquots of sufficient size to support the various test objectives (typically 150- to 600-g subsamples were collected). Coning and quartering were applied to subdivide a sample split into smaller aliquots supporting batch contact testing.

A small quantity of black impurities was observed within the bulk, as-received CST material (see Figure 3.1.a for a representative distribution). A few particles (Figure 3.1.b) were isolated and were found to be responsive to a magnetic field; thus, they were theorized to be iron filings. No attempt was made to further characterize or remove the black particles from the bulk of the CST subsamples. It was understood that these impurities would be present in the full scale TSCR operation and CST laboratory testing should be representative of the full TSCR process. Thus, their presence was maintained in the medium and full height column tests as randomly sampled.

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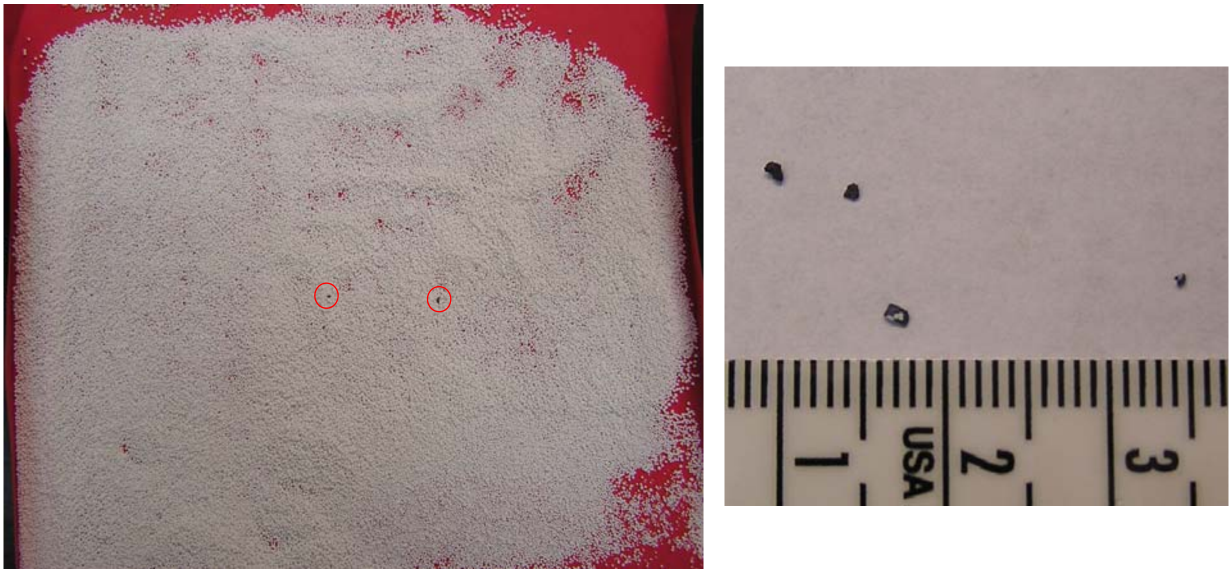
[1] Fiskum SK. TP-TCT-001, Rev.0.0. *TSCR Technology Testing and Support: Tall and Medium Column Test with Crystalline Silicotitanate*. Pacific Northwest National Laboratory, Richland Washington. 2018. This document is internal to PNNL and is not publicly available.

[2] R9140-B is provided in the sodium form by the vendor.

[3] Rovira AM. TI-TCT-005, *Tall and Medium Column CST Preparatory Activities*. Pacific Northwest National Laboratory, Richland Washington. Issued September 2018. This document is internal to PNNL and is not publicly available.



a) Two impurity particles (circled) in a subsample of CST product.

b) Close-up of four collected impurity particles with centimeter scale.

Figure 3.1. Photographs of Impurities in the CST

3.1.2 CST Sieving

The column wall effect (i.e., flow maldistribution) is reduced with increasing number of beads across the column diameter. Helfferich (1962) recommends 30 beads across the column diameter to mitigate the wall effects. Removal of large CST particles was thus required to optimize column performance in the narrow 1.44-cm inner diameter (ID) columns supporting medium column testing. Aliquots of dry CST were passed through a 25-mesh (ASTM E11 specification) sieve to remove >710-µm diameter particles. This approach was similar to previous testing (Fiskum et al. 2018a; Rovira et al. 2018) with the exception that fines (<180 microns) were not removed by passing the CST fines through a 60-mesh sieve. A total of 59-wt% CST was collected in the <25-mesh sieve fraction. Testing in the full height columns used the unseived CST (i.e., as provided by the manufacturer).

3.1.3 CST Pretreatment

The CST was received already in the sodium form; thus, conversion to the sodium form was not necessary. The CST was washed with dilute sodium hydroxide to remove colloidal fines. Aliquots of CST were washed with 0.1 M NaOH in a phase proportion of nominally 1 volume CST to 1.5 volumes 0.1 M NaOH. The CST-NaOH slurry was gently mixed to suspend fines. The aqueous portion was decanted and an additional amount of 0.1 M NaOH was added. This process was repeated seven times until the vast majority of CST fines were removed. Initial contact with 0.1 M NaOH resulted in a large amount of effervescing from the CST accompanied by a crackling sound. By the third wash, the gas production and crackling abated.

3.1.4 Physical Properties Measurements

The physical properties of the pretreated unseived CST (duplicate 19.3 g samples) and the pretreated sieved (<25 mesh) CST (duplicate 9.87 g samples) were measured. These properties included bulk density, bed density, bed void fraction, particle density, surface area, and particle size distribution (PSD).

The bulk density was measured simply from the net mass of dry CST collected in a graduated cylinder after tapping the cylinder with a bung until the CST reached a constant volume. The wet bed density was measured from a 10-mL slurry volume of settled CST in a graduated cylinder and the dry CST mass was measured after removing the CST from the graduated cylinder and taking it to dryness at 100 °C. The CST bed void fraction was determined as previously described (Fiskum et al. 2018a) using water displacement. A known mass of the 100 °C dried CST was slowly added to a known volume and mass of deionized (DI) water in a tared graduated cylinder. Incremental CST addition was paused to allow effervescence to complete before adding the next increment. After all effervescence ceased, the CST was tapped to final constant volume (V_{sl}). The headspace water was removed and the net slurry mass (M_{sl}) calculated. The dry mass of CST (M_{CST}) was subtracted from the net slurry mass; the difference was ascribed to the water content in the slurry volume. The void fraction (VF) was calculated according to Eq. (3.1).

$$\mathrm{VF} = \frac{\mathrm{M_{sl}} - \mathrm{M_{CST}}}{\mathrm{V_{sl}}} \tag{3.1}$$

Particle density was measured using the gas pycnometry using a micromeritics Accupyc II 1340. Samples were dried at 105 °C prior to analysis. Moisture content was determined using a Mettler-Toledo Halogen Moisture Analyzer, HR83, at 105 °C to constant mass. Table 3.1 summarizes the measured physical property characteristics of the two CST mesh sizes.

Table 3.1. Physical Properties of Pretreated R9140-B, Lot 8056202-999 CST

	Full PSD		<25 mesh	
Parameter	Sample 1	Sample 2	Sample 1	Sample 2
Bulk dry density, g/mL	1.02	1.01	1.03	1.01
Wet bed density, g/mL	1.00	1.00	1.01	1.01
Settled bed void fraction, %	68.5	66.7	64.7	67.7
Particle density, g/mL	3.32	3.34	4.13	3.41
Moisture Content, wt %	7.88	7.94	9.34	9.67

Duplicate subsamples of both the pretreated CST and the sieve cut pretreated CST (<25 mesh) in the 0.1 M NaOH suspension fluid were submitted for particle size analysis (PSA). The PSA was conducted using a Malvern Mastersizer 2000 coupled with a HydroG dispersion unit. Measurements were collected pre-sonication, during sonication, and post-sonication. It was observed that applied sonication had marginal impact on the particle size distribution (PSD) (see Appendix A). Table 3.2 summarizes the particle size of select percentiles for the two CST materials analyzed for the pre-sonication condition. Based on the CST d_{50} particle diameter, ~24 beads will fit across the medium column diameter (1.44 cm ID) and ~36 beads will fit across the full height (2.54 cm ID) column diameter. Optimally, at least 30 beads across the column diameter minimizes wall effects and channeling (Helfferich 1962). Testing at the medium scale with <25 mesh CST pushed the lower limit of this goal.

Table 3.2. Cumulative Particle Undersize Fractions of Pretreated R9140-B CST Lot 8056202-999

Undersize Fraction	Full PSD, µm		<25 mesh, µm	
	Sample 1	Sample 2	Sample 1	Sample 2
d_{10}	454	480	429	426
d_{50}	695	722	590	587
d_{90}	1084	1112	812	806

3.1.5 CST Dry Mass Basis

The CST dry mass was based on the achieved constant mass at 100 °C (dry mass divided by sampled mass or F-factor). For batch contact testing, the sampled CST condition was achieved after air drying pretreated wet CST at ambient temperature (~20 °C) typically overnight until the CST was in a free-flowing condition. The CST was then dried to constant mass (<0.5% difference in 4 h) at 100 °C to establish the F-factor. Hamm and McCabe (2018) indicated that an additional 7% mass loss may be obtained when the CST is further dried to 400 °C. The CST subsamples that were dried to 100 °C were further dried at 200 °C; an additional 4.4% mass loss was obtained as shown in Figure 3.2, where CST mass (% of starting mass) is plotted as a function of time for both tested temperatures (100 °C and 200 °C). Incremental mass loss continued after the first 50 h at 100 °C and first 24 h at 200 °C. For data comparability to previous work, the F-factor obtained at 100 °C is used throughout this report. It is noted that using 100 °C F-factors could create a small bias relative to Hamm and McCabe (2018) studies where F-factors were obtained from heating to 400 °C.

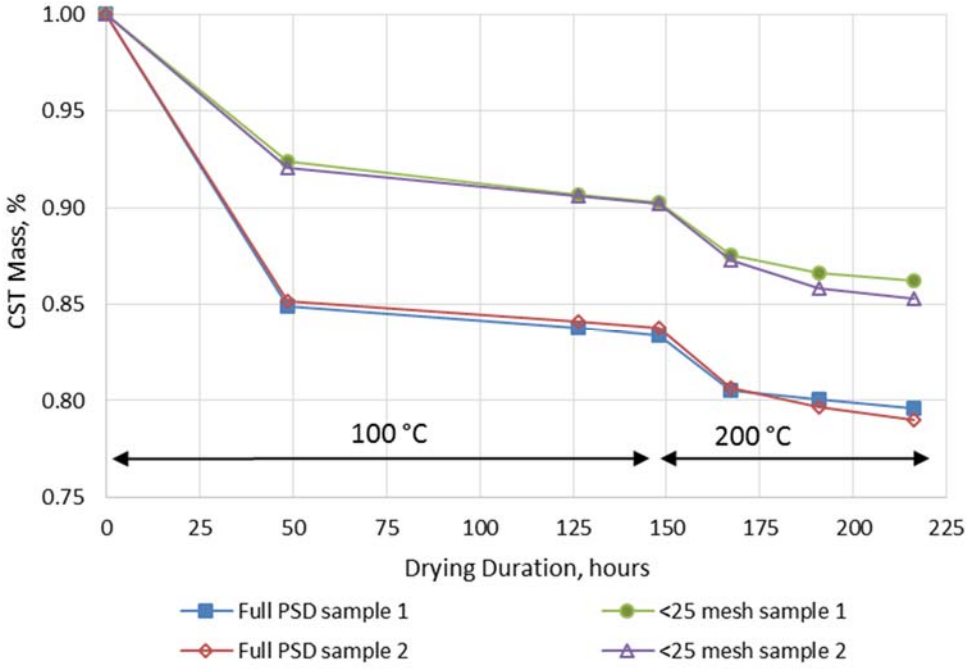


Figure 3.2. CST Mass Loss Profiles to Determine F-factors

3.2 Simulated Tank Waste Ion Exchange Feed

PNNL contracted the production of 680 gallons of 5.6 M Na simulant and 13 gallons of 6.0 M Na simulant to Noah Technologies, Inc. (San Antonio, Texas). The simulant preparations were conducted as defined by Russell et al. (2017), with the exception that the Cs concentration was set to 8 µg/mL (instead of 13.8 µg/mL). This Cs concentration approximated the Cs concentration in AP-107 Hanford tank waste and matched testing reported by Fiskum et al. (2018a). The sodium oxalate component was completely omitted to mitigate solids precipitation. The target component masses and calculated ionic species concentrations are provided in Table 3.3 and Table 3.4. The reagents used to make the simulants were assayed at 99.2% or better. However, the sheer scale of the production process required very large quantities of salts to be used, and a small metal impurity fraction could result in kilogram quantities of insoluble metal hydroxides. Thus, Noah Technologies was directed to wait at least 24 hours after mixing and then filter the simulant through a 0.45 micron pore size filter.

Table 3.3. 5.6 M Sodium Simulant Target Composition

Component	Component Formula Weight, g/mole	Target Component Mass per kg Solution, g	Composition, g Component/ L Solution	Anion / Cation Species	Target Conc., M
$Al(NO_3)_3•9H_2O$	375.13	49.82	62.27	Al as $Al(OH)_4^-$	0.166
NaOH (50%, w/w)	40.00	132.73	165.91	free OH^-	1.41
$CsNO_3$	194.91	0.0094	0.0117	Cs^+	6.00E-05
KCl	74.55	7.28	9.10	K^+ and Cl^-	0.122
Na_2SO_4	142.04	7.51	9.39	SO_4^{2-}	0.0661
$NaNO_2$	69.00	56.30	70.38	NO_2^-	1.02
$NaNO_3$	84.99	87.17	108.97	NO_3^-	1.78
Na_3PO_4-$12H_2O$	380.12	13.14	16.42	PO_4^{3-}	0.0432
Na_2CO_3	105.99	46.33	57.91	CO_3^{2-}	0.467
Deionized water	18.02	598.35	747.94	Na^+	5.60

Table 3.4. 6.0 M Sodium Simulant Target Composition

Component	Component Formula Weight, g/mole	Target Component Mass per kg Solution, g	Composition, g Component/ L Solution	Anion / Cation Species	Target Conc., M
$Al(NO_3)_3•9H_2O$	375.13	52.17	66.78	Al as $Al(OH)_4^-$	0.178
NaOH (50%, w/w)	40.00	138.91	177.80	free OH^-	1.51
$CsNO_3$	194.91	0.0094	0.0117	Cs^+	6.00E-05
KCl	74.55	7.63	9.77	K^+ and Cl^-	0.131
Na_2SO_4	142.04	7.86	10.06	SO_4^{2-}	0.0708
$NaNO_2$	69.00	58.77	75.22	NO_2^-	1.09
$NaNO_3$	84.99	91.39	116.97	NO_3^-	1.91
Na_3PO_4-$12H_2O$	380.12	13.75	17.60	PO_4^{3-}	0.0463
Na_2CO_3	105.99	41.41	53.01	CO_3^{2-}	0.500
NaF	41.99	2.29	2.93	F^-	0.070
Deionized water	18.02	584.38	748.01	Na^+	5.60

Noah Technologies, Inc. provided simulant aliquots to PNNL for analysis; satisfactory results were required before the entire production batch was to be accepted and shipped. A limited analysis consisting of density, Na, K, Al, and Cs was conducted. PNNL staff measured the Na, Al, and K by inductively coupled plasma optical emission spectrometry[1] and the ^{133}Cs by inductively coupled plasma mass spectrometry. Analysis results agreed with the preparation formulation within 11% relative. The solution densities were measured in a volumetric flask at 1.25 and 1.27 g/mL for the 5.6 M Na and 6.0 M Na solutions, respectively. The simulant preparations were considered accurate.

Per direction from PNNL, 80 gal of the 5.6 M Na simulant were shipped in 15- and 30-gal drums to support ion exchange testing with the medium columns. The remaining ~600 gal were shipped in two 330-gal totes each containing nominally 300 gal of simulant for use in the full height column testing. The simulant was shipped overland in September/October 2018 with no expectation of temperature control in the transport truck. Upon delivery to PNNL, settled, rust colored, insoluble solids were noted in the 330-gal totes, likely iron (oxy)hydroxide.

One container of 5.6 M Na simulant was set aside for adjustment with organic constituents in order to test the effect of organic-laden 5.6 M Na simulant on CST Cs exchange. Organic chemicals were selected in consultation with WRPS staff. Selection criteria were based on chemical analysis of Hanford tank waste, known additions of materials to tank waste, and emphasis on the double-shell tank inventory that is likely to be used for TSCR feed. Sodium citrate was selected to represent complexing agents; the target concentration, 5000 ppm citrate, matched the nominal citrate concentration listed in the tank waste inventory database. Sodium oleate and trimethylol propane were selected to represent the breakdown products from Quintolubric® 888-46, which was known to be in tank AN-101, and were added at the approximate concentrations as found in tank AN-101 (Meznarich et al. 2017). Finally, Xiameter® AFE-1520 silicone antifoam emulsion (Dow Silicones Corp. Midland, MI) was added according to the

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[1] Results for Sr and Ca were reported for information only (FIO). The Sr was present at [0.15] µg/mL and Ca was present at [20] µg/mL. The bracketed results indicated that the analyte concentrations were greater or equal to the method detection limit but less than the estimated quantitation limit and uncertainty likely exceeded 15%.

manufacturer's specifications as indicated in its use in the 242-A Evaporator (Conner 2007). All of the organic constituents were added directly to 12 gal of the 5.6 M Na simulant. Table 3.5 summarizes the added organics and estimated final concentrations, assuming complete dissolution. Unfortunately, the bulk of the sodium oleate and the trimethylol propane did not appear to go into solution even after rigorous overhead mixing for an hour; solids were observed floating on the liquid surface. Complete dissolution of the sodium citrate was assumed based on bench scale studies of its addition to 5.6 M Na simulant. The final Na concentration in the organic-laden simulant was slightly increased from 5.6 M to 5.7 M. For discussion purposes, this modified simulant is referred to as "5.6 M simulant with added organics." The dip tube inlet for feeding the column was positioned near the bottom of the drum and thus avoided floating solids.

Table 3.5. 5.6 M Sodium Simulant Amended with Organic Constituents

Component	Component Formula Weight, g/mole	Added Mass, g	Composition, g Component/ L Solution	Anion/ Cation Species	Final Conc., M
Sodium citrate ($C_6H_5O_7Na_3$) Sigma Aldrich ≥99.0%	294.1	353.2	7.79	citrate	0.0264
Sodium oleate ($C_{18}H_{33}NaO_2$) Tokyo Chemical Industry, America, >97%	304.45	72.71	1.60	oleate	5.26E-3
Trimethylol propane ($C_6H_{14}O$) Tokyo Chemical Industry Co., >98%	100.00	0.3701	8.16E-3	--	8.15E-05
Xiameter® AFE-1520 Antifoam Emulsion[(a)] Dow Silicones Corp.	NA	2.38	5.25E-2	--	--
				Na^+	5.68

(a) The antifoam emulsion was composed of undisclosed amounts of water, siloxanes, silicones, and dimethyl/methyl cellulose.

3.3 Batch Contact Study for Kinetics Evaluation

The Cs exchange rate onto CST was assessed in three simulants and two PSDs of CST. This section describes the simulant preparation, CST addition, contact conditions, and post-contact handling. The batch contact processing activities were conducted according to a test instruction (internally prepared and reviewed).[1]

Three simulants were tested: 5.6 M Na simulant, 6.0 M Na simulant, and the 5.6 M Na simulant with added organics as defined in Section 3.2. The Cs concentration was increased to 40 µg/mL by adding 0.05 mL of 1.04 M Cs to 220-mL aliquots of each simulant. A ^{137}Cs tracer was also added to each simulant resulting in nominally 0.25 µCi/mL ^{137}Cs concentration. The simulants were equilibrated

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[1] Fiskum SK. TI-TCT-006, *Kinetic Load Testing of Cs onto Crystalline Silicotitanate in 5.6 M Na Simulant, 5.6 M Na Simulant with Added Organics, and 6.0 M Na Simulant*. Pacific Northwest National Laboratory, Richland Washington. Issued October 2018. This document is internal to PNNL and is not publicly available.

(overnight) with the stable Cs and tracer ^{137}Cs. A 2-mL subsample from each mixture was collected and served to provide the initial ^{137}Cs concentration (C_0) measurement.

Nominal 1-g aliquots of pretreated and air-dried CST were weighed into 500-mL polyethylene bottles. Duplicate samples of CST were also taken for the F-factor determination and to correct for water content of the measured CST used for batch contacts. The two F-factor samples were collected before and after aliquoting CST into the 500-mL bottles. The F-factor samples were dried to 100 °C constant mass, then to 200 °C constant mass (see Figure 3.2). The mass corrected to dry weight at 100 °C is used in the calculations reported herein. An additional 4.4% mass reduction in the CST mass may be applied if the 200 °C dry mass is needed. Table 3.6 shows the batch contact test matrix parameters.

Table 3.6. Batch Contact Test Matrix

Simulant	Initial Simulant Vol., mL[(a)]	Cs Conc., M	CST Modification	Dry CST Mass, g[(b)]
5.6 M Na	225.9	2.85E-4	Full PSD	1.0853
5.6 M Na	219.9	3.02E-4	<25 mesh	1.0910
5.6 M Na with added organics	220.7	2.96E-4	<25 mesh	0.9739
6.0 M Na	222.4	2.89E-4	<25 mesh	0.9739

(a) Volumes before 2-mL comparator samples were collected.
(b) Mass-corrected to 100 °C F-factor.

The designated simulant was added to the bottle containing CST and the contact time clock was immediately started. Small samples (2 mL) were collected after processing for nominally 0.1, 0.5, 2.0, 5.2, 20, 45, and 123 hours and allowing for a brief (~1 min) CST settling period. The first sample was collected after shaking by hand for 6 min in a manner that replicated the shaker table. After sampling, the main batch contact solutions were placed horizontally on an IKA KS125 orbital shaker table with 4-mm shaker amplitude and set to mix at ~400 rpm. The batch contact solutions were maintained at room temperature, ranging from 19 to 22 °C. Each 2-mL sample was transferred directly to a syringe fitted with a syringe filter, 45 µm pore size, 25 mm diameter (Puradisc^{TM} 25NYL, Whatman). The sample was passed through the filter and the filtrate was collected for analysis. Duplicate samples were collected at the 2-h contact time. After all sampling was complete, the final batch contact solution volumes were ~200 mL. Thus, the batch contact solution volume to dry CST mass phase ratio ranged from 225 to 186 over the course of the test.

Each filtered sample was measured by gamma energy analysis (GEA). The samples were counted as long as needed to achieve a ≤1% count uncertainty. The ^{137}Cs tracer concentration in solution directly correlated to the total Cs concentration. Thus, the distribution coefficient (K_d, mL/g) could be directly assessed from the ^{137}Cs concentration. All fluid transfers were tracked by mass; thus, the overall uncertainty in the K_d measurements was estimated to be about ±2%.

The Cs batch K_d values were determined according to the standard formula shown in Eq. (3.2). The changing contact solution volumes (V) with each sampling step were incorporated into each successive K_d calculation.

$$K_d = \frac{(C_0 - C_1)}{C_1} \times \frac{V}{M \times F} \tag{3.2}$$

where C_0 = initial ^{137}Cs concentration (μCi/mL)

C_1 = ^{137}Cs concentration (μCi/mL) at the sampling time

V = volume of the batch contact liquid (mL) at the sampling time

M = mass of CST (g)

F = F-factor, mass of the dried CST divided by the mass of the undried CST (100 °C dry mass basis)

K_d = batch-distribution coefficient (mL/g)

3.4 Ion Exchange Column Testing

Two types of column systems were constructed for testing: 1) a medium column system with a single BV of 44 mL (12% full height) and 2) a full height column system constructed with four columns each with a ~592-mL BV (two columns combined were equivalent to one full height column). A total of six medium column tests and two full height column tests were conducted. Each column system was given a color code to better organize samples and paperwork. The color coding served to minimize errors and enhance recognition in sample management and data recording (minimizing the human factor errors). This section describes these ion exchange column systems and their associated process conditions.

3.4.1 Medium Column Testing

This section describes the system design and associated hardware, CST BV, system fluid volume, and specific test processing parameters for the medium column systems. The preparations and column testing were conducted in accordance with a test instruction[1] (prepared and approved internally).

3.4.1.1 Medium Column System Design

The ion exchange system was set up as shown schematically in Figure 3.3. Each system consisted of one column containing ion exchange media, a small metering pump, three valves, a pressure gauge, and a pressure-relief valve. The valves were three-way valves that could be turned to the flow position (upward) to flow solution through the entire system or a sample position (downward) to collect samples. Valve 1 was placed near the outlet of the pump and was used to isolate the column from the pump and collect initial fluids and to expel air from the lines at the initial setup. Valve 2 was primarily used to obtain samples and closed to isolate the system during storage periods.

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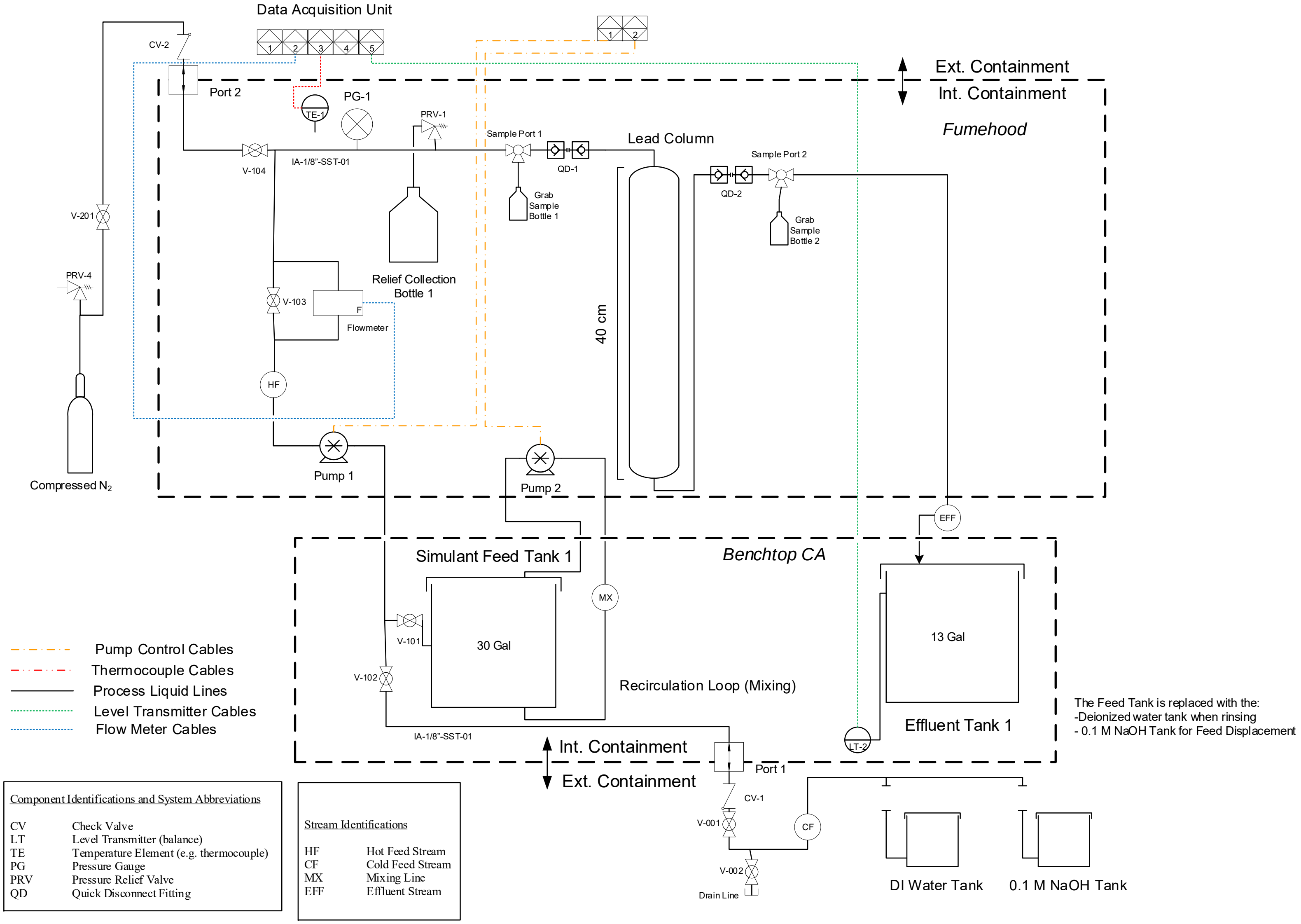
[1] Colburn HA. TI-TCT-004, *Medium Column Crystalline Silicotitanate (CST) Ion Exchange (IX).* Pacific Northwest National Laboratory, Richland, Washington. Issued October 2018. This document is internal to PNNL and is not publicly available.

Column assemblies were purchased from Spectrum Chromatography (Houston, TX), part number 125013. Each glass column was housed in a plastic clamshell for pressure safety purposes. The column assembly included the column plus the top and bottom end fittings. After the first test series (Pink and Red), the top fitting was exchanged for a clone of the bottom fitting to better maintain a system seal. Each column was made of borosilicate glass and was 40 cm tall with an inside diameter of 1.44 cm (corresponding to a CST volume of 1.67 mL/cm). Column fittings were composed of polytetrafluoroethylene (PTFE) and Teflon endplates and ferrule fittings for 1/8 in. outside diameter tubing.



The Feed Tank is replaced with the:
-Deionized water tank when rinsing
- 0.1 M NaOH Tank for Feed Displacement

Component Identifications and System Abbreviations

CV	Check Valve
LT	Level Transmitter (balance)
TE	Temperature Element (e.g. thermocouple)
PG	Pressure Gauge
PRV	Pressure Relief Valve
QD	Quick Disconnect Fitting

Stream Identifications

HF	Hot Feed Stream
CF	Cold Feed Stream
MX	Mixing Line
EFF	Effluent Stream

Figure 3.3. Medium Column System Schematic

The CST bed supports were fabricated in-house. They were made of stainless steel, 200 mesh screens tack-welded onto stainless steel support rings. The support rings were stabilized with snug-fitting O-rings to remain stationary in the column once seated. Figure 3.4 shows replacement CST bed supports similar to those in the columns along with a centimeter scale. The CST bed supports were positioned just above the sight line of the lower column fitting, allowing the entire bed to be viewed.

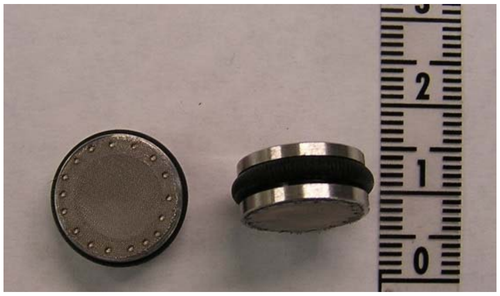


Figure 3.4. CST Bed Supports with Centimeter Scale

The cavity below the screen support was filled with 4-mm-diameter glass beads, reducing the fluid-filled volume from ~4 to ~2 mL. The height of the CST bed was measured with an adhesive centimeter -scale with millimeter subdivisions tape measure (Oregon Rule Co., Oregon City, OR) affixed to the column with the zero-point set at the top of the CST bed support. The associated height measurement error was estimated to be ±2 mm.

The connecting tubing was 1/8-in. outside diameter and 1/16-in. inside diameter and was made of either polyethylene or stainless steel. An in-line flow meter (Micro Motion LF Series, S Burlington, VT) was connected between the pump head and the valve manifold with an optional bypass flow loop. The valve manifold assembly contained an in-line Swagelok Poppet pressure relief check valve with a 10-psi trigger (Solon, OH) and an Ashcroft 15-psi pressure gauge (Stratford, CT) along with Swagelok 3-way ball valves for sampling. Valved quick-disconnects (Cole Parmer, Vernon Hills, IL) were installed in-line to facilitate column removal and switching. A Fluid Metering, Inc. (FMI) QVG50 pump (Syosset, NY) equipped with a ceramic and Kynar® coated low-flow piston pump head was used to introduce all fluids. The feed was piped directly from the drum containing simulant prepared by Noah Technologies. The effluent was collected in a 50-L carboy that was placed on a platform scale (Arlyn Scales, East Rockaway, NY, Model 320D-CR-14) with 225 kg capacity and 0.05 kg readability.

Two system assemblies were prepared; both systems were operated in parallel and each was used sequentially to process three different tests. Figure 3.5 shows photographs of the Pink and Red column assemblies. The FMI pump is shown on the left with the feed line entering the fume hood containment from the feed drum (not shown). The flow meter is shown in the back and the valve manifold in the center. The third valve (taped off) was not used as it supported lag column sampling, which was not conducted in these tests. The packed column is on the right. The effluent line exits the fume hood containment where the effluent is collected in the 50-L carboy (not shown). The pump and column were suspended over secondary containment. The pressure-relief valve was plumbed to a collection bottle capable of collecting an entire shift's worth of process fluid, should the column system plug.

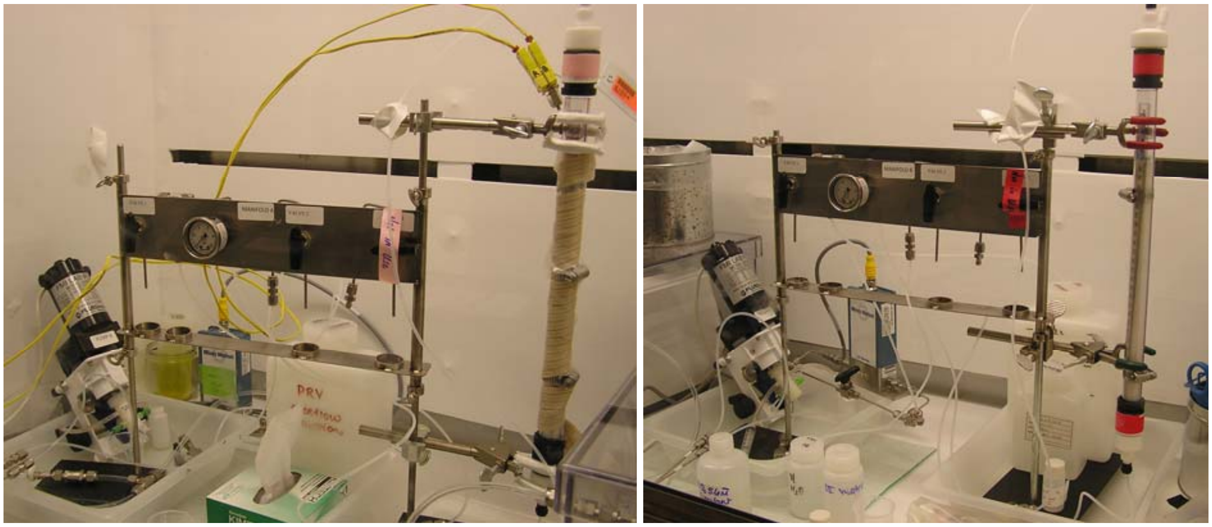


Figure 3.5. Medium Column System Configuration, Pink (left) and Red (right) Columns

One test (Pink) was operated at 35 °C. The column was wrapped in heat tape with a Type K thermocouple affixed between the column and the heat tape (see Figure 3.5). The heat tape wrap extended above the CST bed height and surrounded most of the fluid height above the bed. The heat tape was controlled with a Model 270 temperature controller (J-Kem Scientific, Inc., St. Louis, MO). The column temperature was allowed to equilibrate overnight before feed processing began in an effort to assure the entire CST bed reached the test temperature. Temperature control was maintained within ±2 °C.

3.4.1.2 CST Bed Volume and System Volume

The <25 mesh sieved fraction CST was measured as a slurry in 0.1 M NaOH in a graduated cylinder to reach 44 mL settled CST volume after tapping with a bung. The CST was quantitatively transferred to the ion exchange columns and again settled by tapping with a bung in several increments. The settled CST bed was 27 cm high and the length/diameter ratio was 19. The fluid headspace was adjusted to approximately 3 to 4 cm above the packed bed. The holdup volume of the entire ion exchange system, ~52 mL, was the summed volume of all fluid-filled parts. The CST bed fluid represented ~50% of the fluid filled system volume. The packed column was placed in-line to the flow system. Sodium hydroxide (0.1 M) was processed through the system to fill all fluid lines before starting the simulant processing to avoid potential precipitation of aluminum hydroxide once contacted with simulant.

3.4.1.3 Medium Column Testing

The flowrate was controlled with a remotely operated FMI stroke-rate controller. With additional adjustment of the stroke length, the pump could deliver flowrates from 0.2 to ~15 mL/min. The actual volume pumped was determined using the mass of the fluid collected divided by the fluid density. Flowrate was determined from the calculated volume processed divided by the collection time. Fluid flow was processed through a Micro Motion LF Series flow meter to also assess flowrate. The Micro Motion flow meter and load cell mass were recorded electronically at 1-second intervals. Practical use of the flow meter was challenged from the pulsating action of the positive displacement pump. Fluid flow pulsation through the CST bed was dampened once it reached the fluid head space.

The feeds supporting the medium column testing were delivered in 15-gal and 30-gal drums. The feed in 15-gal drums supported a single column test; the feed in the 30-gal drums supported two concurrent tests. Before processing through the columns, each simulant container was spiked with a ^{137}Cs tracer solution sufficient to provide a measurable DF of ~30,000 when a 10-mL aliquot was measured by gamma spectroscopy. The tracer was added to the simulant by placing ~0.2 Ci ^{137}Cs directly into the mixing recirculation line. The tracer was mixed into the simulant to create a homogenous distribution by recirculating the fluid with a peristaltic pump pulling fluid from the bottom of the container and cycling it back to the top of the container. A filter (Whatman Inc. Polycap 36HD) with 5.0-micron pore size was installed in-line to remove suspended solids from solution.[1] The mixing duration of ~3 h was needed to pump the tank capacity 10 times, at which point 99.9% recirculation had been met. Analytical samples were collected during mixing about 1 h apart to confirm consistency of the ^{137}Cs concentration. After mixing, the simulant remained static at least overnight, allowing any suspended solids to settle.

The six process tests evaluated three different feeds, three different flowrates, and two different temperatures as summarized in Table 3.7. The tests were color-coded as indicated; the color codes are used throughout this report to identify tests. The process order shows which columns were run in parallel (1, 2, or 3) and which manifolds supported the tests (A or B). These manifolds had been used for previous testing (Fiskum et al. 2018a). The Pink, Red, Purple, and White column flowrates were specifically chosen to match the target residence time of the full scale TSCR operation (1.9 BV/h). The Green and Yellow column flowrates were significantly higher and were intended to match the target superficial velocity tested at the full height columns, 7.3 and 5.0 cm/min, respectively. The specific processing parameters achieved for each test are shown in Table 3.8 to Table 3.13; some variation from the targets was realized.

Table 3.7. Variable Test Parameters for the Medium Columns

Feed Material	Flowrate, BV/h	Superficial Velocity, cm/min	Process Temp., ° C	Test Color Code	Process Order	Manifold ID
5.6 M Na Simulant	1.93	0.87	35	Pink	1	Manifold A
5.6 M Na Simulant	1.83	0.82	20	Red	1	Manifold B
5.6 M Na Simulant	15.0	6.76	20	Green	2	Manifold A
5.6 M Na Simulant	11.4	5.13	20	Yellow	2	Manifold B
5.6 M Na Simulant with added organics	1.86	0.84	20	Purple	3	Manifold A
6.0 M Na Simulant	1.88	0.85	20	White	3	Manifold B

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[1] Bug debris from the piping was also removed with this filter.

Table 3.8. Experimental Conditions for the Pink Column, 1.93 BV/h, 35 °C, 10/18/18 Start

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	Liters	BV/h	mL/min	h
Loading	5.6 M Na Simulant	705	--	31.0	1.93	1.41	386
Feed displacement	0.1 M NaOH	6.0	5.1	0.26	3.0	2.2	2.0
Water rinse	DI water	12	10	0.53	5.5	4.0	2.2

BV = bed volume is 44 mL as loaded in the column.
AV = apparatus volume (nominally 54 mL).
DI = deionized.

Table 3.9. Experimental Conditions for the Red Column, 1.83 BV/h, 20 °C, 10/16/18 Start

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	Liters	BV/h	mL/min	h
Loading	5.6 M Na Simulant	967	--	42.6	1.83	1.34	530
Feed displacement	0.1 M NaOH	4.6	3.8	0.20	4.1	3.0	1.1
Water rinse	DI water	14	12	0.60	4.9	3.6	2.8

BV = bed volume is 44 mL as loaded in the column.
AV = apparatus volume (nominally 50 mL).
DI = deionized.

Table 3.10. Experimental Conditions for the Green Column, 15.0 BV/h, 20 °C, 11/12/18 Start

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	Liters	BV/h	mL/min	h
Loading	5.6 M Na Simulant	826	--	36.4	15.0	11.0	53.2
Feed displacement	0.1 M NaOH	5.7	4.8	0.25	2.8	2.1	2.0
Water rinse	DI water	16	14	0.70	7.0	5.1	2.3

BV = bed volume is 44 mL as loaded in the column.
AV = apparatus volume (nominally 56 mL).
DI = deionized.

Table 3.11. Experimental Conditions for the Yellow Column, 11.4 BV/h, 20 °C, 11/12/18 Start

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	Liters	BV/h	mL/min	h
Loading	5.6 M Na Simulant	848	--	37.3	11.4	8.36	74.4
Feed displacement	0.1 M NaOH	6.3	5.3	0.28	2.2/4.7(a)	1.6/3.4(a)	2.2
Water rinse	DI water	11	9.6	0.50	5.7	4.2	2.0

(a) The flowrate was increased part way through processing.
BV = bed volume is 44 mL as loaded in the column.
AV = apparatus volume (nominally 57 mL).
DI = deionized.

Table 3.12. Experimental Conditions for the Purple Column, 1.86 BV/h, 20 °C, 11/28/18 Start

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	Liters	BV/h	mL/min	h
Loading	5.6 M Na Simulant w/ Added Organics	531	--	23.4	1.86	1.36	335[(a)]
Feed displacement	[(b)]	--	--	--	--	--	--
Water rinse	[(b)]	--	--	--	--	--	--

(a) This time duration included ~17 h stop flow condition.
(b) The column plugged and no further processing could be accomplished.
BV = bed volume is 44 mL as loaded in the column.
AV = apparatus volume (nominally 56 mL).
DI = deionized.

Table 3.13. Experimental Conditions for the White Column, 1.88 BV/h, 20 °C, 11/28/18 Start

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	Liters	BV/h	mL/min	h
Loading	6.0 M Na Simulant	989	--	43.5	1.88	1.38	527
Feed displacement	0.1 M NaOH	6.1	5.2	0.27	3.1	2.2	2.0
Water rinse	DI water	12	10	0.54	3.0	2.2	4.0

BV = bed volume is 44 mL as loaded in the column.
AV = apparatus volume (nominally 57 mL).
DI = deionized.

Back pressure was not observed in any of the column systems processed at 1.9 BV/h with one exception. The 5.6 M Na simulant with added organics caused the (Purple test) column to plug after processing about 460 BVs of feed with concomitant back pressure >15 psig.[1] A couple of pulses of 0.1 M NaOH were processed in backflow mode, slightly lifting the CST bed but not fluidizing it. This effort allowed flow to resume through the column for about another 18 h before plugging/pressure buildup was reestablished. Further efforts at backflow processing to reinstate downflow feed were not successful and the test was suspended. Back pressure was observed when processing Green and Yellow column tests at the higher flowrates. The Green column test was operated at ~3 to 4 psig and the Yellow column test was operated at ~1.5 to 2.5 psig.[1] These back pressures were consistent through the test runs.

During the loading phase, nominal 10-mL samples were collected from the columns at the sample collection port (valve 2). Samples were collected after the first ~10 BVs were processed and again at nominal ~40- to 100-BV increments. Feed displacement and water rinse were collected in bulk except for the White column test, where intermittent samples were collected. Each sample was submitted for GEA. The fluid was expelled from the column systems with pressurized nitrogen gas. No attempt was made to thoroughly dry the CST in the columns with gas flow.

Discoloration was not observed on any of these columns. The tests conducted at 1.9 BV/h resulted in some gas evolution near the top of the bed several days after simulant processing commenced. The

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[1] Back pressures were read from pressure gages and are reported for information only (FIO) because they had not undergone formal calibration meeting PNNL calibration requirements.

bubbles were observed at the top 3 to 4 cm of the CST bed—no bubbles were observed below this level (see Figure 3.6). Some minor disturbance of the bed caused some of the bubbles to rise from the bed and break at the fluid surface. The Green and Yellow column tests did not result in any observable bubbles or void spaces. It was assumed that the pressurization caused any gas evolution to dissolve in the fluid and be swept away. The added ^{137}Cs (~0.2 to 0.3 µCi) was not considered high enough to result in radiolysis of the fluid medium and create bubbles. The cause of bubble formation is not understood; it was not observed previously (Fiskum et al. 2018a).

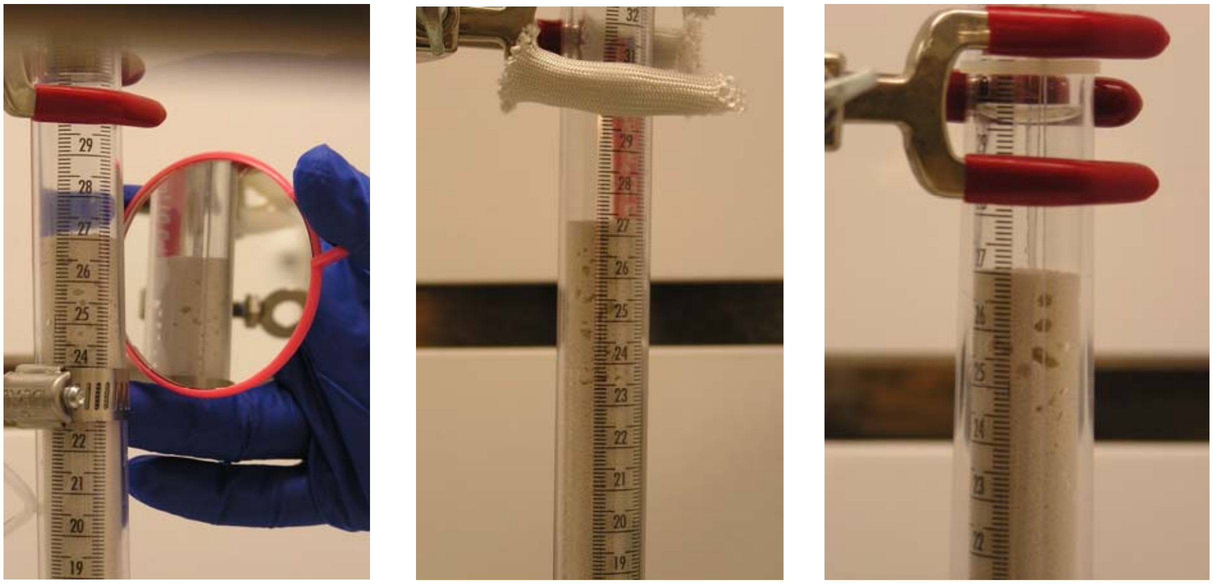
Red Column Pink Column White Column

Figure 3.6. Bubbles Observed at the Top of Selected CST Beds

Selected samples were filtered for reanalysis by GEA to assess if fines bearing Cs were present. Sample selection was based largely on anomalies in the Cs load profile, i.e., uptick in the ^{137}Cs concentration. The sample was transferred directly to a syringe filter and passed through a 0.45-µm pore size, 25-mm-diameter syringe filter (Puradisc^{TM} 25NYL, Whatman). The filtrate was analyzed by GEA and the results compared directly to the unfiltered sample results.

3.4.2 Full Height Column System

This section describes the system design and associated hardware, CST BV, system fluid volume, and specific test processing parameters for the full height column systems. All preparations and column testing were conducted in accordance with a test instruction[1] (prepared and approved internally).

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[1] Rovira AM. TI-TCT-003, *Cesium Removal from 5.6 M Na Simple Simulant Using Crystalline Silicotitanate in a Full Height Dual-Column Format.* Pacific Northwest National Laboratory, Richland, Washington. Issued September 2018. This document is internal to PNNL and is not publicly available.

3.4.2.1 Full Height Column System Design

The ion exchange system was set up as shown schematically in Figure 3.7. The system contained four 2.5-cm-ID by 120-cm-tall columns each containing 592 mL of CST media. The first two columns were collectively considered the lead column and the second two columns were collectively considered the lag column. The lead and lag column CST beds were ~226 cm tall, with a length/diameter ratio of ~89. The system also included two positive displacement pumps, one for feed processing and one for simulant mixing, a flow meter, pressure relief valves, pressure gauges, valves for sampling, and effluent collection containers. Column assemblies were purchased from Kimble Chase (Rochester, NY), part number 420830. The column assembly included the column plus the top and bottom end fittings and flangeless fitting system. Each column was made of Type I, Class A borosilicate glass; end fittings were PTFE with a high-density polyethylene bed support. The borosilicate glass columns were housed in a plastic clamshell for pressure safety purposes.

Manual valve alignment allowed for the transfer between processing solutions (i.e., feed and rinse solutions). Sample port 1 was placed at the outlet of the pump and was used to sample feed, eliminate air from the system lines, or isolate the columns from the pump. Sample port 2 was used for obtaining samples from column 1 (half height lead); sample port 3 was used primarily for obtaining samples from column 2 (full height lead column). Sample port 4 was used to collect samples from column 3 (half height lag column), and sample port 5 was used primarily for obtaining samples from column 4 (full height lag column). Double isolation valves were located before and after every column, allowing for column maintenance, column isolation, and column switching.

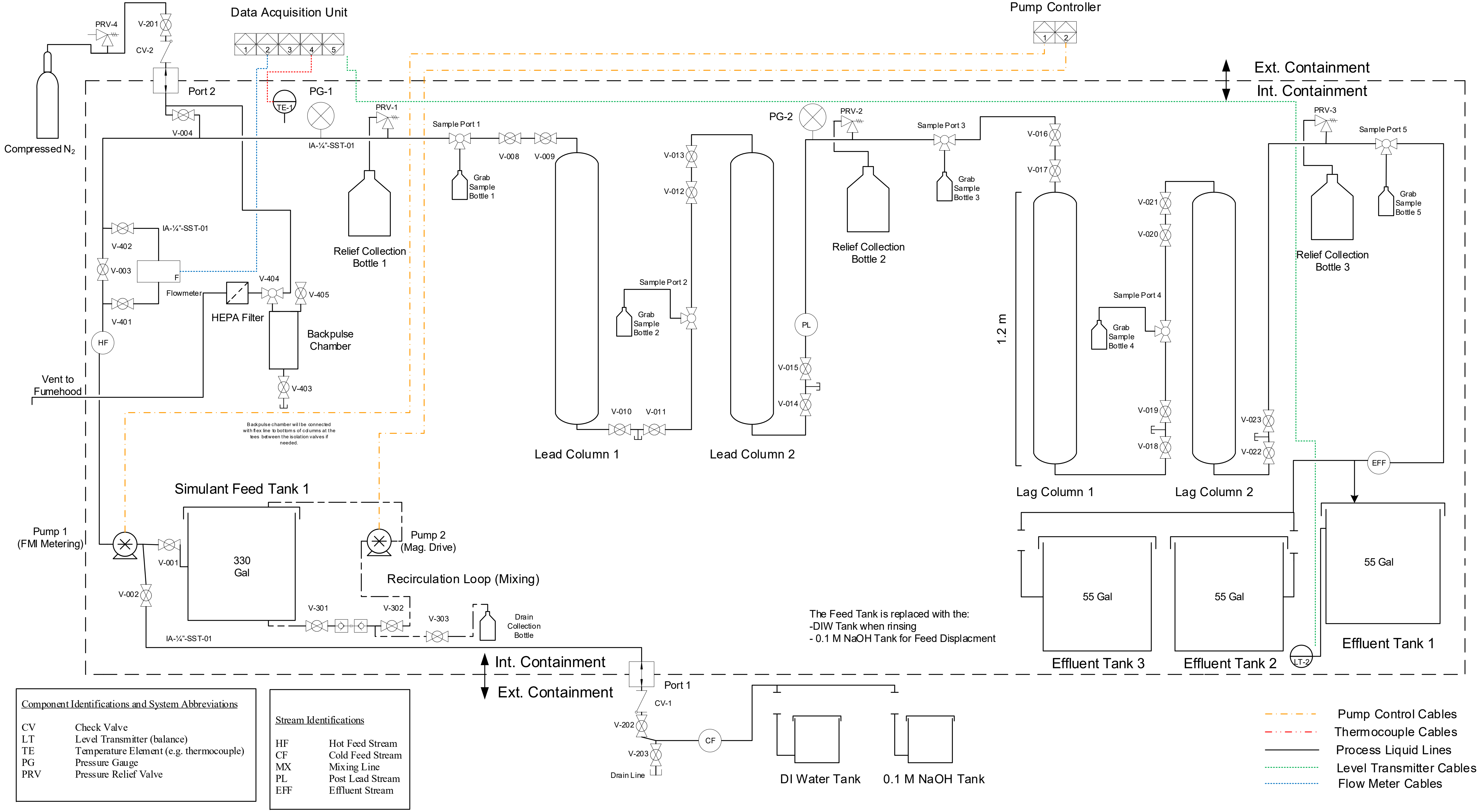

Figure 3.7. Full Height Column System Schematic

The CST bed supports were fabricated in-house. They were made of stainless steel, 100 mesh screens tack-welded onto stainless steel support rings. The support rings were stabilized with snug-fitting O-rings to remain stationary in the column once seated. The support screen rested directly on the bottom column fitting. The entire CST bed surface could be observed through the glass column walls.

The height of the CST bed was measured with an adhesive millimeter-scale (Oregon Rule Co., Oregon City, OR). The scale was affixed to the column with the zero-point set at the top of the CST bed support ring and extending vertically upward. The packed CST bed height measurement uncertainty was about ±2 mm. The high superficial velocities cause a slight disturbance at the top of the CST bed resulting in an uneven CST surface. Thus, any potential change in bed height during processing was confounded.

All connecting tubing was 1/4-in. outside diameter and 1/8-in. inside diameter and was made of either polyethylene, PTFE, or stainless steel. An in-line flow meter (Micro Motion LF Series, S Burlington, VT) was connected between the pump head and the valve manifold with an optional bypass flow loop. The valve manifold assembly contained an in-line Swagelok Poppet pressure relief check valve with a 30-psi trigger (Solon, OH) and a 50-psi pressure gauge (Swagelok) along with Swagelok 3-way ball valves for sampling. An FMI QVG50 pump (Syosset, NY) equipped with a 3/8-in.-diameter ceramic and Kynar®-coated piston pump head was used to introduce all fluids. The feed was piped directly from the 330-gal tote containing simulant prepared by Noah Technologies, Inc. The effluent was collected in a series of 55-gallon drums that were placed on a platform scale (Arlyn Scales, East Rockaway, NY, Model 320M-CR) with 450 kg capacity and 0.1 kg readability.

The column system manifold was assembled with a column changeout capability for multiple tests. Figure 3.8 shows a photograph of the Blue column assembly. The 330-gal feed tote on the left was retrofitted with a feed line inlet positioned at the bottom of the tote to the FMI pump in the benchtop contamination-controlled area. The flow meter is shown on the far left side of the manifold located vertically. The four packed columns are centered on the manifold with additional space available for a polishing column (not used in this test). The effluent line exits the benchtop contamination-controlled area, where the effluent is collected in the 55-gallon drum tucked behind the manifold. All components were contained within a 10-ft by 12-ft plastic berm used as secondary containment. Additional containment was placed underneath the pump and below the columns. The pressure-relief valves were plumbed to collection bottles capable of collecting an entire shift’s worth of process fluid, should the column system plug (shown below the column manifold).

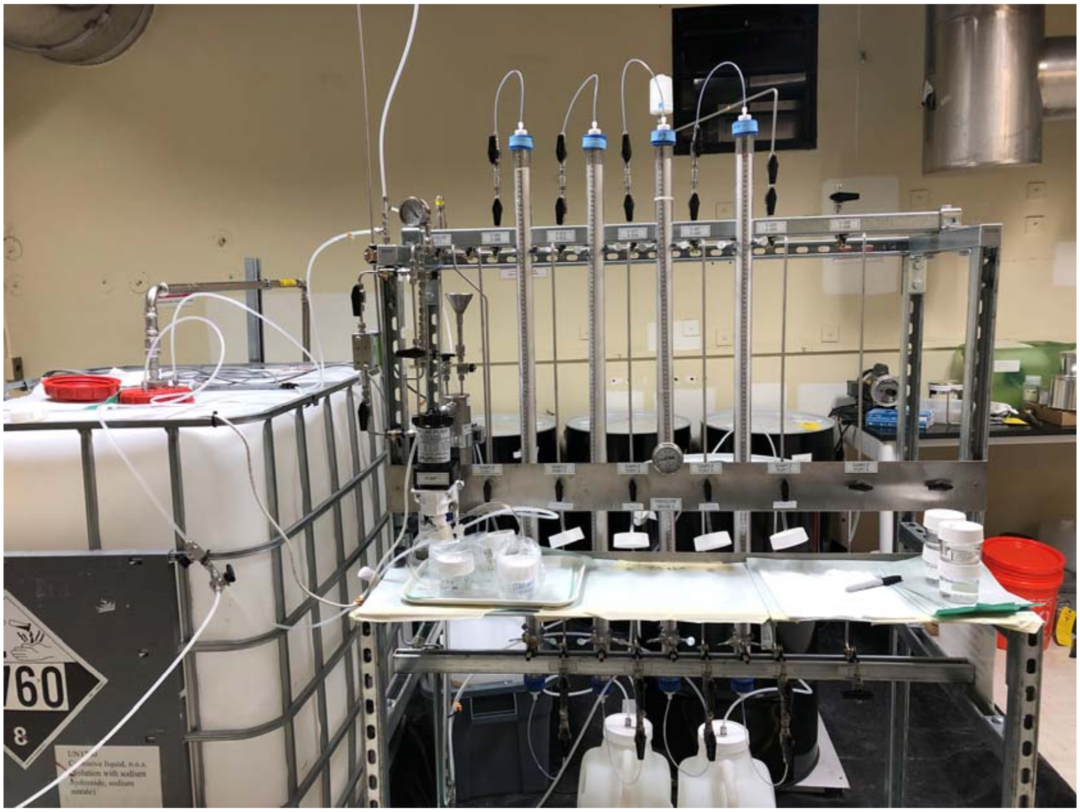

Figure 3.8. Tall Column System Configuration, Blue Columns

3.4.2.2 CST Bed Packing, Bed Volume, and System Volume

Column packing was performed by initially adding 0.1 M NaOH to the column (filling to the ~100 cm level). An aliquot of the pretreated CST (~580 g dry CST), slurried in 0.1 M NaOH, was quantitatively transferred into the column in discrete increments. Each increment was allowed to settle before adding the next increment. No gas bubbles were observed during packing. The column was tapped with a bung to help settle the bed with each 3- to 5-increment transfers until all of the CST was added, resulting in a nominal CST bed height of 113 cm and CST volume of ~573 mL per column. The lead column (columns 1 and 2) and lag column (columns 3 and 4) were thus each ~226 cm tall with a ~1.15 L CST BV.

The fluid headspace was adjusted to approximately 3 to 4 cm above the packed bed. The small air gap above the fluid head disappeared by the third day of simulant processing as the gas was slowly dissolved into the simulant. The fluid holdup volume of the entire system was ~2.1 L. The fluid filled volume in the lead column CST bed represented 38% of the total fluid filled volume.

The packed columns were placed in-line to the flow system. Sodium hydroxide (0.1 M) was processed through the system to fill the lines before testing with simulant to avoid potential precipitation of aluminum hydroxide once contacted with the feed and to calibrate the FMI pump.

3.4.2.3 Feed Preparation

The feeds supporting the tall column testing were delivered in 330-gal totes. Before processing through the columns, each simulant container was spiked with 1.0 mCi and 1.3 mCi (Orange and Blue tests, respectively) ^{137}Cs tracer solution. This was sufficient to provide a measurable DF of ~30,000 when a 100-mL sample aliquot was measured by gamma spectroscopy. The tracer solution was added directly to the mixing recirculation loop. The simulant was mixed for 3 h by turning over the contents of the tote by in-tank mixing. The simulant was drawn out of the bottom of the tote by pump, then added back in through the recirculation line with a spray nozzle at the bottom of the tote. Analytical samples were collected during mixing about 1 h apart to confirm consistency of the ^{137}Cs concentration. After mixing, the simulant was allowed to stand for 12 to 48 h and solids largely settled to the container bottom.

3.4.2.4 Full Height Column Testing

The FMI pump stroke length was set to the maximum position; flows of 1 to 4 BV/h could be accommodated by adjusting the pump head turn or stroke rate. Volume passed through the system was determined using the mass collected on the load cell divided by the fluid density. Flowrate was calculated by dividing the collected volume by the collection time. Fluid flow was also passed through a Micro Motion LF Series flowmeter as a secondary means to assess flowrate. The load cell mass and Micro Motion flowrate were recorded electronically through a data acquisition system along with a time stamp every second. The pump processing resulted in a pulsation of fluid into the system. Pulsation affected the top of the lead column most with some CST disturbance. Once the airgap above the CST bed was eliminated, the pulsation effect on the CST bed disturbance abated.

The 5.6 M Na simulant was processed through the ion exchange media beds, lead to lag. Two different simulant flowrates were tested; the process volumes and flowrates for each test are summarized in Table 3.14 and Table 3.15. The Orange column test was performed first and lasted 31 days. The Blue column test, performed after Orange column test, lasted 22 days. Each test processed nearly 300-gal of feed. Effluent was collected in 55-gallon drums. After processing 356 BVs feed through the Blue column, the flowrate noticeably slowed to 1.7 BV/h despite increasing the stroke rate. After processing 432 BVs, the flowrate slowed to 1.3 BV/h. The decreased flowrate was directly related to pump head deterioration. The flow was stopped after processing 466 BVs of feed for 27 h, allowing for pump head replacement during next normal day shift. Figure 3.9 shows the achieved flowrate versus the BVs processed for both the Orange and Blue column tests along with the flowrate targets. Clearly, more flowrate control was attained with new pump heads (Orange column test and Blue column after head replacement), and pump head replacement after processing 300 gal of feed is recommended.

Table 3.14. Orange System Flow Description Summary, 10/19/18 Start

Step	Feed Material	Volume, BV	Flowrate, BV/h	Superficial Velocity, cm/min
Shakedown testing	0.1 M NaOH	as needed	variable	--
Feed processing[(a)]	5.6 M Na Simulant	951	1.30[(a)]	4.88[(a)]
Feed displacement	0.1 M NaOH	7.1	~3.0[(b)]	--
Water rinse	Deionized water	10.3[(c)]	~3.7[(c)]	--
Fluid displacement	Compressed gas	NA	NA	--

BV = bed volume, 1.15 L.

(a) Flowrate varied between 1.25 and 1.36 BV/h. The last 84 BVs processed reduced flowrate to 1.22 BV/h; this was not included in the average flowrate.

(b) Flowrate was estimated; changing effluent density confounded exact calculation.

(c) The columns had run dry after processing 8.3 BVs DI water; the last 2 BVs collected were associated with re-filling the CST beds with water.

Table 3.15. Blue System Flow Description Summary, 11/28/18 Start

Step	Feed Material	Volume, BV	Flowrate, BV/h	Superficial Velocity, cm/min
Shakedown testing	0.1 M NaOH	as needed	variable	--
Feed processing[(a)]	5.6 M Na Simulant	895	1.82[(a)]	6.94
Feed displacement	0.1 M NaOH	6.4	~3.0[(b)]	--
Water rinse	Deionized water	10.7	~3.3[(c)]	--
Fluid displacement	Compressed gas	NA	NA	--

BV = bed volume, 1.15 L.

(a) Flowrate varied between 1.31 and 2.07 BV/h. The last 24 BVs processed purposefully reduced flowrate to 1.63 BV/h and was not included in the flowrate average. See text for discussion.

(b) Flowrate was estimated; changing effluent density confounded exact calculation.

(c) The calculated flowrate jumped to 3.67 BV/h between 7 and 9 BVs processed.

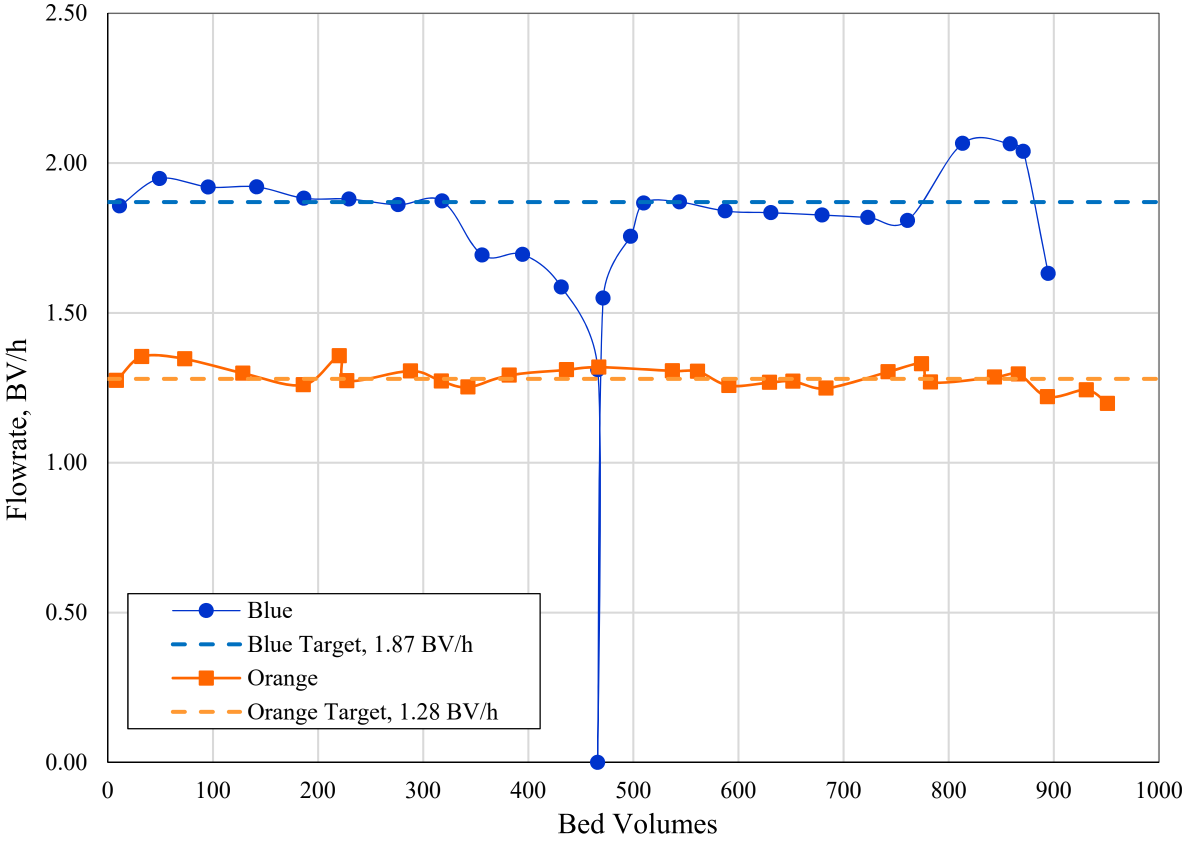

Figure 3.9. Flowrate vs. BVs Processed

Flowrate in the Orange column test was decreased from 1.3 to 1.2 BV/h after processing 866 BVs to the end of test. The Blue column test flowrate was similarly decreased from 2.0 BV/h to 1.6 BV/h after processing 871 BVs feed to the end of the test. The decreased flowrates near the end of the test runs were implemented to ensure the columns would not run dry during unattended operations as the feed volumes were nearing depletion. Samples were collected before and after each change in flow conditions to assess impact on Cs ion exchange.

After simulant loading, 6 to 7 BVs of 0.1 M NaOH (feed displacement) followed by 8 to 11 BVs of DI water rinse were processed to displace residual feed from the system. After 8 BVs of water rinse processing in the Orange column test, the feed water had gone dry and the fluid in the four-column set was displaced. The pump was stopped, additional DI water was added to the feed container, and the pump was restarted. The two samples collected from the Orange column after it went dry contained a small amount of suspended solids. After the water rinse, the fluid was then expelled from the column systems with pressurized nitrogen gas. No attempt was made to thoroughly dry the CST in the columns with gas flow.

During the loading phase, nominal 100-mL samples were collected from each column at the sample port (see Figure 3.7, sample ports 2, 3, 4, and 5). A sample was collected from column 1 after the first ~10 BVs of processing. Lead column samples (column 2) were taken in nominal 40-BV increments with all other columns being sampled in 40- to 80-BV increments. Feed displacement and water rinse samples were collected sequentially from sample port 5 in nominal 1-BV to 2-BV increments, respectively. Samples were sent for GEA to assess the effluent ^{137}Cs concentrations.

Back pressures were observed and recorded for information only (FIO) from both Orange and Blue column systems (all four columns combined). The back pressures were measured from pressure gage 1 located before column 1 (see Figure 3.7). They ranged from ~10 to 12 psig and ~14 to 18 psig, for the Orange and Blue systems, respectively, throughout the test runs. During periodic discrete sampling events from individual columns, the pressure readings from pressure gage 1 were noted.

3.4.2.5 Full Height Column Gamma Scans

Each of the four Orange columns were scanned to assess the overall nature of the Cs loading onto the CST.[1] The column measurements were conducted using a purpose-built detection system incorporating a St. Gobain BriLance-380 $LaBr_3$(Ce) detector (Model 38 S 38) coupled to a Canberra Osprey digital MCA tube base. Detector parameters, data acquisition and data reduction were performed on a Win7 personal computer running Canberra's Genie 2K gamma spectroscopy suite (V3.4). The collimator consisted of a near standard lead brick (10 x 17.8 x 4.5 cm, width, length, thickness) with a 3 mm deep by 9.5 cm wide channel machined into the top, center surface of the brick. This was placed on top of a standard lead brick (nominally 10 x 20 x 5 cm) with the machined surface down, resulting in a 3 mm high by 9.5 cm wide by 10 cm deep channel between the bricks. A third lead brick (10 x 10 x 5 cm) with a 4.13-cm diameter hole machined through the 10 cm x 10 cm face was placed behind the collimator. The $LaBr_3$(Ce) detector was inserted into the hole until it was approximately 2 cm from the horizontal collimator slit. Figure 3.10 provides a general schematic of the collimator and detector configuration with respect to the column.

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[1] The gamma scan data were collected as "for information only" (FIO) because the data did not undergo the technical review rigor as normally applied to the project, the staff performing the analysis had not been trained to the project QA procedures, and the system setup and data acquisition were conducted per discussion and not a project approved test instruction.

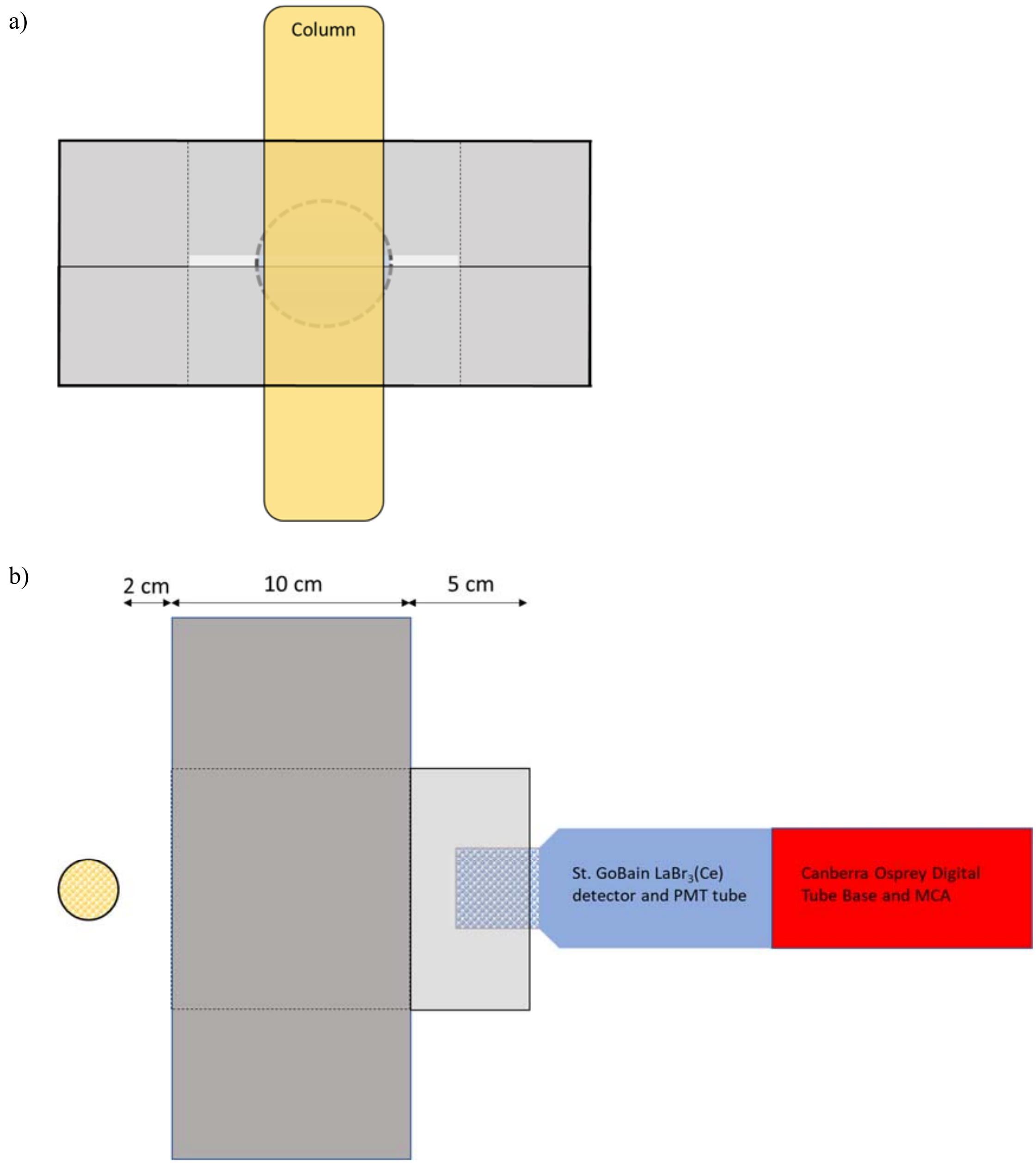

Figure 3.10. Schematic Diagram of Column Gamma Scan System

Figure notes: Schematic shows construction of the collimator and positioning of the LaBr$_3$(Ce) detector relative to the collimator and column (not to scale).

(a) Elevation view of collimator from the front (column depicted in yellow)
(b) Top view of collimator assembly (column in yellow), detector in blue

The detector and collimator were shielded with lead bricks providing a minimum of 10 cm of lead around the detector, thus preventing radiation streaming from the column and the general laboratory background. The detector/collimator assembly along with the rest of the lead shielding weighed approximately 700 kg. It was assembled upon a CE Mobile Lift Table with a 1000-kg capacity. A linear mover providing approximately 63 cm of vertical travel was secured to a table placed alongside the lift table. It provided approximately 2.15 mm vertical travel for each full revolution of the threaded shaft screw. A 20-cm-long ring-stand rod was attached to the linear mover. Two clamps held the column securely to the ring stand rod in vertical orientation, perpendicular to the lift table.

As the column was nearly twice as long as the available linear mover travel, the columns were scanned in a two-step process. With the detector lift table at the low position (collimator approximately 81 cm above floor), the linear mover was put into the bottom position. The columns were clamped into place with the mid-point of the packed column (~55 cm) at the collimator slit. The column was repositioned by moving the linear mover up (clockwise turn), raising the column relative to the collimator and exposing a lower section. This allowed scanning from roughly the column mid-point down to the column bottom (i.e., ~55 to 0 cm) as marked on the column. Data for the upper section of the column were obtained by positioning the lift table to the ‘high’ position (collimator ~150 cm above floor), which placed the collimator and detector near the column mid-point again. The linear mover was lowered (counter clockwise turn) such that the column passed the collimator to scan up the column (i.e., ~55 to 115 cm). Figure 3.11 shows the entire system with the detector and collimator assembly in the high position. Figure 3.12 provides a close-up view of the collimator and column.

Figure 3.11. ^{137}Cs Column Scanning System

Figure notes: The detector and collimator assembly are shown on the blue lift table, which is in the ‘high’ position. The collimator is at the bottom of the copper strip in the lead stack. The column is attached to the vertical linear mover, which is roughly 1/3 down. As the linear mover was lowered, the collimator effectively scanned up the column.

Figure 3.12. Close-up View of the 3-mm Collimator Opening and the Column

Figure note: The column is 1.9 cm away from the collimator slit and approximately 14 cm from the face of the $LaBr_3(Ce)$ detector.

Data were acquired and spectra saved at various positions along the length of the column as denoted by the column's adhesive centimeter scale. The net count rate in counts per second (cps) was recorded along with the net peak area (counts) in a fixed region of interest (ROI) in the spectrum that included the ^{137}Cs 661 keV gamma line. The data were obtained directly from the G2K "Display Info" Status Page without additional spectrum analysis. Count times varied from 20 minutes to 20 hours in an effort to keep uncertainty in the net peak area at <2% for one standard deviation. The $LaBr_3(Ce)$ has an intrinsic background as a result of long-lived ^{138}La and ^{227}Ac impurities; however, a channel per channel background spectrum subtraction was not performed. The ^{137}Cs region of interest was confirmed to have a net zero cps (i.e., no ^{137}Cs) on scans of the unpacked section of the columns, as well as the column ends. These measurements confirmed that the ^{137}Cs in the column outside of the view of the collimator was not streaming through the lead shield and influencing the measurement.

3.5 Sample Analysis

Cesium load performance was determined from the ^{137}Cs tracer concentration in the collected samples relative to the ^{137}Cs tracer in the feed. The collected samples (10 mL for the medium columns and 100 mL for the full height columns) were analyzed directly to determine the ^{137}Cs concentration using GEA. Cesium load breakthrough curves were generated based on the feed ^{137}Cs concentration (C_0) and the effluent Cs concentration (C) in terms of % C/C_0.

The Cs breakthrough curves are plotted on linear-linear plots as well as on probability-log plots, the latter to better show the load characteristics at both ends of the breakthrough curve. Both the contract limit and 50% breakthrough lines are marked and used to compare performance between tests. The contract limit was derived from AP-107 tank waste processing (Rovira et al. 2018) and is 0.0114% C/C_0 or a Cs DF of 877. This value was based on the 5.6 M Na and 156 µCi/mL ^{137}Cs concentration in AP-107 tank waste. The final ^{137}Cs concentration in the low-activity glass is targeted to be at or below 3.18E-5 Ci ^{137}Cs/mole of Na.[1]

The water rinse samples associated with the Blue column processing were filtered using Nalgene™ Rapid-Flow™ disposable filter units equipped with 0.2-µm pore size nylon membranes (Thermo-Scientific). An additional 0.2-µm pore size nylon membrane filter was placed on the top of the filter unit filter so that it could be easily removed. The filtrates and the associated removable nylon filters were counted by GEA to assess the ^{137}Cs contents in each fraction—soluble Cs in filtrate and particulate (bound) Cs on the filter.

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[1] 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.

4.0 Batch Contact Test Results

This section provides and compares the batch contact kinetic results for the <25 mesh CST contacted with 5.6 M Na simulant, 6.0 M Na simulant, and 5.6 M Na simulant with added organics, and the full PSD CST contacted with 5.6 M Na simulant. The effective Cs capacity at the equilibrium feed condition (hereafter called effective capacity) was not determined on this lot of CST. Fiskum et al. (2018a) determined the effective capacity on a different CST production lot (Batch 2081000057, 30 x 60 mesh) at 6.16 mg Cs/g dry CST. Based on this effective capacity, the equilibrium Cs concentration in a solution of 40 µg/mL Cs would result in an ~8-µg/mL Cs solution given the phase ratio of 200; the 5.6 M Na simulant matched this Cs concentration.

Table 4.1 identifies the simulant, initial Cs concentration, contact time, contact volumes, final Cs concentration, K_d values, and Cs loading onto the CST for testing with <25 mesh CST. Table 4.2 provides the same set of data for testing with the full PSD CST. Note that duplicate samples were collected at the 2-h contact time. The 2-h duplicate K_d values varied within ±3 to 14% and represented the overall experimental K_d uncertainty; the duplicate Q values (mmoles Cs/g CST) varied within ±2 to 8% and represented the overall experimental Q uncertainty, mass basis relative to the 100 °C dried CST. If the 200 °C dry CST mass basis is used instead of the 100 °C dry CST mass basis, the K_d and Q values increase by 5%.

Table 4.1. Kinetic Batch Contact Testing Results with <25 Mesh CST

Simulant Description	Initial [Cs], µg/mL	Contact Time, h	Simulant Volume, mL	Final [Cs], µg/mL	K_d, mL/g	Eq. Cs in CST, mmole Cs/g CST (Q)
5.6 M Na	40.2	0.10	219.0	38.7	7.66	2.22E-3
		0.67	216.3	33.9	36.9	9.49E-3
		2.00	213.9	25.8	109	2.16E-2
		2.00	213.9	24.8	121	2.32E-2
		5.17	209.6	16.1	287	3.63E-2
		20.4	207.6	8.48	713	4.79E-2
		45.1	205.3	7.37	841	4.95E-2
		123	203.3	5.71	1128	5.20E-2
6.0 M Na	38.5	0.10	219.5	34.5	23.4	6.04E-3
		0.65	217.1	30.1	56.2	1.28E-2
		1.98	214.7	19.8	188	2.84E-2
		1.98	214.7	20.2	179	2.77E-2
		5.15	210.4	13.9	343	3.73E-2
		20.4	208.4	7.84	754	4.65E-2
		45.1	206.2	6.93	869	4.79E-2
		123	204.1	6.44	941	4.87E-2

Simulant Description	Initial [Cs], µg/mL	Contact Time, h	Simulant Volume, mL	Final [Cs], µg/mL	K_d, mL/g	Eq. Cs in CST, mmole Cs/g CST (Q)
5.6 M Na with added organics	39.4	0.10	219.4	36.5	16.0	4.39E-3
		0.50	216.8	33.9	32.3	8.33E-3
		1.85	214.4	23.7	131	2.39E-2
		1.85	214.4	24.0	127	2.34E-2
		5.10	210.2	15.9	287	3.58E-2
		20.2	207.9	8.68	679	4.67E-2
		44.8	206.0	7.31	833	4.88E-2
		123	203.7	6.02	1041	5.08E-2

Table 4.2. Kinetic Batch Contact Testing Results with Full PSD CST

Simulant Description	Initial [Cs], µg/mL	Contact Time, h	Simulant Volume, mL	Final [Cs], µg/mL	K_d, mL/g	Eq. Cs in CST, mmole Cs/g CST (Q)
5.6 M Na	37.8	0.10	224.8	33.4	27.4	6.85E-3
		0.50	222.2	31.2	43.6	1.03E-2
		1.85	219.8	21.7	151	2.51E-2
		1.85	219.8	23.0	131	2.31E-2
		5.10	215.9	14.8	312	3.59E-2
		20.2	214.0	8.70	663	4.54E-2
		44.8	211.8	6.61	926	4.86E-2
		123	209.6	6.20	989	4.93E-2

The data from Table 4.1 and Table 4.2 are plotted in Figure 4.1 (K_d versus time) and Figure 4.2 (Q versus time) on linear-linear scales. Rapid Cs exchange occurred from 0 to 20 h. The exchange rate after 20 h contact time, measured by Q, started leveling off; the rate measured by K_d was still increasing, albeit more gradually. These results mirror those previously reported (King et al. 2018), where the Cs concentration loading in the CST solids was essentially complete after 24 h yet the K_d values continued to change significantly up to 96 h. As King et al. (2018) previously described, the K_d values are more responsive than Q values to small changes at low Cs concentrations.

The 45-h K_d value from this current equilibrium test (5.6 M Na, <25 mesh CST) was 841 mL/g (see Table 4.1). This value may be directly compared to the 45-h K_d value of 785 mL/g reported by Fiskum et al. (2018) using a different CST production lot (Batch 2081000057) and different processing conditions (20-mL solution volume, phase ratio of 189). The newer CST production batch (Lot 8056202-999) resulted in a 7% higher K_d value. Although 7% difference cannot be excluded from overall experimental uncertainty, it indicates that the Cs effective capacity and/or kinetics may be slightly higher for the newer CST production batch; this is supported by the column testing results.

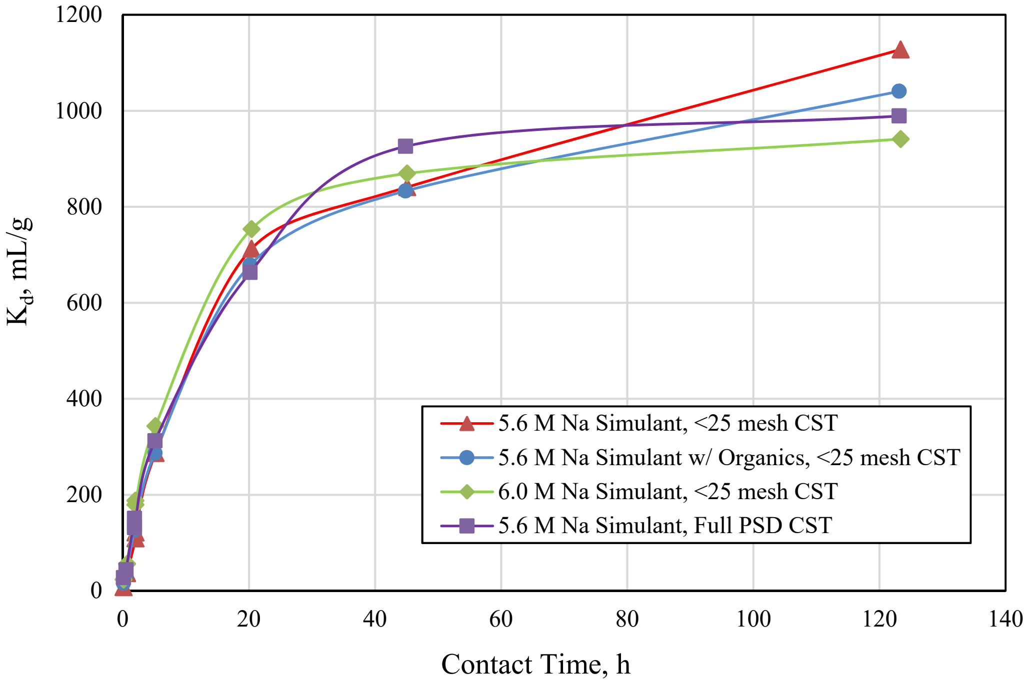

Figure 4.1. K_d as Function of Time in Various Simulants and CST Size Fractions

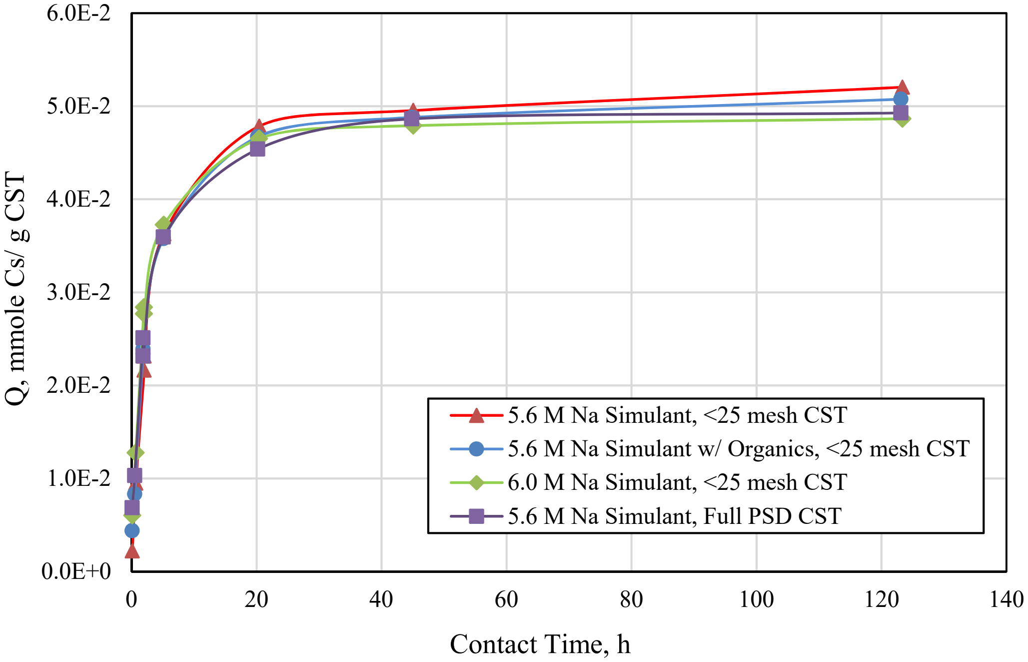

Figure 4.2. Cs Loading as a Function of Time in Various Simulants and CST Size Fractions

Close examination of the data tables shows the primary differences between the variable tests conditions and the <25 mesh CST results in 5.6 M Na simulant (baseline) occurred at the first 0.1 h contact measurement. The 0.1-h measurements showed higher K_d and Q values for the variable tests. However, the 0.1-h contact time condition included hand-mixing and required closely matched sampling times, which were hard to exactly match test to test. Further, slow wetting of the CST may further confound the 10-min tests. These variables could significantly impact the precision of 0.1-h contact time Cs concentration given the rapidly changing Cs concentration and slow CST wetting in this time region.

The 6.0 M Na simulant matrix showed initially higher K_d and Q values relative to that of the 5.6 M Na simulant through the first ~2-h contact time; the K_d values converged after 5 h. The full PSD CST test results were similar to those of the 6.0 M Na simulant results in that the initial (0.1- to 2-h) K_d results were higher than the 5.6 M Na simulant, then K_d results converged from 5 h onward. The K_d and Q results for the 5.6 M Na simulant with added organics were not distinguishable from those of the 5.6 M Na simulant with <25 mesh CST within experimental uncertainty. The variable test conditions did not significantly affect the Cs exchange rates onto the CST.

Based on the changing Cs concentrations and K_d values between the 45-h and the 123-h contact times, final Cs equilibrium conditions at 123 h could not be confirmed. At 45 h, 83% to 84% of the Cs was removed from solution; at 123 h, 84% to 87% of the Cs was removed from solution. The difference in Cs content appears small, but Cs was still being removed from solution as of the 123-h contact time.

5.0 Medium Column Test Results

The Cs load behavior was evaluated at a range of conditions: three different flowrates with the 5.6 M Na simple simulant, 5.6 M Na simulant at elevated temperature (35° C), 5.6 M Na simulant with added organics, and 6.0 M Na simulant. This section discusses the Cs load behavior for the six tests. The Cs content in the feed displacement and water rinse was evaluated on one test (6.0 M Na simulant). Tabulated data for each test are provided in Appendix B.

5.1 Cs Load Results

The Red column, processed at 1.8 BV/h with 5.6 M Na simulant, was considered the standard comparative reference point for evaluating the effects of variables. Figure 5.1a shows the Cs load profile on a linear-linear plot. The x-axis shows the BVs processed and the y-axis shows the effluent Cs concentration (C) relative to the feed concentration (C_0) in terms of % C/C_0. In this graphing format, the Cs breakthrough from the column appears to start at ~240 BVs and continues to 967 BVs. The 50% breakthrough was extrapolated to be at ~1000 BVs. The breakthrough profile in relation to the contract limit is not discernable on this linear-linear scale. Figure 5.1b shows the same Cs load data provided in Figure 5.1a on a probability-log scale plot. Much more detail of the Cs load performance at low and high % C/C_0 values is discernable, especially in relation to the contract limit. Further, the Cs breakthrough appears linear on the probability-log plot, allowing for more accurate forward and backward extrapolations. The contract limit was assigned 0.114 % C/C_0.[1] Figure 5.1b shows that Cs breakthrough starts off high (above the contract limit) for the first 40 BVs; however, this was attributed to an artifact from sample port Cs contamination associated with previous use with the manifold on ^{137}Cs-spiked simulant. After processing 40 BVs, the effluent Cs concentration dropped below the contract limit. Clearly, the effluent Cs concentration started to rise after processing 200 BVs of feed. The contract limit was reached at 242 BVs processed and the 50% breakthrough was extrapolated to 1000 BVs.

Figure 5.2 and Figure 5.3 show the Cs breakthrough profiles for the Yellow (11.4 BV/h) and Green (15.0 BV/h) columns using both scale presentations. These two column tests were intended to match the superficial velocity of the full height columns (4.88 cm/min for the Orange system and 6.90 cm/min for the Blue system). Figure 5.4 shows the Cs load profile while processing at 35 °C (Pink column) and Figure 5.5 shows the Cs load profile with the 5.6 M Na simulant with added organics (Purple column). Figure 5.6 shows the Cs load results for the 6.0 M Na simulant along with the Cs concentration associated with the feed displacement and the water rinse. Results of the filtered effluent sample are also shown in each figure.

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[1] The contract limit was based on AP-107 tank waste with 5.61 M Na and 157 µCi/mL ^{137}Cs and a maximum loading of 3.18E-5 Ci ^{137}Cs/mole Na in the glass (from the ICD 30 Waste Acceptance Criterion).

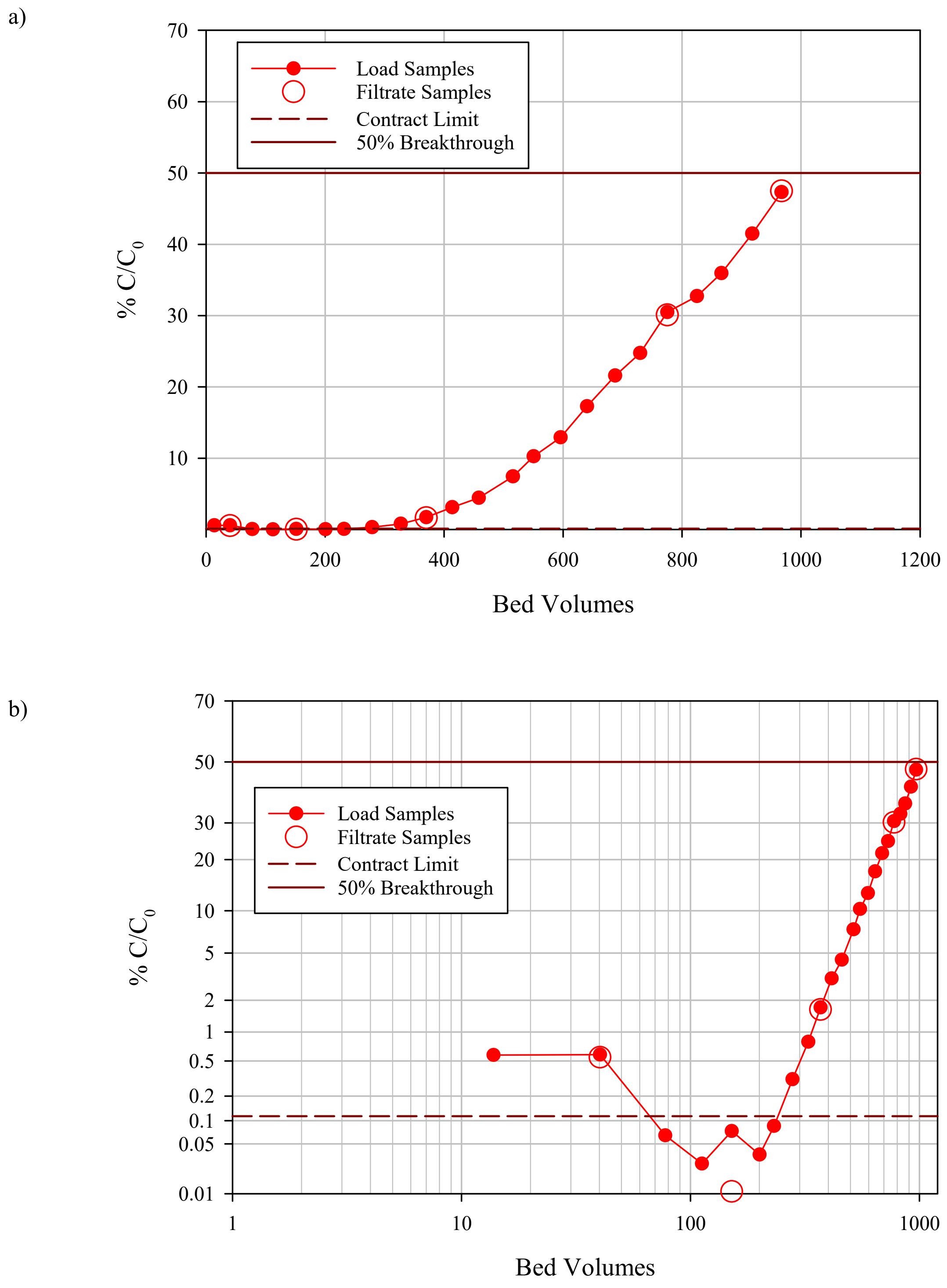
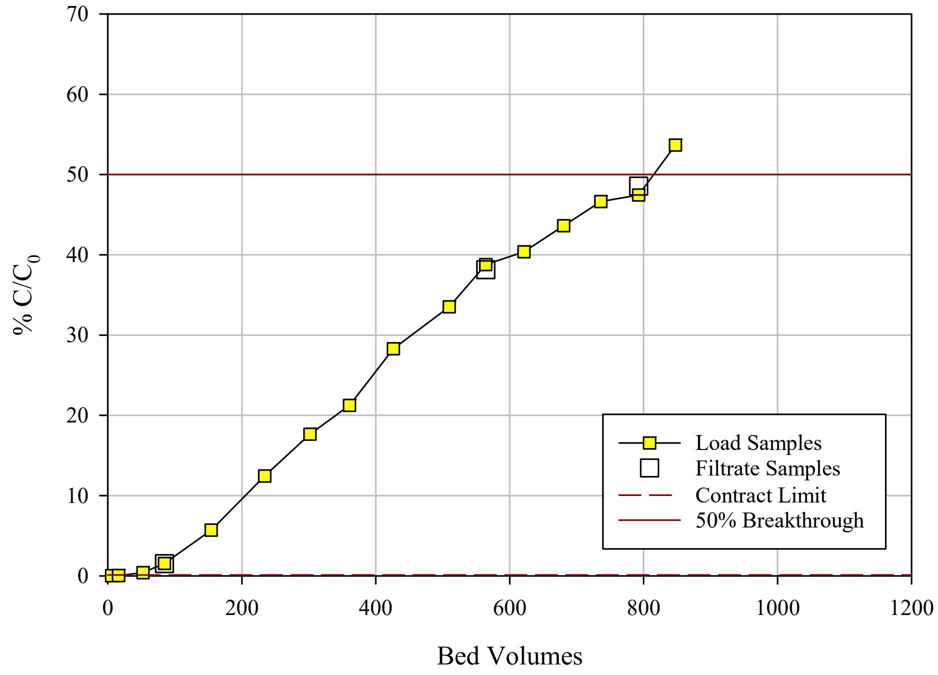


Figure 5.1. Red Column a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant 20 °C, Flowrate 1.83 BV/h, Superficial Velocity 0.82 cm/min

a)



b)

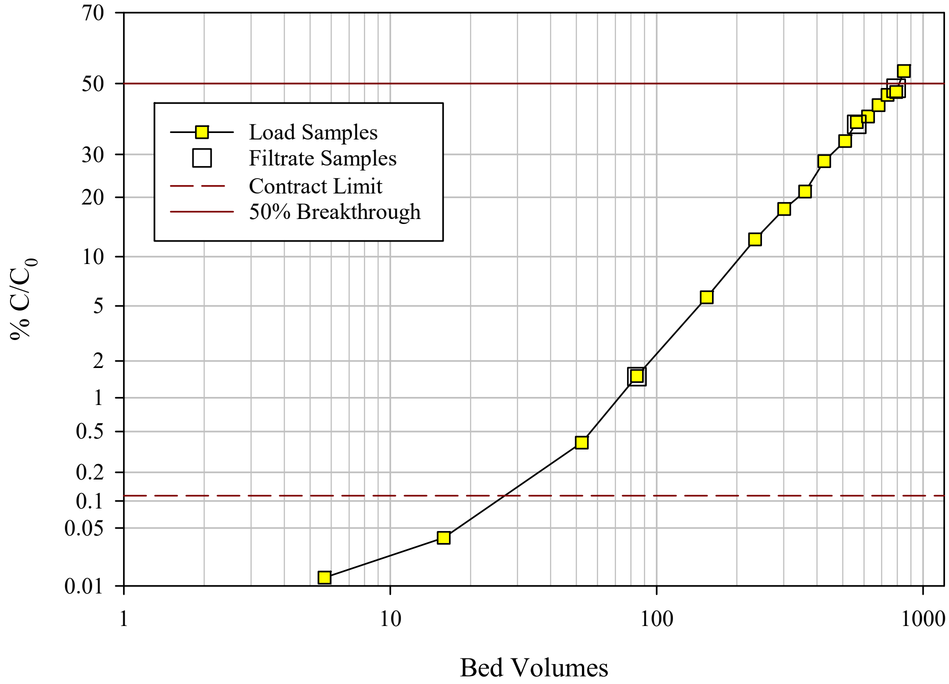


Figure 5.2. Yellow Column a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant 20 °C, Flowrate 11.4 BV/h, Superficial Velocity 5.1 cm/min

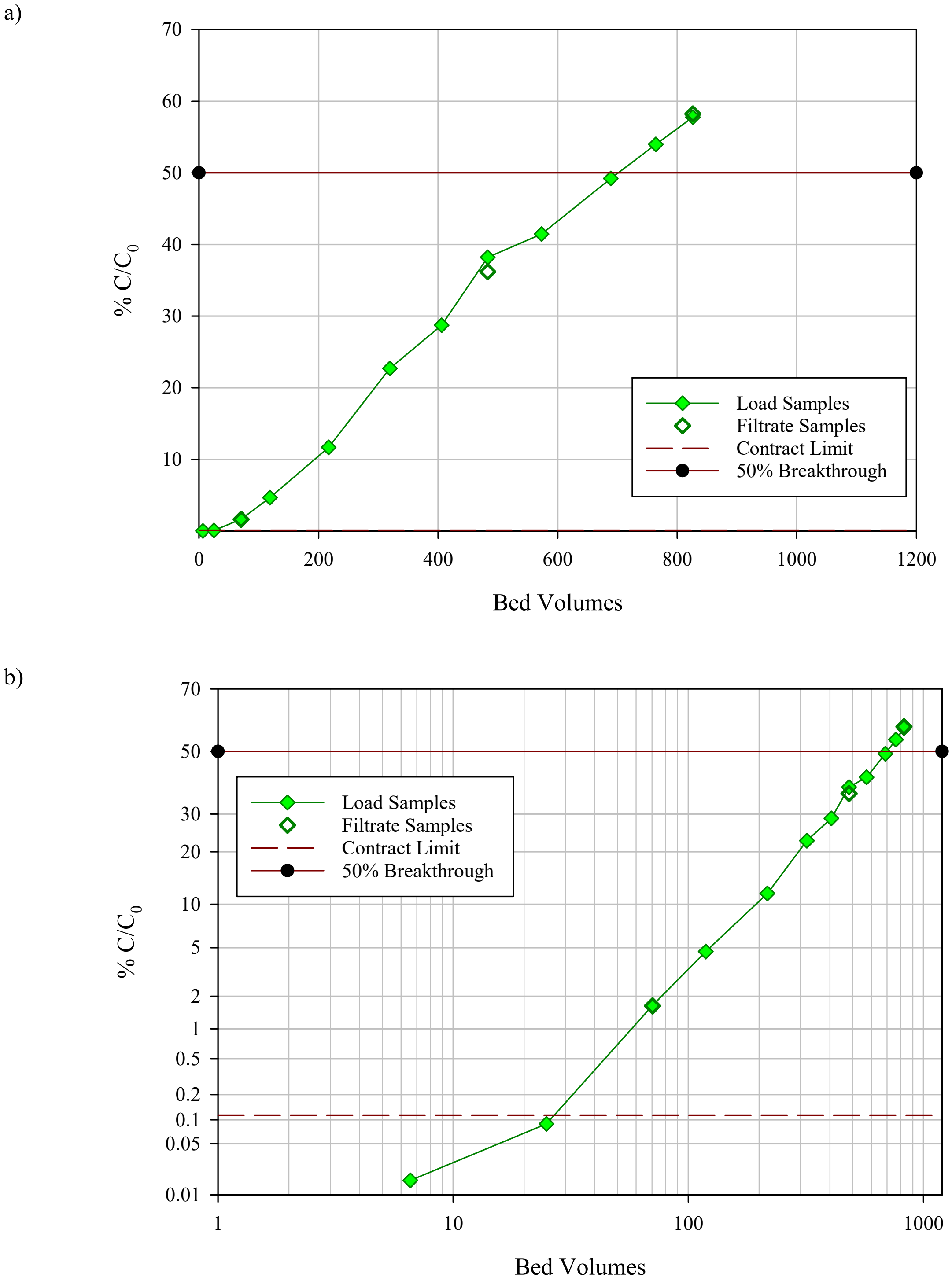
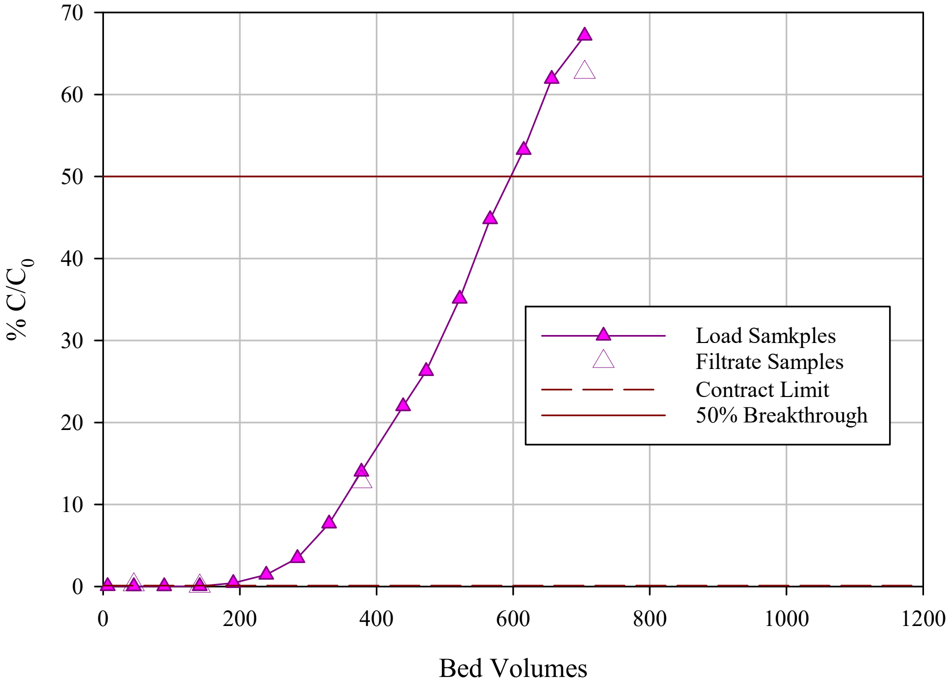


Figure 5.3. Green Column a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant 20 °C, Flowrate 15.0 BV/h, Superficial Velocity 6.8 cm/min

a)



b)

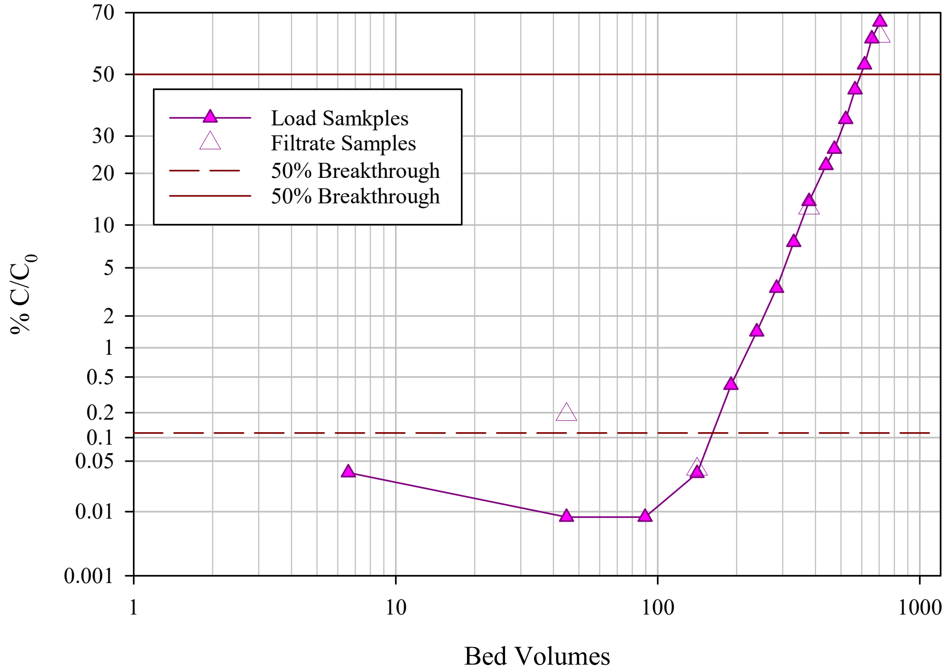
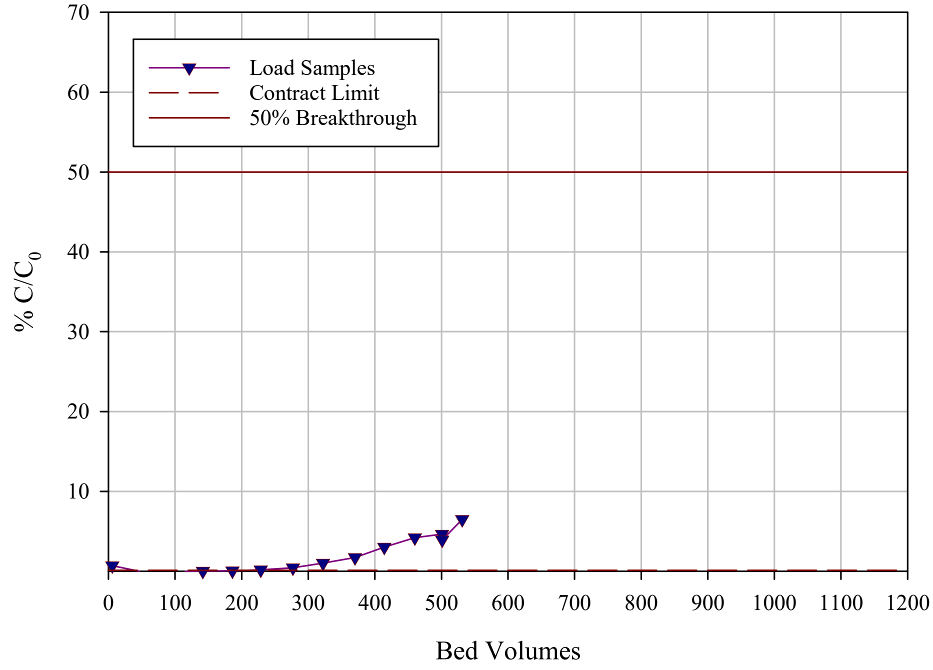


Figure 5.4. Pink Column a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant 35 °C, Flowrate 1.93 BV/h, Superficial Velocity 0.87 cm/min

a)



b)

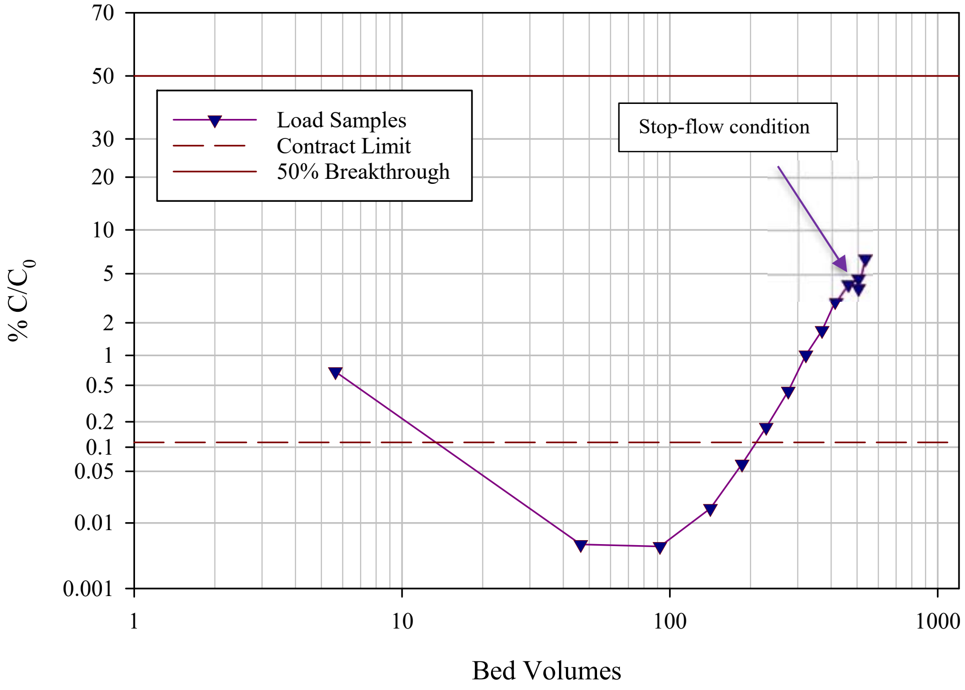
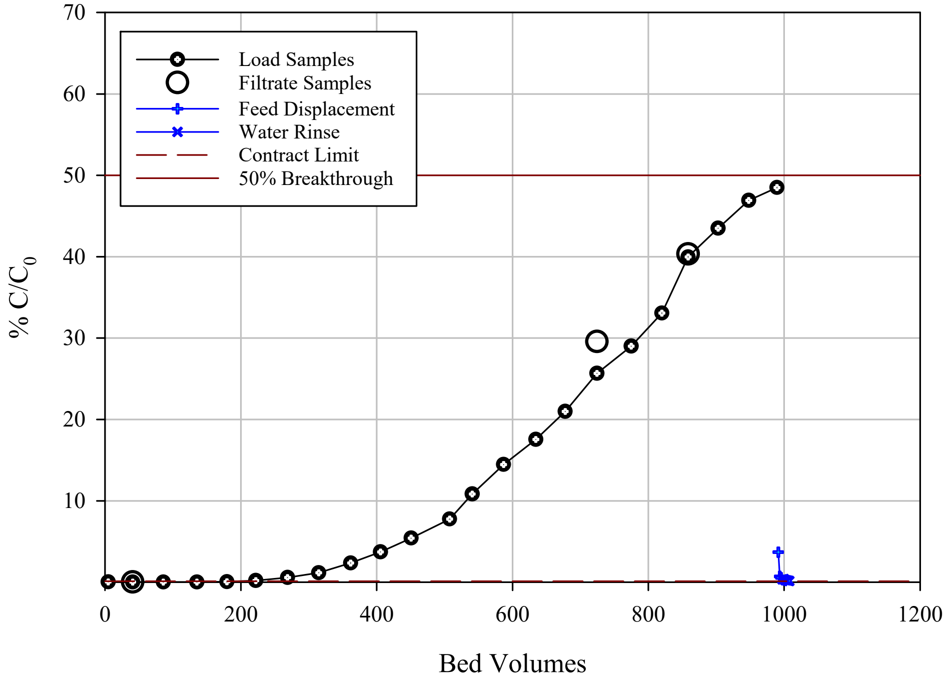


Figure 5.5. Purple Column a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant with Added Organics ~20 °C, Flowrate 1.86 BV/h, Superficial Velocity 0.84 cm/min

a)



b)

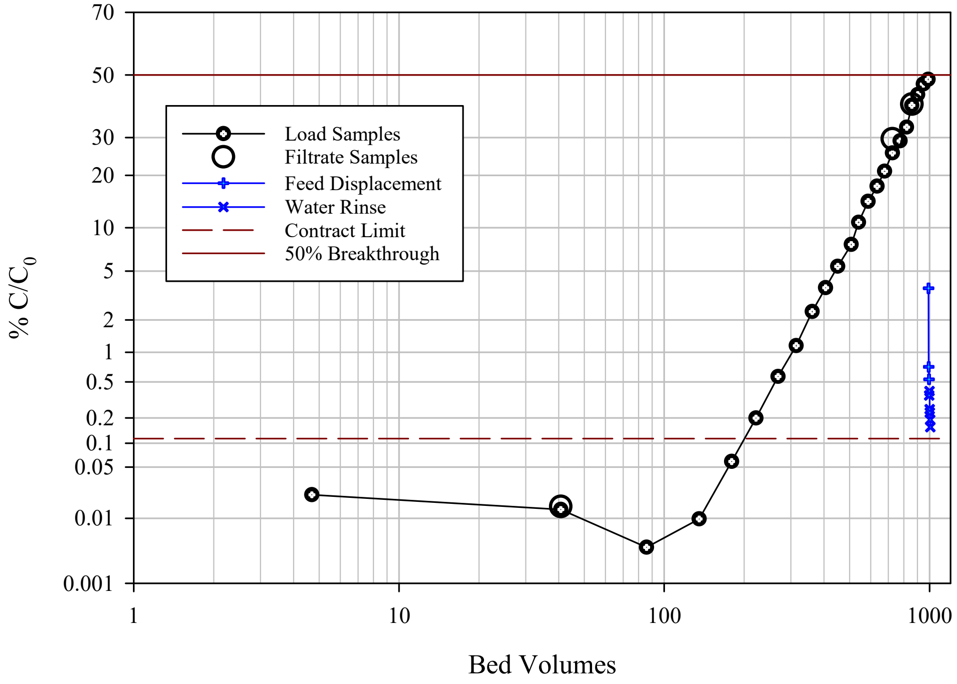


Figure 5.6. White Column a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 6.0 M Na Simulant 20 °C, Flowrate 1.88 BV/h, Superficial Velocity 0.85 cm/min,
Feed Displacement and Water Rinse 3.0 BV/h, Superficial Velocity 1.34 cm/min

In most cases, the Cs load curves were not completely smooth as presented on the linear-linear plots. The reason for these aberrations was not clear. In contrast, breakthrough profiles measured with spherical resorcinol-formaldehyde resin were smooth, allowing for simple interpolation between data points and backward and forward extrapolations (Fiskum et al. 2018b). Samples were targeted from peak “bumpy” regions for filtration and re-analysis by GEA to assess if fines carrying Cs might be associated with them. Generally, the filtrate analysis confirmed the original results, with a few that were slightly below or above the original result. The filtrate result at 45 BVs from the Pink column was an anomaly and was attributed to cross-contamination. The deviations between unfiltered and filtered sample results were attributed to the random analytical uncertainty and not to the presence/removal of CST fines.

Sample analysis from the feed displacement processing following 6.0 M Na simple simulant feed processing resulted in a nearly one order of magnitude drop in the Cs concentration. This indicated that Cs was well retained by CST when the Na concentration and ionic strength dropped to that of 0.1 M NaOH. The subsequent water wash effluent continued to drop in Cs concentration, but the rate of change in Cs concentration slowed. The effluent Cs concentration did not drop below the contract limit after processing 6.1 BVs of 0.1 M NaOH and 12 BVs of DI water.

5.2 Medium Column Tests Performance Comparison

Figure 5.7 provides all medium column load profiles on one graph for direct comparison. The Red column test was used as the comparison or reference condition (5.6 M Na simulant, 1.83 BV/h, 20 °C). Rapid flowrates (Yellow at 11.4 BV/h and Green at 15.0 BV/h column tests) resulted in early Cs breakthroughs and longer mass transfer zones. The higher processing temperature of 35 °C (Pink column test) resulted in early Cs breakthrough with a shortened mass transfer zone. The 5.6 M Na simulant with added organics (Purple column test) Cs exchange was not appreciably different from that of the reference condition within the range tested, 0 to 531 BVs. The Cs exchange associated with the higher 6.0 M Na concentration (White column test) was also similar to that of the reference condition. Thus, the presence of organic constituents or increased Na molarity to 6.0 M is not expected to affect the Cs exchange kinetics, Cs load capacities, or Cs mass transfer zones with CST. Increasing temperature and flowrate have a distinct negative effect on Cs exchange kinetics, Cs load capacities, and Cs mass transfer zones.

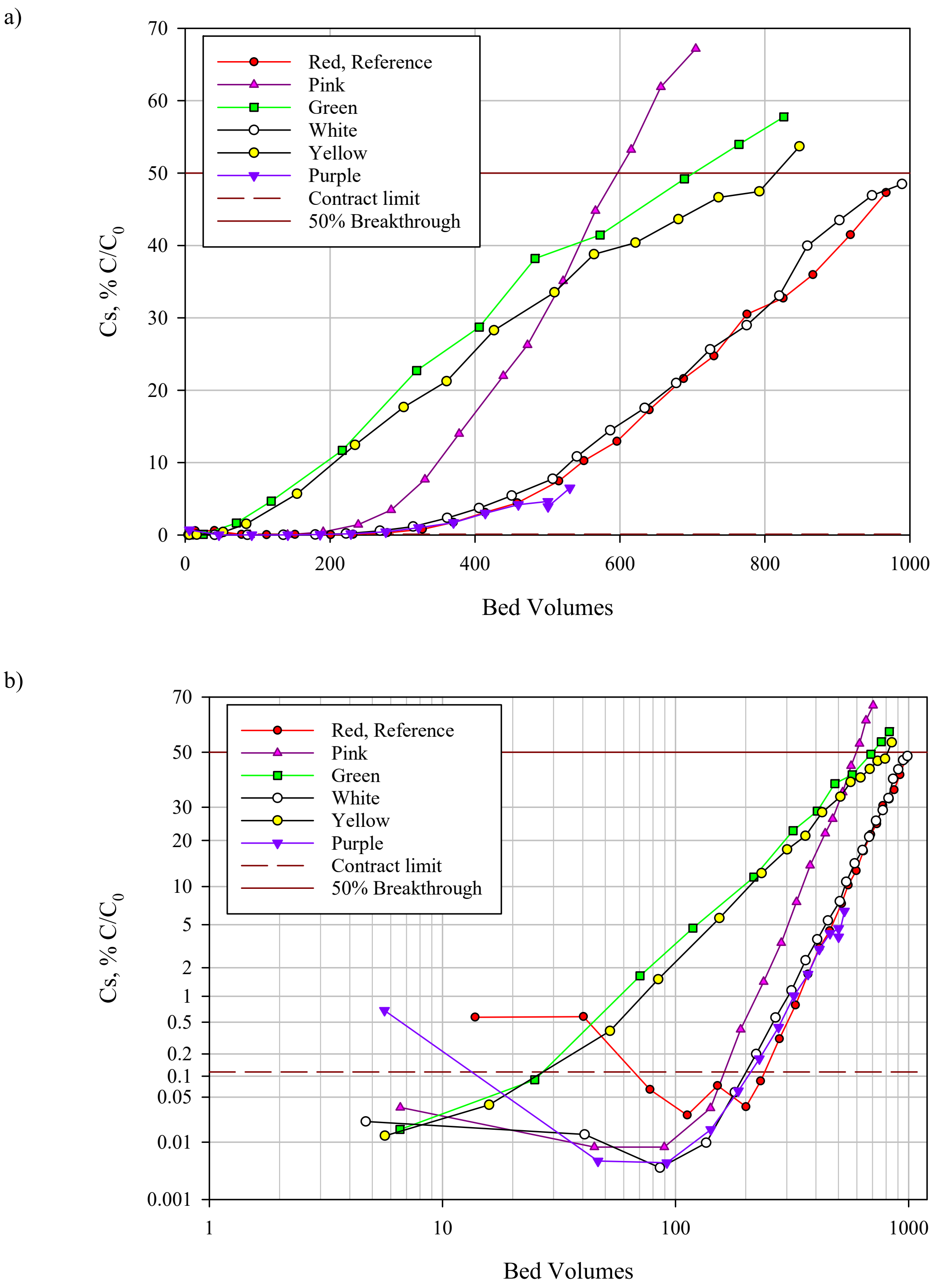


Figure 5.7. Comparative Cs Breakthrough Performance for Medium Column Tests
a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: Red Baseline, 5.6 M Na simulant, 1.8 BV/h, 20 °C; Yellow 11 BV/h; Green 15 BV/h; Pink 1.9 BV/h, 35 °C; Purple Added Organics, 1.9 BV/h; White, 6.0 M Na, 1.9 BV/h

Table 5.1 summarizes the ^{137}Cs fractionation between the effluent, samples, and CST for each column test. The quantity of Cs loaded onto the column was determined by subtracting the Cs measured in the samples and the effluent composite from the total quantity fed to the column.

Table 5.1. ^{137}Cs Activity (Cs) Fractionation in the Medium Column Tests

Column ID	Units	Input Feed	Effluent	Samples	Feed Disp. and Water Rinse	CST Loading
Red	µCi ^{137}Cs	260	30.2	0.188	NA	230
	%	100	11.6	0.072		88.3
Yellow	µCi ^{137}Cs	225	62.1	0.25	NA	163
	%	100	27.6	0.11		72.3
Green	µCi ^{137}Cs	218	61.9	0.191	NA	156
	%	100	28.4	0.087		71.5
Pink	µCi ^{137}Cs	194	32.4	0.215	NA	162
	%	100	16.7	0.110		83.2
Purple	µCi ^{137}Cs	138	1.96	0.016	NA	137
	%	100	1.41	0.012		98.6[(a)]
White	µCi ^{137}Cs	236	32.4	0.19	1.47	202
	%	100	13.7	0.082	0.92	85.6

(a) The Cs loading fraction was relatively high for the Purple column test because it processed only 54% to 75% of the amount of feed processed during the other tests.

The total Cs loading was calculated from the total ^{137}Cs loaded onto the column; at 50% Cs breakthrough, this represents the effective capacity. It is noted that Cs loading varied between tests ranging from 47.3 to 67.2 % C/C_0 Cs breakthrough (excluding the 5.6 M Na simulant with added organics test). This range was considered narrow enough to allow for gross comparisons in the Cs loading behavior between tests. The Cs mass loaded into the CST bed was calculated according to Eq. (5.1).

$$\mathrm{C} = \frac{\mathrm{A_{Cs}} \times \mathrm{CF}}{\mathrm{M}} \tag{5.1}$$

where A_{Cs} = activity of ^{137}Cs, µCi on the column

CF = conversion factor, mg Cs/µCi ^{137}Cs, specific to the Cs and ^{137}Cs spike conditions of each test

M = mass of dry CST (44.0 g)

C = Cs loading, mg Cs/g CST

Table 5.2 summarizes the CST Cs loading performance for each column test. Batch contact testing with a different CST lot number (2081000057) resulted in a measured Cs loading of 6.16 mg Cs/g CST at 8.0 µg/mL Cs equilibrium condition and the associated column test processed at 1.99 BV/h (89.1% Cs breakthrough) resulted in a measured Cs loading of 6.38 mg Cs/g CST (Fiskum et al. 2018a). The CST lot tested herein showed a higher Cs loading of 6.95 mg Cs/g CST (Red column).

Table 5.2. CST Cs Load Performance Summary in the Medium Column Tests

Column Test	BV Processed	Flowrate, BV/h	Cs Loading, mg Cs/g CST[(a)]	Cs Loading, mmoles Cs/g CST[(a)]
Red	967	1.83	6.95	0.0523
Yellow	848	11.4	4.99	0.0375
Green	826	15.0	4.80	0.0362
Pink, 35 °C	705	1.93	4.77	0.0359
Purple	531	1.86	4.26	0.0320
White (6.0 M Na)	989	1.88	6.89	0.0518

(a) This value is close to the effective Cs capacity.

The decreased CST Cs capacities of the Yellow and Green column tests were attributed to the fast flowrates and the slow pore diffusion of Cs exchange into the CST particles. Longer fluid residence times in the CST bed allow time for the Cs to diffuse into the CST particle tunnel network.

The CST Cs loading from the 6.0 M Na simulant test was essentially equivalent to that of the 5.6 M Na simulant test. The higher Na concentration had no measurable effect on Cs loading, similar to the results of the kinetic study batch contact testing (Section 4.0).

No inference of the column test total Cs loading while processing 5.6 M Na with added organics can be made because the test was stopped early after processing 531 BVs. This CST bed had effectively plugged from entrained colloidal-like solids in the feed. This clearly demonstrated that the presence of solids, like those observed in the feed, may be expected to plug the CST bed. The colloidal solids were most likely a sodium phosphate phase (see Appendix E) and the plugging phase was most likely a combination of alumino-silicate phase (cancrinite) and sodium phosphate phase. Cancrinite formation in the CST bed had been previously observed with a 5.6 M Na simulant solution (Taylor and Mattus 2001).

Processing at 35 °C (15 °C higher than the reference condition) resulted in a 31% decrease in Cs loading and significantly earlier Cs breakthrough. Therefore, within the range tested, increased temperature was shown to have a profound negative effect on Cs load behavior.

Table 5.3 provides pertinent Cs exchange performance with respect to BVs to contract limit, to 5% Cs breakthrough, to 20% Cs breakthrough, and to 50% Cs breakthrough. Estimated mass transfer zones were evaluated in two approaches. Evaluation of transfer zone between 20% and 80% Cs breakthrough allowed for comparison to previously reported data (Fiskum et al. 2018a). Evaluation of the transfer zone between 5% and 95% Cs breakthrough provides a more realistic estimation of the whole transfer zone. In both cases, the 50% Cs breakthrough point is the inflection point around which the transition zone pivots. The BV interval from 5% to 50% Cs breakthrough was calculated and then doubled to account for the identical range from 50% to 95% Cs breakthrough. A similar approach was used for the 20% to 50% Cs breakthrough range.

Table 5.3. CST Cs Breakthrough and Transition Zone Summary in the Medium Column Tests

		BVs to Breakthrough				Transition Zone, BVs	
Column Test	Flowrate, BV/h	0.1%	5%	20%	50%	20-80% Cs BT[(a)]	5-95% Cs BT[(b)]
Red	1.83	240	470	680	~1000	~640	~1060
Yellow	11.4	27	150	340	800	920	1300
Green	15.0	29	125	300	700	800	1150
Pink, 35 °C	1.93	162	306	430	600	340	588
Purple (Organics)	1.86	210	480	na	na	na	na
White (6.0 M Na)	1.88	200	440	670	~1000	~660	~1120

(a) The transition zone was estimated by doubling the BVs processed between 20% and 80% Cs breakthrough to compare with previously reported data (Fiskum et al. 2018a).

(b) The transition zone was estimated by doubling the BVs processed between 5% Cs breakthrough (contract limit) to 50% breakthrough.

BT = breakthrough

na = not applicable

The Red column process condition at 1.83 BV/h was similar to the Fiskum et al. (2018a) Blue lead column processed at 1.99 BV/h. In both cases, the 20% to 80% Cs breakthrough transition zone was 640 BVs. However, the Fiskum et al. (2018a) Blue column only loaded 129 BVs to the contract limit, significantly reduced from that of the Red column (240 BVs), indicating lower Cs load behavior for the previously tested production batch.

The Red column results were used as a reference comparison point for other test variables. The following effects were inferred from these test results.

1. Rapid flowrates (Yellow and Green columns), targeting superficial velocities similar to those of the tall column tests, showed earlier Cs breakthroughs with respect to the contract limit (~28 BVs vs. 240 BVs) and 100 to 300 BVs longer transition zones.

2. The 35 °C test (Pink column) resulted in 30% reduced BVs to contract limit, 40% reduced BVs to 50% Cs breakthrough, and 32% decreased Cs load behavior. The transition zone was nearly half that of the reference point.

3. The 5.6 M Na simulant with added organics test (Purple column) feed reduced the interpolated BVs to contract limit by only 12%. Except for this offset, the general load curve tracked with that of the reference point, indicating similar Cs load performance. However, the column plugging negated any other comparisons.

4. Increasing the Na concentration to 6.0 M (White column) reduced the BVs to contract limit by 17% with no obvious effect on the BVs to 20% and 50% Cs breakthrough. The increased Na molarity might have had a slight effect (~5%) on lengthening the transition zone; however, this difference cannot be discounted from normal test variability.

6.0 Full Height Column Test Results

The Cs load behavior was evaluated at two different flowrates and superficial velocities with the 5.6 M Na simulant in the full height column format: 1.30 BV/h and 4.88 cm/min for the Orange column test and 1.82 BV/h and 6.94 cm/min for the Blue column test. This section discusses the Cs load, feed displacement, water rinse and Cs mass balance results for the two tests. Raw data are provided in Appendix C.

6.1 Cs Load, Feed Displacement, and Water Rinse Results

The Cs load profiles for Orange and Blue column testing are shown in Figure 6.1 and Figure 6.2, respectively. The Cs breakthrough is plotted on a linear-linear plot and a probability-log plot, where ^{137}Cs concentration (C) is normalized to the feed concentration (C_0). The C_0 value for ^{137}Cs was determined to be ~1 µCi/mL. Combined columns 1 and 2 represent the lead column and combined columns 3 and 4 represent the lag column. Data are shown for all four column segments.

The initial Cs breakthroughs from Orange and Blue columns 1 manifested at the first data collection point (8 and 11 BVs) at 0.02 % C/C_0, an order of magnitude above the detection limit corresponding to ~0.002 % C/C_0. Thus, a small amount of Cs leaked through column 1 immediately. Initial samples collected from the Blue column 2 (lead column) and column 3 each had high initial ^{137}Cs concentrations. These values were attributed to cross contamination from residual ^{137}Cs in the valve effluent ports associated with the Orange column testing (conducted in the same apparatus, before Blue column testing) and should be discounted as artifacts.

After processing 318 BVs in the Blue column test, the pump head started failing, manifested by a drop in the flowrate from 1.9 to 1.7 BV/h. The flow was stopped at 466 BVs as pump head deterioration increased. The system remained stagnant for 27 h (Sunday to Monday) before the FMI pump head was replaced and flow resumed. The extra contact time during the 27-h stop flow condition appears in Figure 6.2 as a vertical black dashed line; pointers to the slowed flowrates are also indicated (see also Figure 3.9 for flowrate vs. BV processed).

The Cs load profiles were responsive to each low-flow and stopflow condition. As the flowrate decreased, the Cs effluent concentration also decreased. Following the stopflow condition, a marked bending of the load curve or decrease in the Cs effluent concentration was also evident. The ensuing Cs breakthrough trajectories (see probability-log plots) following these low-flow and stopflow conditions shifted right. These results indicated that CST was pore diffusion limited; allowing additional contact time resulted in enhanced Cs ion exchange. Hamm et al. (2001) also has defined CST to be pore diffusion limited. It is noted that the low flow and stop flow conditions may improve Cs loading onto CST, however, in a full-scale column with actual tank waste, there may be insufficient flow to remove hydrogen gas and heat.

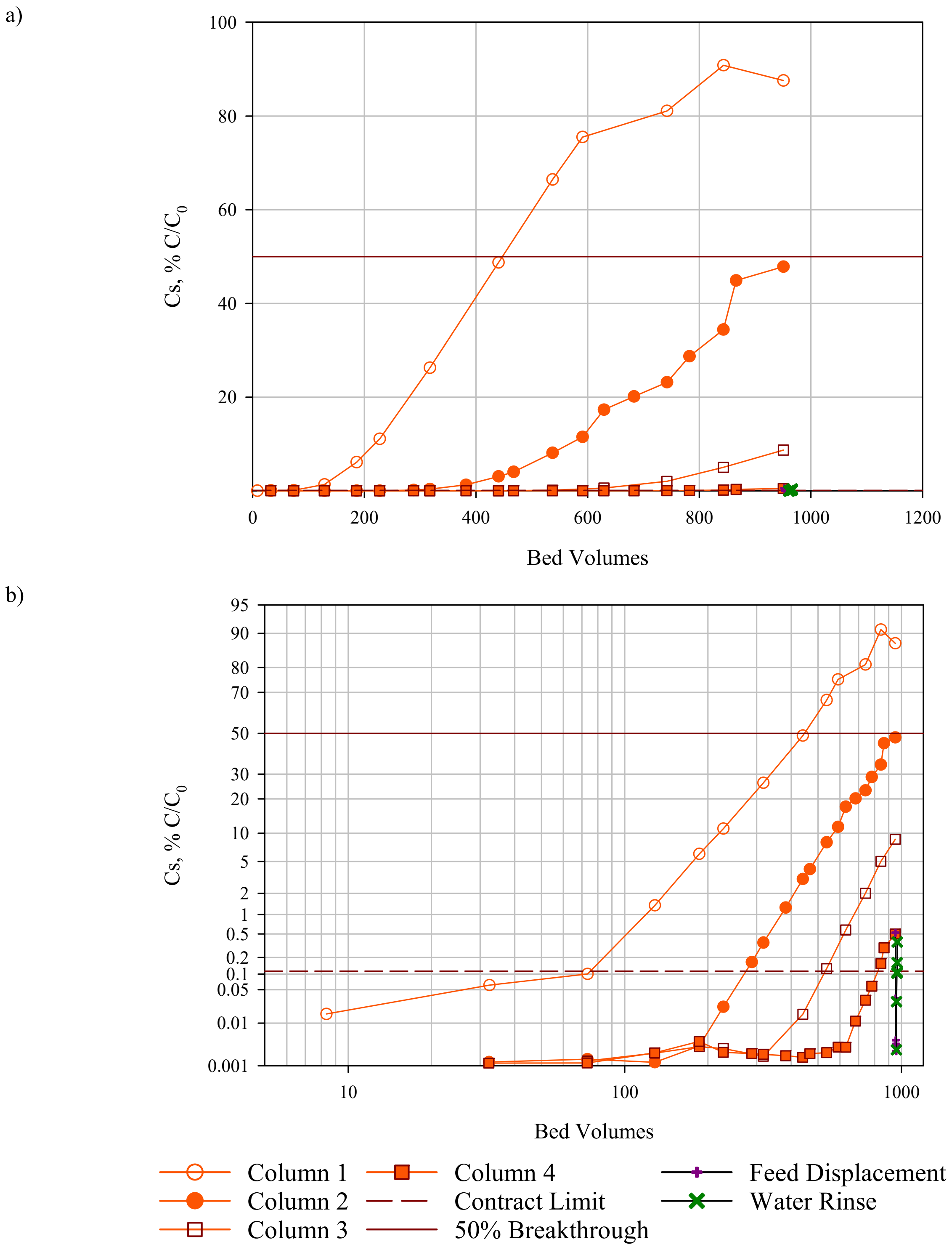


Figure 6.1. Orange Column Test Cs Load Profiles a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant 20 °C, Flowrate 1.30 BV/h, Superficial Velocity 4.88 cm/min

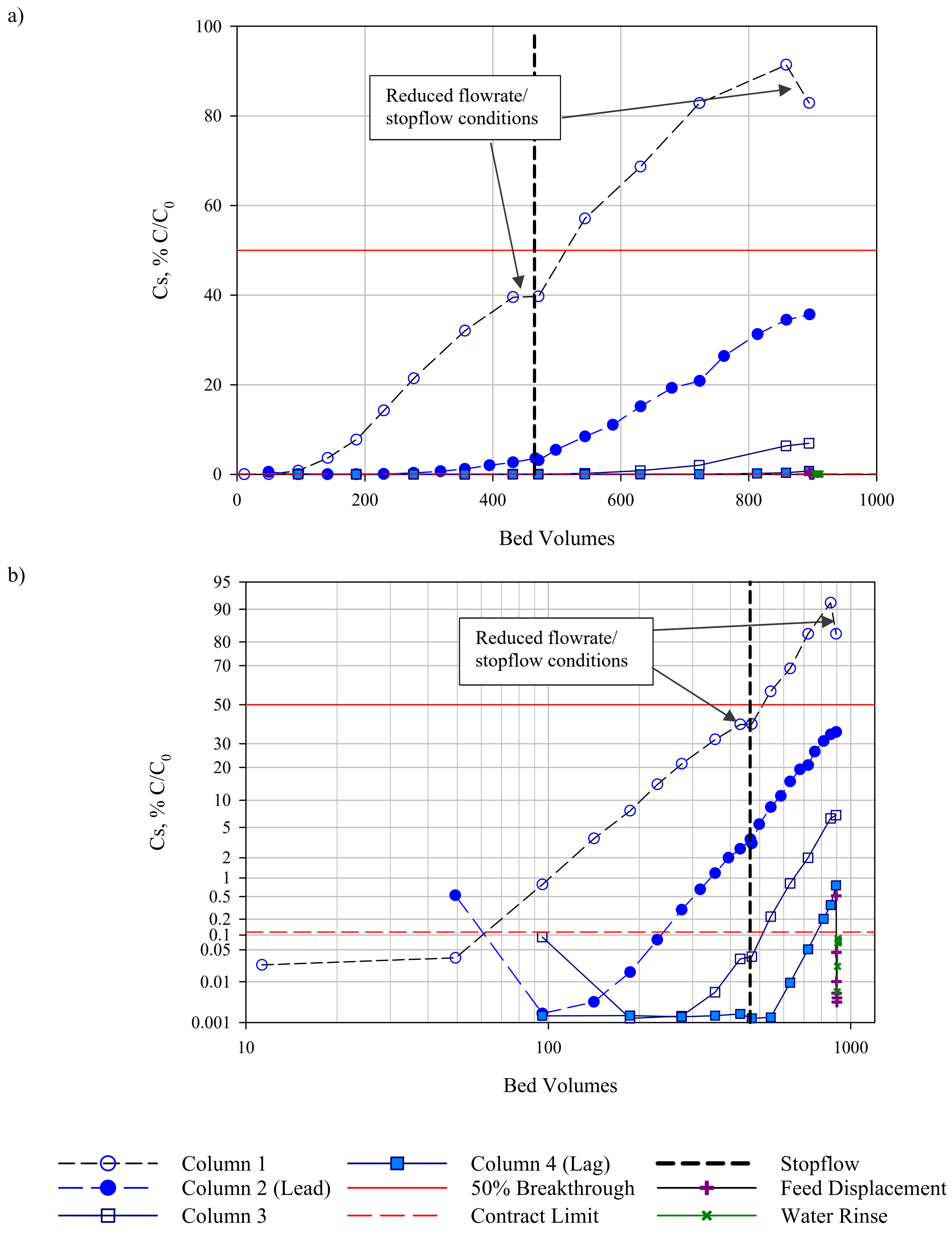


Figure 6.2. Blue Column Test Cs Load Profiles a) Linear-Linear Plot; b) Probability-Log Plot

Figure notes: 5.6 M Na Simulant 20 °C, Flowrate 1.82 BV/h, Superficial Velocity 6.94 cm/min

Table 6.1 summarizes salient features (onset of Cs breakthrough, contract limit breakthrough, and 50% breakthrough) of the Orange and Blue column tests. Extrapolated values are provided where the measured breakthrough was close to the designated limit and the extrapolation was relatively short; extrapolations were conducted visually and the uncertainties of the extrapolated values are not known. Direct comparison between the Orange and Blue column tests was confounded by the Blue column low-flow and stopflow conditions where enhanced Cs exchange onto CST occurred. The best head-to-head comparison between the column tests is associated with the lead column contract limit Cs breakthrough, before the low-flow/stopflow conditions occurred; the lower flowrate Orange column test was 40 BVs better (delayed) than that of the Blue column test. In contrast, the 50% Cs breakthrough for the lead Orange column was ~960 BVs and that of the Blue column was higher at ~1050 BVs (extrapolated). Slowing and/or stopping the feed flowrate improved the Cs ion exchange performance.

Table 6.1. Tall Column Tests Breakthrough Points Summary

	BVs to Cs Breakthrough					
	Orange Column Test (1.30 BV/h)			Blue Column Test (1.82 BV/h)		
Column	Onset	Contract Limit	50%	Onset	Contract Limit	50%
1	≤8	75	450	≤11	66	510[(b)]
2 (Lead)	185	280	~960[(a)]	140	240	~1050[(a,b)]
3	320	530	nm	300	520[(b)]	nm
4 (Lag)	630	820	nm	620[(b)]	770[(b)]	nm

(a) Extrapolated value

(b) Value affected (delayed BV) by the low-flow and stopflow conditions; see text for further discussion.

nm = not measured, not extrapolated

Following the Orange column test simulant load, 7 BVs of 0.1 M NaOH solution were passed through the system as a feed displacement. The first sample off the lag column, taken after 1 BV was processed, continued the Cs breakthrough profile, as was expected because simulant was still in the system. The Cs concentration dropped significantly in the remaining feed displacement samples (about two orders of magnitude) below the contract limit. The DI water rinse Cs concentrations started at the same concentration as the last feed displacement sample and then gradually increased nearly two orders of magnitude above the feed displacement Cs concentration and eventually approached the contract limit over the 8 BVs of DI water processed. The last two samples, collected after the column had gone dry, exceeded the contract limit and solids were found in each of them. The increasing Cs concentration in the DI water effluent indicated that some Cs had not remained bound to the CST in the presence of DI water or that small CST particles containing Cs escaped the system. The Blue column test feed displacement and water rinse results were similar to those of the Orange column test.

The Blue column DI water rinse samples were filtered and the filtrates and filtered solids were measured for ^{137}Cs content in an effort to better understand the nature of the increased ^{137}Cs content. Table 6.2 summarizes the results of the initial ^{137}Cs concentration, the filtrate ^{137}Cs concentration, and the filtered solids ^{137}Cs concentration normalized to the filtered sample volume. The percent ^{137}Cs recoveries found in the filtrate and filtered solids, relative to the unfiltered samples, are also provided. The filtered solids from the first sample (2.1 BVs) appeared anomalously high (198% recovery) and the filtrate sample result had a very high counting uncertainty such that a calculated recovery was not reasonable to perform. The 3.8-BV sample showed no measurable Cs in the filtered solids. The last three samples indicated an even split between ^{137}Cs present in the aqueous phase and the solids phase. Solids were barely visible in these samples; those that were observed were very fine and wispy. The increased Cs content in the last three water rinse samples was present as very fine solids and in filtrate that passed through a 0.2-micron filter. In contrast, Walker et al. (1999) found that all ^{137}Cs could be removed from selected effluent samples (of the Savannah River Site Tank 44F waste processed through CST) when passed through a 0.2-micron filter indicating that fines were carrying Cs.

Table 6.2. Cs Fractionation in Blue Column Filtered DI Water Rinse Samples

BV Processed	Initial ^{137}Cs, µCi/mL	Filtrate ^{137}Cs, µCi/mL	% Recovered	Filter Solids ^{137}Cs, (Normalized) µCi/mL	% Recovered
2.1	7.44E-8	[3.2E-8][(a)]	--[(a)]	1.48E-7	198%
3.8	2.86E-7	2.23E-7	78%	<1.70E-8	<6%
5.5	8.86E-7	4.71E-7	53%	5.18E-7	58%
7.1	1.09E-6	4.77E-7	44%	4.86E-7	45%
9.1	1.00E-6	4.08E-7	41%	4.80E-7	48%

(a) The sample result had a 48% count uncertainty; recovery could not be calculated.

The back pressures for both the Orange and Blue column test systems were recorded for information only (FIO) from the on-line pressure gage 1 (dial indicator). The nominal back pressures for both 4-column systems, including the final solution lift to the effluent collection drum, were nominally 8 to 12 psig between pump actions; the back pressure increased to nominally 18 to 21 psig when the pump piston pushed solution into the system. The back pressures increased by a few psig as processing continued over the 526- to 741-h processing times. The pressure gage readings were also recorded during the sampling events from each of the four columns to get a sense of the incremental pressure drops. Table 6.3 summarizes the results and Figure 6.3 shows the linear relationship of the back pressure as a function of the CST bed depth. At a depth of up to 86 cm, no measurable back pressure is expected in the full PSD CST at a linear flow velocity of up to 6.94 cm/min. The cause of the pressure increase is indeterminate. Potential causes include fouling of the bed by solids suspended in the feed solution, precipitation of solids from the feed solution upon contact with the CST, or formation of fines in the CST bed during processing. However, the back-pressure data in Table 6.3 suggest that the increase in pressure drop was not associated with the feed solution, as there was negligible increase in the pressure drop across the first column (column 1), where presumably feed solids would be deposited. Likewise, any solids formation from precipitation from the feed would likely be associated with column 1 as well. Thus, the likely source of increase pressure drop is associated with fines production during the test, resulting in reduced hydraulic permeability.

Table 6.3. Back Pressure Ranges at Each Column Sample Port (FIO)

Test ID	Column 1 (psig)	Column 2 (psig)	Column 3 (psig)	Column 4 (psig)
Orange	0-0.5	1-5	5-10	8-12
Blue	0-2	4-5	9-10	12-14

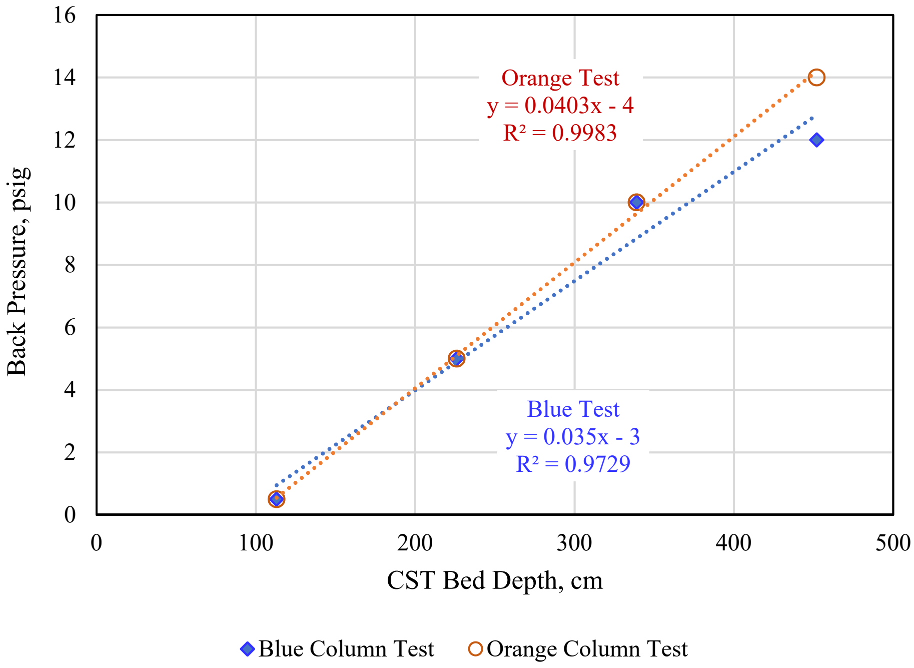


Figure 6.3. Back Pressure as a Function of CST Bed Depth, Unsieved CST (FIO)

6.2 ^{137}Cs Activity Balance

Table 6.4 and Table 6.5 provide the Cs-decontaminated effluent composite results in terms of ^{137}Cs concentration and overall DF for the Orange and Blue tests. A DF of 877 was needed to meet the waste acceptance criteria. The effluents met the DF limit through 770 BVs and 760 BVs processed, Orange and Blue column tests, respectively.

Table 6.4. Orange Effluent Composites ^{137}Cs Content and Decontamination Factor

Effluent Container	^{137}Cs, µCi/mL	Decontamination Factor
Effluent-1 (0-127 BVs)	<2.3E-8	>4.2E+4
Effluent-2 (128-219 BVs)	<2.1E-8	>4.6E+4
Effluent-3 (220-340 BVs)	<1.8E-8	>5.2E+4
Effluent-4 (341-434 BVs)	<2.1E-8	>4.5E+4
Effluent-5 (435-558 BVs)	<1.8E-8	>5.4E+4
Effluent-6 (559-648 BVs)	<2.3E-8	>4.2E+4
Effluent-7 (649-770 BVs)	2.07E-07	4590
Effluent-8 (771-861 BVs)	1.12E-06	847
Effluent-9 (862-973 BVs) plus feed displacement and water rinse	3.13E-06	304

Table 6.5. Blue Effluent Composites ^{137}Cs Content and Decontamination Factor

Effluent Container	^{137}Cs, µCi/mL	Decontamination Factor
Effluent-1 (0-95 BVs)	<2.6E-8	>5.0E+4
Effluent-2 (96-230 BVs)	<2.2E-8	>5.7E+4
Effluent-3 (231-317 BVs)	<2.1E-8	>6.0E+4
Effluent-4 (318-395 BVs)	<2.2E-8	>5.9E+4
Effluent-5 (396-465 BVs)	<2.2E-8	>5.8E+4
Effluent-6 (466-543 BVs)	<1.9E-8	>6.7E+4
Effluent-7 (544-630 BVs)	5.78E-08	22,200
Effluent-8 (631-760 BVs)	4.83E-07	2660
Effluent-9 (761-858 BVs)	2.72E-06	472
Effluent-10 (859-893 BVs) and feed displacement and water rinse	4.08E-06	314

The ^{137}Cs fractionation between the effluent composites, load samples, and lead and lag columns relative to the input ^{137}Cs was determined. The quantities of ^{137}Cs loaded onto the lead and lag columns were determined by integrating the product of ^{137}Cs concentration measured in the associated samples and the process volume between samples. Table 6.6 and Table 6.7 summarize the ^{137}Cs fractions found in the various effluents as well as the calculated lead and lag column ^{137}Cs loading for Orange and Blue tests, respectively. As expected, most of the ^{137}Cs was adsorbed onto the lead column. The Blue column test, despite the higher intended flowrate, resulted in a higher Cs loading than the Orange column test. The increased Cs loading was a direct consequence of the low-flow and stopflow conditions associated with the Blue column test and concomitant enhanced Cs ion exchange onto the CST.

Table 6.6. ^{137}Cs Activity Balance for Orange Column Test

Input	mCi	%
Feed sample	1.04	100
Output		
Effluent-1 (0-127 BVs)	<3.3E-06	<3.2E-04
Effluent-2 (128-219 BVs)	<2.1E-06	<2.1E-04
Effluent-3 (220-340 BVs)	<2.6E-06	<2.5E-04
Effluent-4 (341-434 BVs)	<2.3E-06	<2.2E-04
Effluent-5 (435-558 BVs)	<2.5E-06	<2.4E-04
Effluent-6 (559-648 BVs)	<2.3E-06	<2.3E-04
Effluent-7 (649-770 BVs)	2.89E-05	2.79E-03
Effluent-8 (771-861 BVs)	1.18E-04	1.14E-02
Effluent-9 (862-973 BVs) and feed displacement and water rinse	3.60E-04	3.48E-02
Load samples	7.46E-04	7.20E-02
Total ^{137}Cs Column Loading		
Lead column Cs loading	0.907	87.5
Lag column Cs loading	0.129	12.4
Activity balance	1.04	100%

Table 6.7. ^{137}Cs Activity Balance for Blue Column Test

Input	μCi	%
Feed sample	1.33	100
Output		
Effluent-1 (0-95 BVs)	<2.8E-06	<2.1E-04
Effluent-2 (96-229 BVs)	<3.5E-06	<2.6E-04
Effluent-3 (230-317 BVs)	<2.2E-06	<1.6E-04
Effluent-4 (318-394 BVs)	<1.9E-06	<1.5E-04
Effluent-5 (395-465 BVs)	<1.8E-06	<1.3E-04
Effluent-6 (466-542 BVs)	<1.7E-06	<1.3E-04
Effluent-7 (543-629 BVs)	5.76E-06	4.34E-04
Effluent-8 (630-759 BVs)	7.23E-05	5.44E-03
Effluent-9 (760-857 BVs)	3.06E-04	2.30E-02
Effluent-10 (858-892 BVs) and feed displacement and water rinse	2.42E-04	1.82E-02
Load samples	1.01E-03	7.57E-02
Total ^{137}Cs Column Loading		
Lead column Cs loading	1.20	90.3
Lag column Cs loading (calculated)	0.13	9.6
Activity balance	1.33	100%

The total Cs loaded per gram CST was calculated from the total Cs loaded onto the lead column (which was not assumed to be fully saturated under these load conditions) and the dry CST mass loaded into the lead column according to Eq. (6.1).

$$\frac{A_{Cs} \times CF}{M} = C \tag{6.1}$$

where A_{Cs} = activity of ^{137}Cs, μCi on the lead column

CF = conversion factor, μg Cs/μCi ^{137}Cs

M = mass of dry CST (592 g)

C = Cs loading, mg Cs/g CST

A total of 6.77 mg Cs/g CST (0.0509 moles Cs/g CST) was loaded on the Orange lead column after processing to 47.9% breakthrough. A total of 7.27 mg Cs/g CST (0.0547 moles Cs/g CST) was loaded on the Blue lead column after processing to 35.7% breakthrough. Contrary to expectation that increased flowrate will result in decreased Cs exchange, the Blue column (1.82 BV/h) outperformed the Orange column (1.30 BV/h) with respect to total Cs loading. Again, the enhanced Blue column Cs loading performance was attributed directly to the low-flow and stopflow conditions of the test.

Table 6.8 shows BVs processed to reach 0.1% (contract limit), 5%, 20%, 50% Cs breakthrough and estimated mass transfer zones to compare Cs exchange performance. Evaluation of data at BVs to 20% Cs breakthrough allows for comparison to the medium column testing as well as previously reported data (Fiskum et al. 2018a). The 50% breakthrough point is the inflection point around which the transition zone pivots. The BV interval from 5% to 50% Cs breakthrough was calculated and then doubled to account for the identical range from 50% to 95% Cs breakthrough. A similar approach was used for the 20% to 50% Cs breakthrough range so that direct comparisons to medium column and previously reported data (Fiskum et al. 2018a) can be made.

Table 6.8. Lead Column CST Cs Breakthrough and Transition Zone Summary in the Full Height Column Tests

		BVs to Breakthrough				Transition Zone, BVs	
Column Test	Flowrate, BV/h	0.1% (Contract Limit)	5%	20%	50%	20-80% Cs Breakthrough(a)	5 to 95% Cs Breakthrough(b)
Orange	1.30	280	484	680	~960(c)	~560(c)	~950(c)
Blue	1.82	240	492(d)	700(d)	~1050(c,d)	~700(d)	1120(d)

(a) The transition zone was estimated by doubling the BVs processed between 20% and 50% Cs breakthrough to compare with previously reported data (Fiskum et al. 2018a).

(b) The transition zone was estimated by doubling the BVs processed between 5% Cs breakthrough (contract limit) to 50% breakthrough.

(c) Extrapolated value.

(d) Affected by low-flow and stopflow conditions.

6.2.1 Cesium Distribution on Orange Column Test CST Beds

Figure 6.4 shows a plot of the measured ^{137}Cs net peak count rate as a function of position in a single "effective" column that is the combined length of the four individual columns. Individual raw column data are provided in Appendix D. ^{137}Cs was detected in all the scans above the background condition. Activity upticks were detected 13 cm from the top of column 2 and at the top of column 3 relative to the bottom of columns 1 and 2, respectively. Genesis of these upticks is not understood. The Cs mass transfer zone can be estimated from 13 cm (the top of column 1) through at least 350 cm (into the top of column 4) assuming that the top of column 1 from 0 to 13 cm deep represents the fully loaded CST.

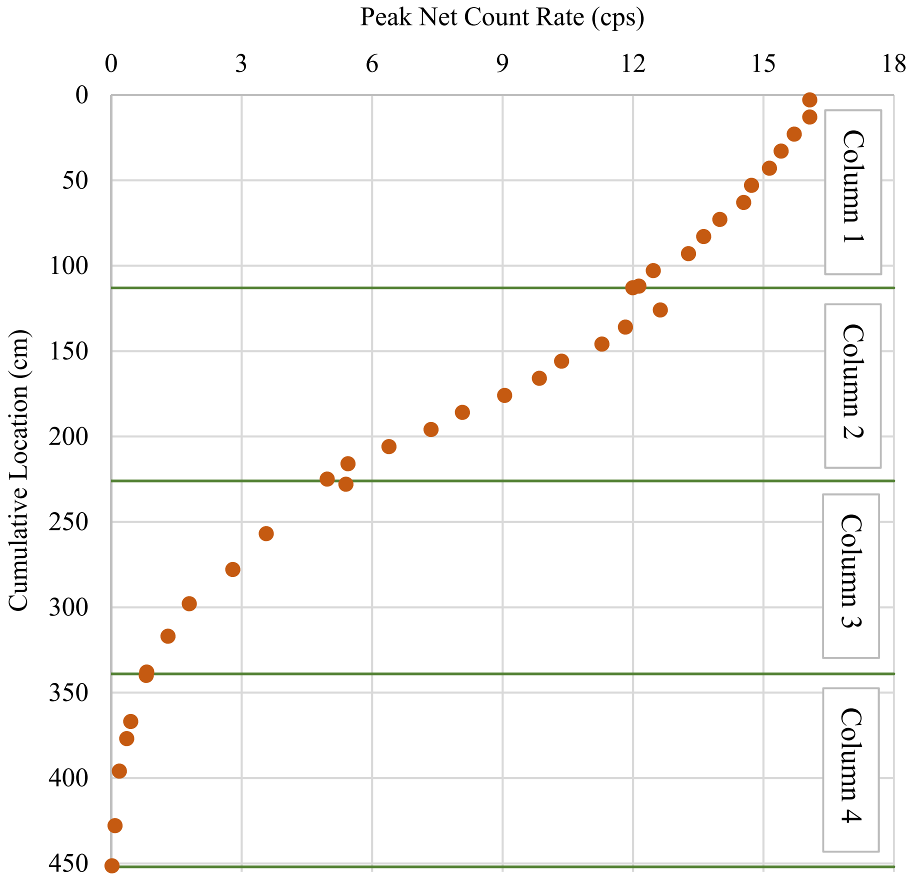


Figure 6.4. ^{137}Cs Data for the Orange Columns 1-4 Plotted as a Single Effective Column

7.0 Medium and Full Height Column Result Comparisons

This section compares results of the medium (12% of full height) and the full height columns to differentiate the effect of residence time (in terms of BV/h) from superficial velocity (cm/min) on Cs ion exchange performance. It also discusses efficacy of using the medium scale columns to predict full height column Cs exchange performance.

7.1 Flowrate Effect

The effect of flowrate on the BVs required to reach the contract limit was examined, in part, with the plurality of Orange and Blue test columns. The flowrates through the following systems of columns were examined:

1. Column 1
2. Column 1 – 2 combined
3. Column 1 – 3 combined
4. Column 1 – 4 combined

Thus, for a given superficial velocity, the flow through column 1 in terms of BV/h was twice the flowrate of the column 1-2 combined (i.e., the lead column). Similarly, the flowrate in terms of BV/h dropped for the columns 1-3 combination and dropped again for the columns 1-4 combination. Similarly, the BVs processed to contract limit was normalized relative to the redefined systems. Column 1 was half the volume of the lead column (which consists of columns 1 and 2 combined) and thus the BVs processed twice that shown in Figure 6.1 and Figure 6.2. Similar adjustments were made with respect to columns 3 and 4. Table 7.1 summarizes the column system description, CST BV (liters), superficial velocity (cm/min), effective flowrate (BV/h) for the system, and BVs processed to reach the contract limit. The Red, Yellow, and Green medium column test data are also shown as they were included in the system comparisons.

Table 7.1. Column System Performance

System ID	CST BV, L	Superficial Velocity, cm/min	Flowrate, BV/h	Normalized BVs to Contract Limit
Orange 1	0.573	4.88	2.58	150
Orange 1-2	1.15	4.88	1.30	280
Orange 1-3	1.72	4.88	0.87	353
Orange 1-4	2.29	4.88	0.65	410
Blue 1	0.575	6.94	3.64	132
Blue 1-2	1.15	6.94	1.82	240
Blue 1-3	1.73	6.94	1.21	347[a]
Blue 1-4	2.30	6.94	0.91	385[a]
Red	0.044	0.82	1.83	240
Yellow	0.044	5.13	11.4	27
Green	0.044	6.76	15.0	29

(a) Value is confounded by the stop-flow condition.

The simplest approach to conduct medium and full height column comparisons was to match the relevant process condition. The medium and full height column paired conditions were as follows (where the medium column was effectively considered the lead column). The paired test superficial velocities did not exactly match, but they were considered close enough to make valid comparisons.

1. Red and Blue 1-2 (lead column) matched residence times (1.83 and 1.82 BV/h, respectively); superficial velocities differed (0.82 and 6.94 cm/min, respectively)

2. Yellow and Orange 1-2 (lead column) similar superficial velocities (5.13 and 4.88 cm/min, respectively); residence times differed (11.4 and 1.81 BV/h, respectively)

3. Green and Blue 1-2 (lead column) matched superficial velocities (6.76 and 6.90 cm/min, respectively); residence times differed (15.0 and 1.81 BV/h, respectively)

Figure 7.1 shows the Cs load profiles for condition 1, matched residence times (Red and Blue columns 1-2 systems). They are virtually identical from 0 to ~400 BVs. They diverged where the Blue column experienced a flowrate reduction followed by a stopflow condition. Once the flowrate was re-established at ~471 BVs, the load curves were only slightly offset a few BVs. After the stopflow condition, the Cs load curves tracking was quickly reestablished despite the extra Cs loading accomplished with added contact time during low-flow and stopflow conditions. The close tracking of the medium and full height scales indicated that the residence time (pore diffusion limitation), not the superficial velocity (film diffusion limitation), dominated Cs exchange into the CST.

Figure 7.2 and Figure 7.3 compare the effects of constant superficial velocity (and concomitant variation in residence time) at the two process scales. Figure 7.2 compares Orange and Yellow columns (condition 2); Figure 7.3 compares Blue and Green columns (condition 3). In both cases, the medium column tests poorly modeled the full height column Cs breakthrough performance. These results further demonstrated that fluid residence time with the CST bed drives the Cs removal efficiency.

Film diffusion, which is minimized at high superficial velocities, was not a controlling effect on the Cs ion exchange performance. Increased residence time allows more time for Cs diffusion into the CST pores. The medium (12% height) column scale results accurately predicted the full height column results (condition 1), despite processing at different superficial velocities (0.82 cm/min for Red and 6.9 cm/min for Blue).

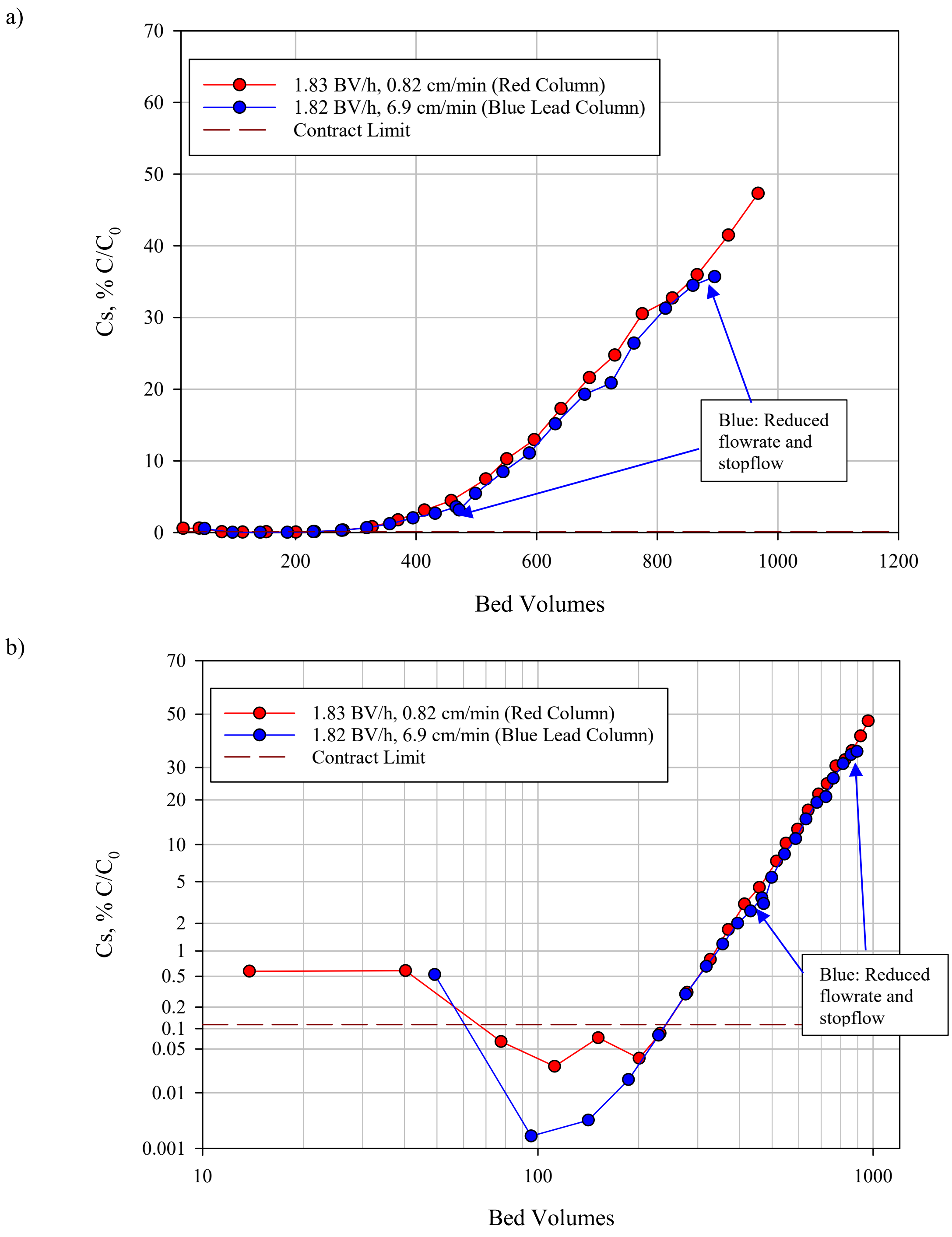


Figure 7.1. Cs Load Profiles at Two Different Linear Velocities and Constant Residence Time

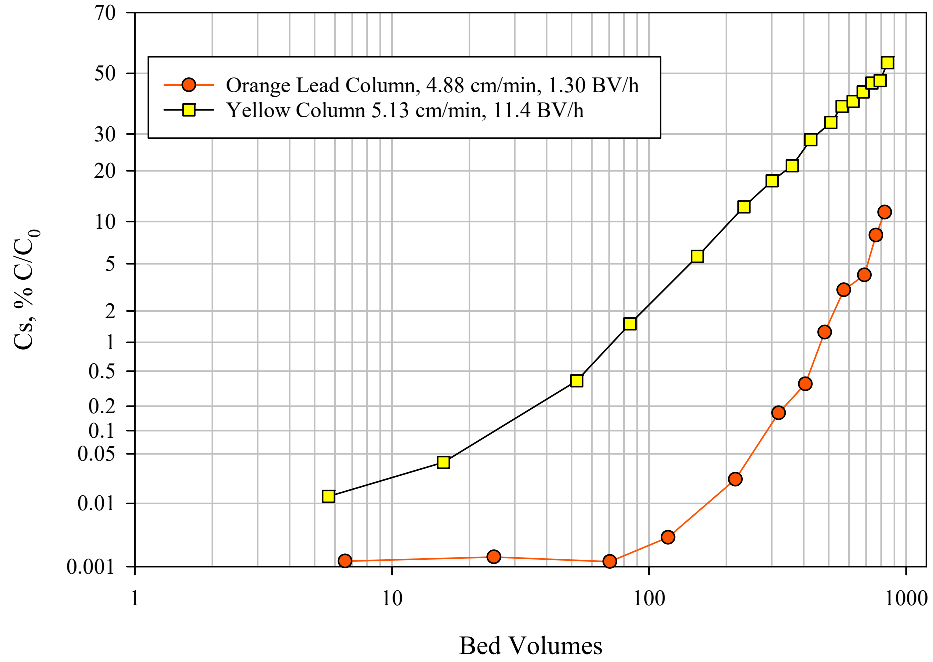


Figure 7.2. Cs Load Profiles at ~5.0 cm/min Superficial Velocity but Different Residence Times

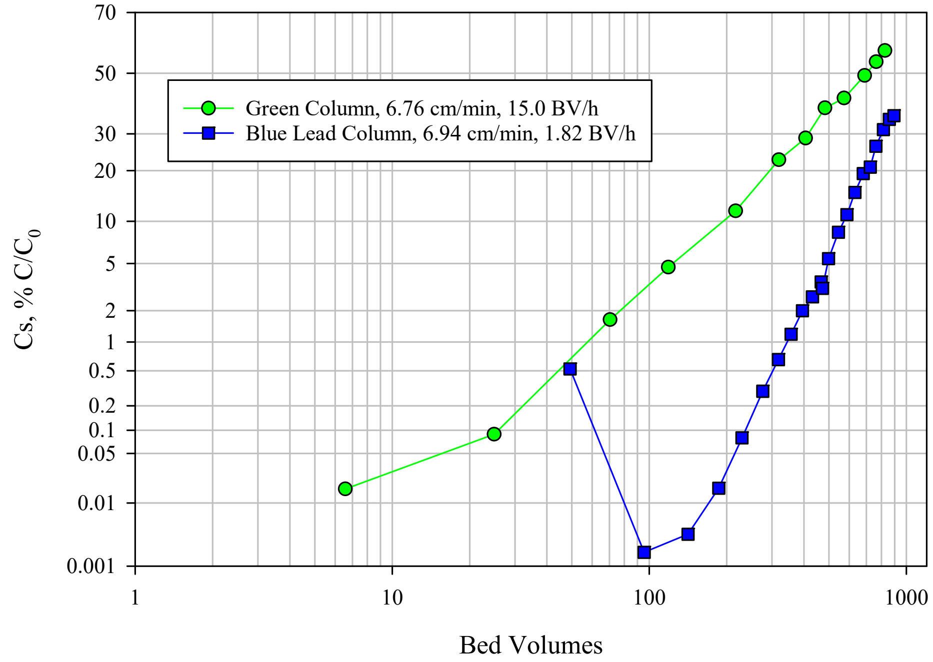


Figure 7.3. Cs Load Profiles at ~6.8 cm/min Superficial Velocity and Different Residence Times

Figure 7.4 shows the relationship of the volume processed to reach contract limit as a function of flowrate including the Orange and Blue full height column data (four systems per test as shown in Table 7.1) and Red, Yellow, and Green medium column data. In this case, the combined data set was fit to a power curve. (A logarithmic curve fit did not fit this data set.) The data set provided by Fiskum et al. (2018a) is also provided for comparison and refitted to a power curve. The Orange and Blue column data are circled in orange and blue, respectively; the data from the medium column tests are circled in green. This figure clearly shows that slowing the flowrate will improve performance of the Cs loading onto the CST. As evidenced by the Orange test (4-column composite), 410 BVs may be processed at a flowrate of 0.65 BV/h before exceeding the contract limit from a single column.

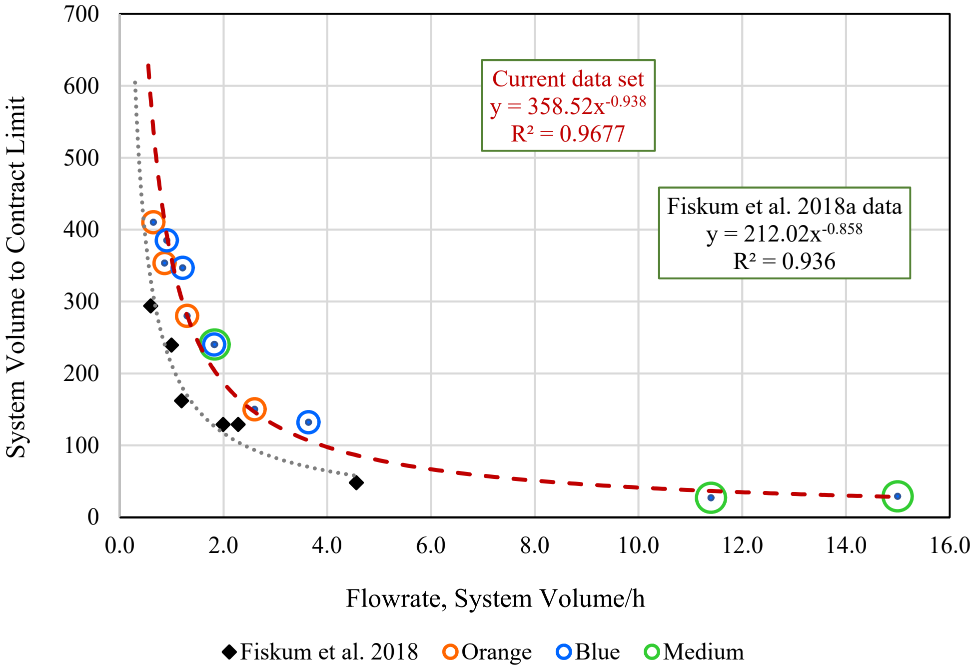


Figure 7.4. Volume Processed to Reach Contract Limit vs. Flowrate

The different curve fits for the Fiskum et al. (2018a) data and from the current data set were attributed primarily to the performance difference of the two lots of CST. The effective Cs loading of CST Lot 8056202-999 was higher than that of 2081000057 (6.95 vs. 6.38, mg Cs/g CST, respectively, see Section 5.2). It is also possible that the smaller CST bed size used by Fiskum et al. (2018a) may have had some negative influence on Cs loading. The Fiskum et al. data were collected with 10-mL CST beds as opposed to the 44-mL CST medium column beds of the current study (same column inner diameter). It is noted that the Red medium and Blue full height column test results matched well. There was also a substantial CST PSD difference between the tests where the smaller column used smaller CST PSD (<25 mesh). Thus, it is possible that another, smaller CST sieve cut may be applicable to the smaller 10-mL BV in order to again match performance to that of the full height column.

7.2 CST Cs Loading

The Cs loading, measured on the Orange and Blue lead columns, compared generally well for the full height and medium column tests; Table 7.2 provides the measured Cs capacities. The Cs loading decreased with decreasing BVs processed. Despite this trend, the standard deviation of the Cs capacities was only 2.6%, indicating that all three lead columns were nearly equally loaded. This again indicated that the medium scale testing with <25 mesh CST in the 27-mL CST bed duplicated the full height column test well.

Table 7.2. Full and Medium Height Column Test Cs Capacities

Column ID	Flowrate, BV/h	Process Volume, BVs	Cs Loading, mg/g CST
Red (medium)	1.83	967	6.95
Orange (full)	1.30	951	6.77
Blue (full)	1.82	895	6.60

8.0 Conclusions

Cesium ion exchange batch contact and column testing with CST was conducted to assess Cs exchange performance. Batch contact testing was conducted to assess exchange kinetics at three different feed conditions and two CST PSDs. The column testing was conducted at two column sizes, medium (12% full height) and full height, to assess Cs load performance behavior. The medium scale testing was conducted in a single column format examining six different process conditions. The full height testing was conducted with a series of four half-height columns examining feed processing at two different flowrates in a lead-lag configuration. The following conclusions have been established.

8.1 CST Physical Characteristics

The CST physical properties of IONSIV R9140-B, Lot 8056202-999 were characterized and are as follows:

- The <25 mesh (ASTM E11) sieve fraction represented 59 wt% of the as-received material. The sieved fraction was loaded into the medium columns and the full size PSD (unsieved) CST was loaded into the full height columns.
- The CST d50 of the <25 mesh fraction was 588 μm and the d50 of the full PSD CST was 708 μm.
- The full PSD CST particle density averaged 3.33 g/mL <25 mesh CST particle density averaged 3.77 g/mL.
- The dry mass basis of CST was based on measurement to 100 °C. An additional mass correction of ~4.5% applies if the dry mass is taken to 200 °C.
- The dry CST bed densities were 1.01 g/mL for both full size PSD and <25 mesh CST. The CST bed void fractions were 67.6 and 66.2% for the full size PSD and <25 mesh CST, respectively.

8.2 Batch Contact Testing

The Cs initially loaded rapidly onto the CST exchanger with ~80% of the available Cs mass loaded within ~20 h. Evaluation of the K_d values showed that residual Cs continued to be removed from solution up to 123-h contact time. Testing beyond 123 h was not conducted; therefore, it was not clear if equilibrium K_d was achieved. The Cs kinetic exchange performance differences between the test variables and the <25 mesh CST in 5.6 M Na simulant were minimal.

- The 6.0 M Na simulant solution showed initially higher Cs exchange performance than the 5.6 M Na simulant; after 5-h contact time, the K_d values converged. At 123-h contact time, the 6.0 M simulant K_d value was 17% lower than that of the 5.6 M Na simulant. It is noted that the K and hydroxide concentrations, along with the Na concentration, were 7% higher than that of the baseline 5.6 M Na simulant and may also affect Cs loading.
- The 5.6 M Na simulant with added organics Cs exchange performance was indistinguishable from that of the 5.6 M Na simulant. The final difference at 123-h contact time between the two tests was 8%, well within experimental uncertainty.

- The full PSD CST Cs exchange performance trended very similar to that of the <25 mesh PSD CST. However, the final K_d value at 123-h contact time was 12% lower than that of the <25 mesh CST.

8.3 Column Testing

The full height column test evaluated two flowrates (1.30 BV/h and 1.82 BV/h; 4.88 cm/min and 6.94 cm/min, respectively) with 5.6 M Na simulant in a lead-lag column format (each column in two sections). The 1.82 BV/h test incorporated low-flow and stopflow conditions. The following can be concluded from these tests.

- Cs exchange was pore-diffusion limited and therefore slowing the flowrate in terms of BV/h or contact time with CST is imperative to obtain high Cs DFs.
- 820 BVs of 5.6 M Na simulant can be processed through a lead-lag column at 1.30 BV/h to reach the contract limit with a CST Cs loading of 6.77 mg Cs/g CST.
- In-process slowing of the flowrate and stopflow conditions have a slight positive effect on Cs ion exchange into the CST. It should be noted, however, that the low flow and stop flow conditions in a full-scale column with actual tank waste may insufficiently remove hydrogen gas and heat.

The medium column tests evaluated 5.6 M Na simulant, 6.0 M Na simulant, 5.6 M Na simulant with added organics, three process flowrates, and an elevated process temperature to 35 °C using 44-mL, <25 mesh CST beds. The comparative basis column, 5.6 M Na simulant processed at 20 °C at 1.83 BV/h, resulted in 6.95 mg Cs per g CST and 240 BVs processed to the contract limit and ~1000 BVs to 50% Cs breakthrough. The following can be inferred using the 5.6 M Na simulant test as a comparative basis.

- Processing at 35 °C resulted in 31% decreased Cs loading (4.77 mg Cs/g CST) and the contract limit was reached sooner at 162 BVs.
- Processing with 5.6 M Na simulant with added organics did not appreciably alter the Cs load profile. The BVs to contract limit was 210 BVs (12% sooner). Due to in situ precipitation and column plugging, comparable Cs loading onto the CST could not be assessed.
- Processing with 6.0 M Na simulant (with concomitant higher K and hydroxide concentrations) decreased the BVs processed to contract limit at 200 BVs by 17%. However, the 50% Cs breakthrough Cs loading was essentially unchanged at 6.89 mg Cs/g CST.
- Increasing flowrate to match the full height column superficial velocity resulted in markedly poorer Cs load performance with early Cs breakthrough and longer transition zones.

The Cs load profile of the medium test at 5.6 M Na simulant feed processed at 1.83 BV/h matched the Cs load profile of the full height column test. The Cs loading at the equilibrium condition on the medium column test at 6.95 mg Cs/g CST was near the range established by the full height tests (6.77 and 6.60 mg Cs/g CST). These results showed that medium column testing can reasonably predict the full height column test results. Use of the medium columns can help reduce overall test costs relative to full height column testing by reducing the CST BVs to more manageable sizes, which in turn reduces the required simulant feed volumes.

9.0 References

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Appendix A

CST Particle Size Distribution

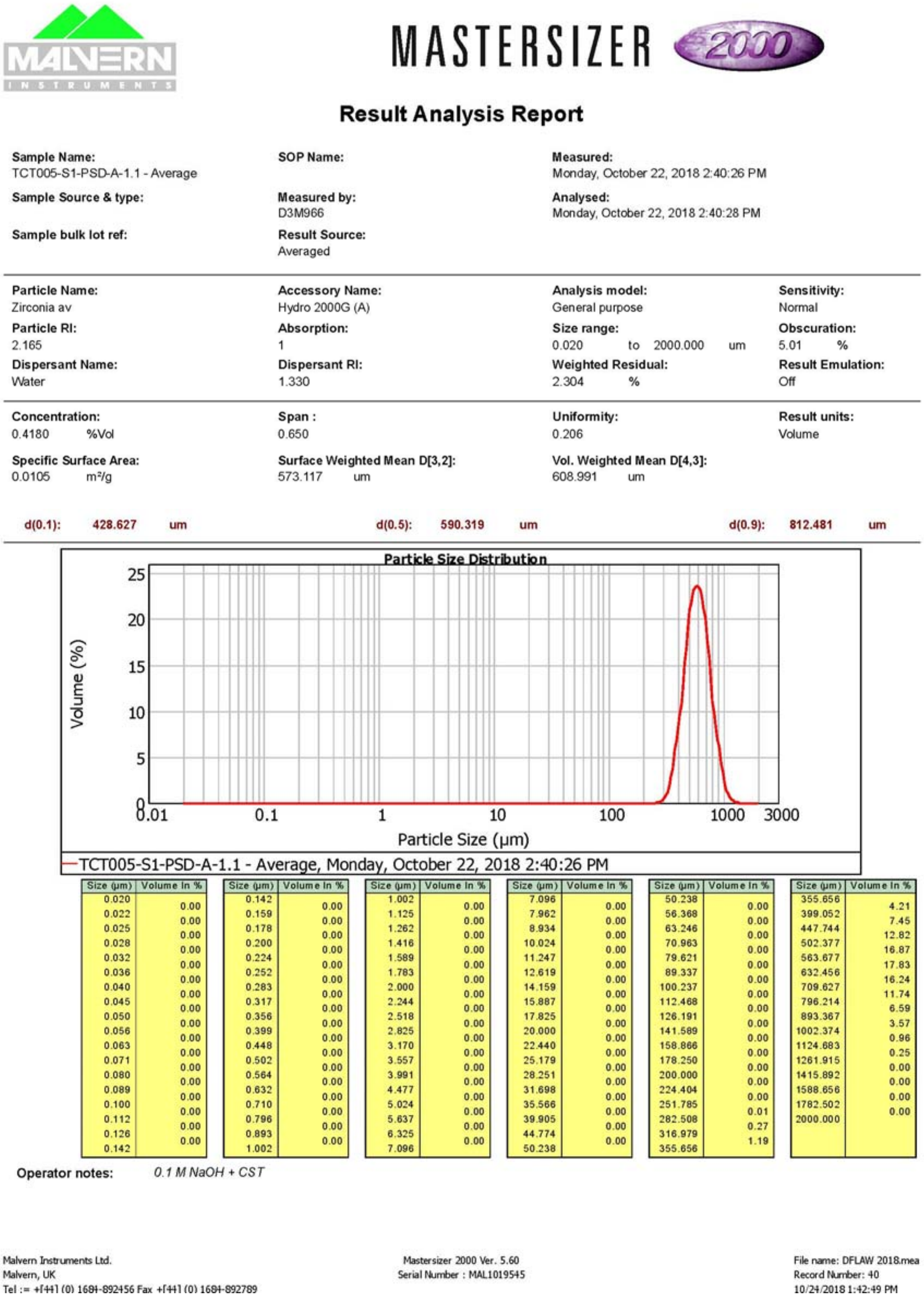
Appendix A

CST Particle Size Distribution

This appendix provides the particle size distribution (PSD) for the <25 mesh, washed crystalline silicotitanate (CST) and as-received, washed CST. Each sample was analyzed in duplicate. The PSDs of the sample duplicate pairs were measured pre-sonication, during sonication, and post-sonication. Table A.1 provides a cross-reference for each sample, process condition, and figure identification where the results are shown.

Table A.1. Cross-Reference of PSD Samples, Process Conditions, and Appendix Figure

Sample ID	Sieve Cut	Sonication Status	Figure
TCT005-S1-PSD-A-1.1 - Average	<25 mesh	Pre-sonication	A.1
TCT005-S1-PSD-A-1.2 - Average	<25 mesh	Sonicated	A.2
TCT005-S1-PSD-A-1.3 - Average	<25 mesh	Post-sonication	A.3
TCT005-S1-PSD-B-1.1 - Average	<25 mesh	Pre-sonication	A.4
TCT005-S1-PSD-B-1.2 - Average	<25 mesh	Sonicated	A.5
TCT005-S1-PSD-B-1.3 - Average	<25 mesh	Post-sonication	A.6
TCT005-CST-PSD-03-1.1 - Average	Full PSD	Pre-sonication	A.7
TCT005-CST-PSD-03-1.2 - Average	Full PSD	Sonicated	A.8
TCT005-CST-PSD-03-1.3 - Average	Full PSD	Post-sonication	A.9
TCT005-CST-PSD-04-1.1 - Average	Full PSD	Pre-sonication	A.10
TCT005-CST-PSD-04-1.2 - Average	Full PSD	Sonicated	A.11
TCT005-CST-PSD-04-1.3 - Average	Full PSD	Post-sonication	A.12



MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name: TCT005-S1-PSD-A-1.1 - Average	**SOP Name:**	**Measured:** Monday, October 22, 2018 2:40:26 PM	
Sample Source & type:	**Measured by:** D3M966	**Analysed:** Monday, October 22, 2018 2:40:28 PM	
Sample bulk lot ref:	**Result Source:** Averaged		
Particle Name: Zirconia av	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 2.165	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 5.01 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.304 %	**Result Emulation:** Off
Concentration: 0.4180 %Vol	**Span :** 0.650	**Uniformity:** 0.206	**Result units:** Volume
Specific Surface Area: 0.0105 m²/g	**Surface Weighted Mean D[3,2]:** 573.117 um	**Vol. Weighted Mean D[4,3]:** 608.991 um	

d(0.1): 428.627 um **d(0.5):** 590.319 um **d(0.9):** 812.481 um

Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	0.00	355.656	4.21
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	0.00	399.052	7.45
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	63.246	0.00	447.744	12.82
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.00	70.963	0.00	502.377	16.87
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	0.00	563.677	17.83
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	0.00	632.456	16.24
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.00	100.237	0.00	709.627	11.74
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	0.00	796.214	6.59
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	0.00	893.367	3.57
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589	0.00	1002.374	0.96
0.063	0.00	0.448	0.00	3.170	0.00	22.440	0.00	158.866	0.00	1124.683	0.25
0.071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	0.00
0.080	0.00	0.564	0.00	3.991	0.00	28.251	0.00	200.000	0.00	1415.892	0.00
0.089	0.00	0.632	0.00	4.477	0.00	31.698	0.00	224.404	0.00	1588.656	0.00
0.100	0.00	0.710	0.00	5.024	0.00	35.566	0.00	251.785	0.01	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	0.00	282.508	0.27	2000.000	
0.126	0.00	0.893	0.00	6.325	0.00	44.774	0.00	316.979	1.19		
0.142		1.002		7.096		50.238		355.656			

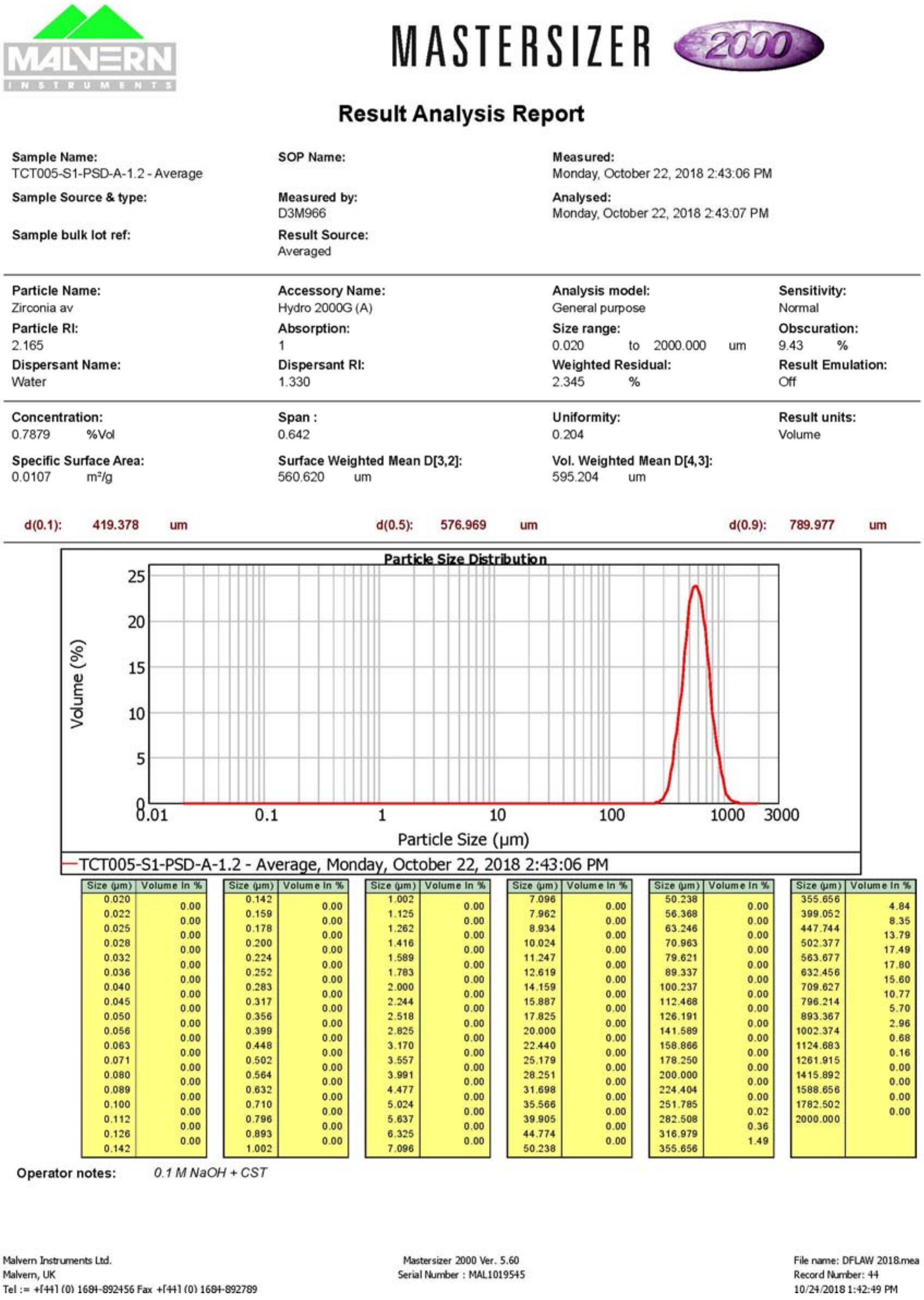
Operator notes: *0.1 M NaOH + CST*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 40
10/24/2018 1:42:49 PM

Figure A.1. Pre-sonication, <25 mesh CST Lot 8056202-999



Result Analysis Report

Sample Name: TCT005-S1-PSD-A-1.2 - Average

Sample Source & type:

Sample bulk lot ref:

SOP Name:

Measured by: D3M966

Result Source: Averaged

Measured: Monday, October 22, 2018 2:43:06 PM

Analysed: Monday, October 22, 2018 2:43:07 PM

Particle Name: Zirconia av

Particle RI: 2.165

Dispersant Name: Water

Accessory Name: Hydro 2000G (A)

Absorption: 1

Dispersant RI: 1.330

Analysis model: General purpose

Size range: 0.020 to 2000.000 um

Weighted Residual: 2.345 %

Sensitivity: Normal

Obscuration: 9.43 %

Result Emulation: Off

Concentration: 0.7879 %Vol

Specific Surface Area: 0.0107 m²/g

Span : 0.642

Surface Weighted Mean D[3,2]: 560.620 um

Uniformity: 0.204

Vol. Weighted Mean D[4,3]: 595.204 um

Result units: Volume

d(0.1): 419.378 um **d(0.5):** 576.969 um **d(0.9):** 789.977 um

—TCT005-S1-PSD-A-1.2 - Average, Monday, October 22, 2018 2:43:06 PM

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	0.00	355.656	4.84
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	0.00	399.052	8.35
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	63.246	0.00	447.744	13.79
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.00	70.963	0.00	502.377	17.49
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	0.00	563.677	17.80
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	0.00	632.456	15.60
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.00	100.237	0.00	709.627	10.77
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	0.00	796.214	5.70
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	0.00	893.367	2.96
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589	0.00	1002.374	0.68
0.063	0.00	0.448	0.00	3.170	0.00	22.440	0.00	158.866	0.00	1124.683	0.16
0.071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	0.00
0.080	0.00	0.564	0.00	3.991	0.00	28.251	0.00	200.000	0.00	1415.892	0.00
0.089	0.00	0.632	0.00	4.477	0.00	31.698	0.00	224.404	0.00	1588.656	0.00
0.100	0.00	0.710	0.00	5.024	0.00	35.566	0.00	251.785	0.02	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	0.00	282.508	0.36	2000.000	
0.126	0.00	0.893	0.00	6.325	0.00	44.774	0.00	316.979	1.49		
0.142		1.002		7.096		50.238		355.656			

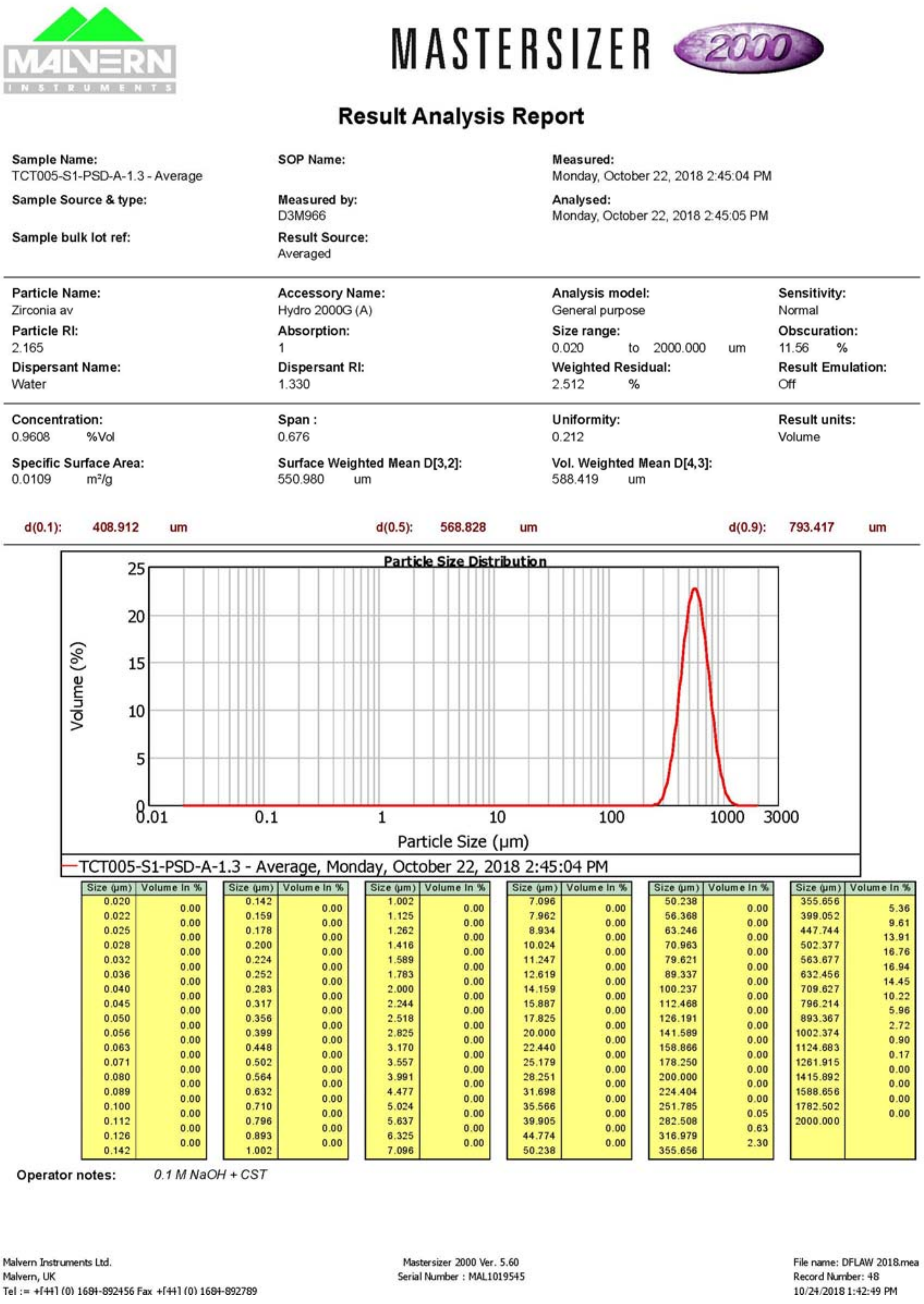
Operator notes: *0.1 M NaOH + CST*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 44
10/24/2018 1:42:49 PM

Figure A.2. During Sonication, <25 mesh CST Lot 8056202-999



Result Analysis Report

Sample Name:
TCT005-S1-PSD-A-1.3 - Average

Sample Source & type:

Sample bulk lot ref:

SOP Name:

Measured by:
D3M966

Result Source:
Averaged

Measured:
Monday, October 22, 2018 2:45:04 PM

Analysed:
Monday, October 22, 2018 2:45:05 PM

Particle Name:
Zirconia av

Particle RI:
2.165

Dispersant Name:
Water

Accessory Name:
Hydro 2000G (A)

Absorption:
1

Dispersant RI:
1.330

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
2.512 %

Sensitivity:
Normal

Obscuration:
11.56 %

Result Emulation:
Off

Concentration:
0.9608 %Vol

Specific Surface Area:
0.0109 m²/g

Span :
0.676

Surface Weighted Mean D[3,2]:
550.980 um

Uniformity:
0.212

Vol. Weighted Mean D[4,3]:
588.419 um

Result units:
Volume

d(0.1): 408.912 um **d(0.5):** 568.828 um **d(0.9):** 793.417 um

Size (μm)	Volume In %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	

Size (μm)	Volume In %
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.00
0.796	0.00
0.893	0.00
1.002	

Size (μm)	Volume In %
1.002	0.00
1.125	0.00
1.262	0.00
1.416	0.00
1.589	0.00
1.783	0.00
2.000	0.00
2.244	0.00
2.518	0.00
2.825	0.00
3.170	0.00
3.557	0.00
3.991	0.00
4.477	0.00
5.024	0.00
5.637	0.00
6.325	0.00
7.096	

Size (μm)	Volume In %
7.096	0.00
7.962	0.00
8.934	0.00
10.024	0.00
11.247	0.00
12.619	0.00
14.159	0.00
15.887	0.00
17.825	0.00
20.000	0.00
22.440	0.00
25.179	0.00
28.251	0.00
31.698	0.00
35.566	0.00
39.905	0.00
44.774	0.00
50.238	

Size (μm)	Volume In %
50.238	0.00
56.368	0.00
63.246	0.00
70.963	0.00
79.621	0.00
89.337	0.00
100.237	0.00
112.468	0.00
126.191	0.00
141.589	0.00
158.866	0.00
178.250	0.00
200.000	0.00
224.404	0.00
251.785	0.05
282.508	0.63
316.979	2.30
355.656	

Size (μm)	Volume In %
355.656	5.36
399.052	9.61
447.744	13.91
502.377	16.76
563.677	16.94
632.456	14.45
709.627	10.22
796.214	5.96
893.367	2.72
1002.374	0.90
1124.683	0.17
1261.915	0.00
1415.892	0.00
1588.656	0.00
1782.502	0.00
2000.000	

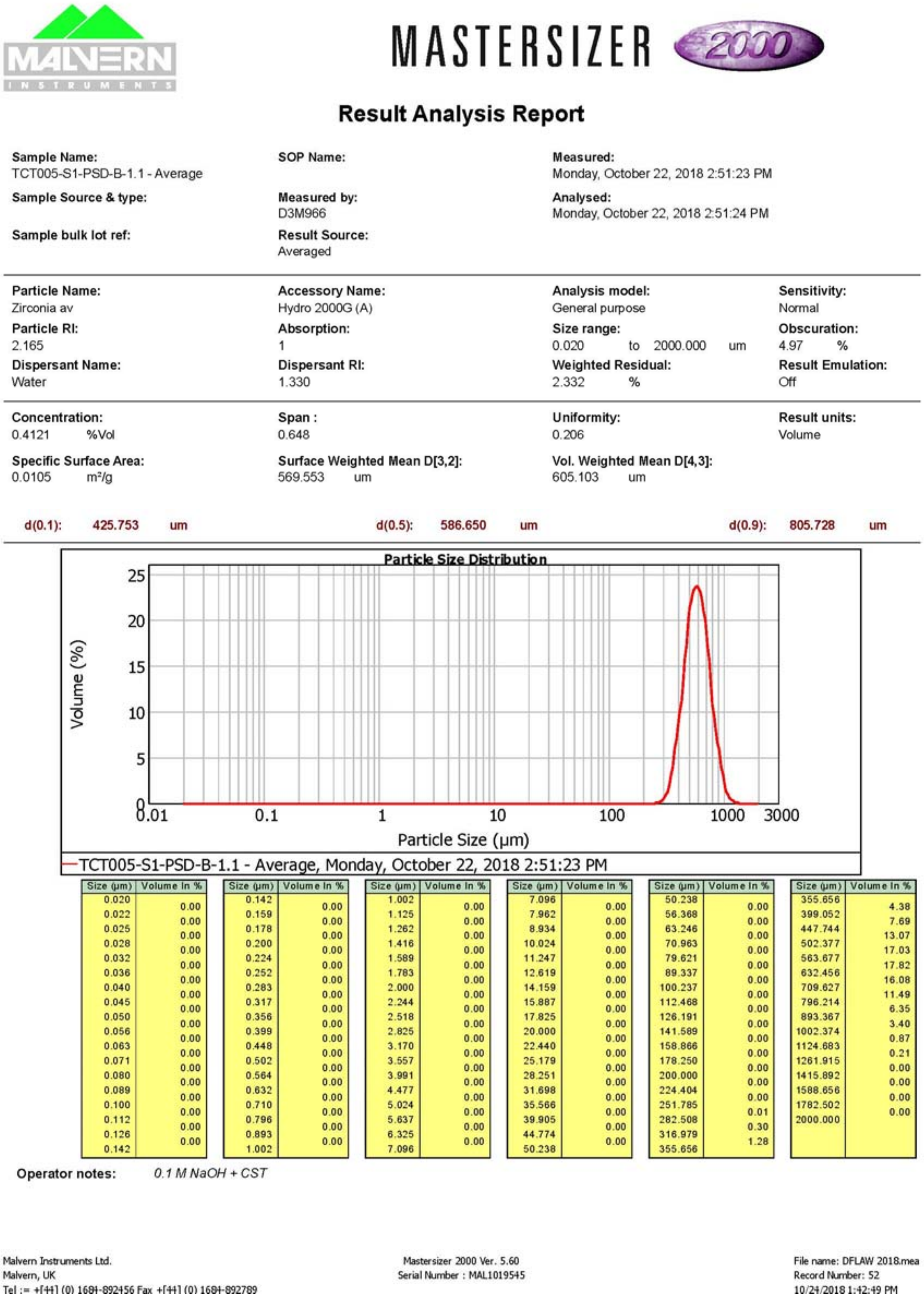
Operator notes: *0.1 M NaOH + CST*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 48
10/24/2018 1:42:49 PM

Figure A.3. Post-sonication, <25 mesh CST Lot 8056202-999



Result Analysis Report

Sample Name: TCT005-S1-PSD-B-1.1 - Average	**SOP Name:**	**Measured:** Monday, October 22, 2018 2:51:23 PM	
Sample Source & type:	**Measured by:** D3M966	**Analysed:** Monday, October 22, 2018 2:51:24 PM	
Sample bulk lot ref:	**Result Source:** Averaged		
Particle Name: Zirconia av	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 2.165	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 4.97 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.332 %	**Result Emulation:** Off
Concentration: 0.4121 %Vol	**Span :** 0.648	**Uniformity:** 0.206	**Result units:** Volume
Specific Surface Area: 0.0105 m²/g	**Surface Weighted Mean D[3,2]:** 569.553 um	**Vol. Weighted Mean D[4,3]:** 605.103 um	

d(0.1): 425.753 um **d(0.5):** 586.650 um **d(0.9):** 805.728 um

Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	0.00	355.656	4.38
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	0.00	399.052	7.69
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	63.246	0.00	447.744	13.07
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.00	70.963	0.00	502.377	17.03
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	0.00	563.677	17.82
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	0.00	632.456	16.08
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.00	100.237	0.00	709.627	11.49
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	0.00	796.214	6.35
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	0.00	893.367	3.40
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589	0.00	1002.374	0.87
0.063	0.00	0.448	0.00	3.170	0.00	22.440	0.00	158.866	0.00	1124.683	0.21
0.071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	0.00
0.080	0.00	0.564	0.00	3.991	0.00	28.251	0.00	200.000	0.00	1415.892	0.00
0.089	0.00	0.632	0.00	4.477	0.00	31.698	0.00	224.404	0.00	1588.656	0.00
0.100	0.00	0.710	0.00	5.024	0.00	35.566	0.00	251.785	0.01	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	0.00	282.508	0.30	2000.000	
0.126	0.00	0.893	0.00	6.325	0.00	44.774	0.00	316.979	1.28		
0.142		1.002		7.096		50.238		355.656			

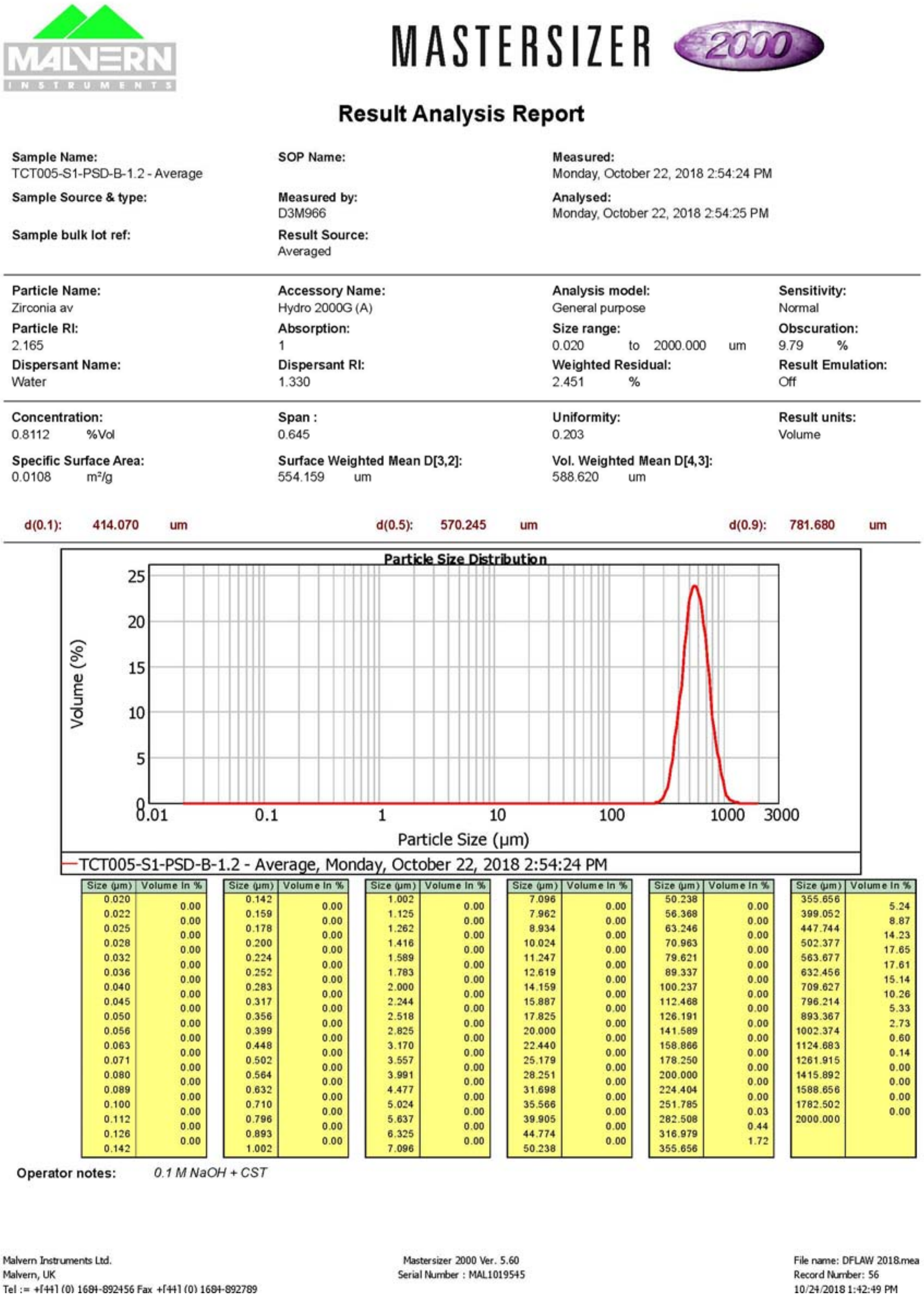
Operator notes: *0.1 M NaOH + CST*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 52
10/24/2018 1:42:49 PM

Figure A.4. Pre-sonication, <25 mesh CST Lot 8056202-999, Duplicate



Result Analysis Report

Sample Name:
TCT005-S1-PSD-B-1.2 - Average

Sample Source & type:

Sample bulk lot ref:

SOP Name:

Measured by:
D3M966

Result Source:
Averaged

Measured:
Monday, October 22, 2018 2:54:24 PM

Analysed:
Monday, October 22, 2018 2:54:25 PM

Particle Name:
Zirconia av

Particle RI:
2.165

Dispersant Name:
Water

Accessory Name:
Hydro 2000G (A)

Absorption:
1

Dispersant RI:
1.330

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
2.451 %

Sensitivity:
Normal

Obscuration:
9.79 %

Result Emulation:
Off

Concentration:
0.8112 %Vol

Specific Surface Area:
0.0108 m²/g

Span :
0.645

Surface Weighted Mean D[3,2]:
554.159 um

Uniformity:
0.203

Vol. Weighted Mean D[4,3]:
588.620 um

Result units:
Volume

d(0.1): 414.070 um **d(0.5):** 570.245 um **d(0.9):** 781.680 um

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	0.00	355.656	5.24
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	0.00	399.052	8.87
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	63.246	0.00	447.744	14.23
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.00	70.963	0.00	502.377	17.65
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	0.00	563.677	17.61
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	0.00	632.456	15.14
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.00	100.237	0.00	709.627	10.26
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	0.00	796.214	5.33
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	0.00	893.367	2.73
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589	0.00	1002.374	0.60
0.063	0.00	0.448	0.00	3.170	0.00	22.440	0.00	158.866	0.00	1124.683	0.14
0.071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	0.00
0.080	0.00	0.564	0.00	3.991	0.00	28.251	0.00	200.000	0.00	1415.892	0.00
0.089	0.00	0.632	0.00	4.477	0.00	31.698	0.00	224.404	0.00	1588.656	0.00
0.100	0.00	0.710	0.00	5.024	0.00	35.566	0.00	251.785	0.03	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	0.00	282.508	0.44	2000.000	
0.126	0.00	0.893	0.00	6.325	0.00	44.774	0.00	316.979	1.72		
0.142		1.002		7.096		50.238		355.656			

Operator notes: *0.1 M NaOH + CST*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 56
10/24/2018 1:42:49 PM

Figure A.5. During-sonication, <25 mesh CST Lot 8056202-999, Duplicate

MALVERN
INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name: TCT005-S1-PSD-B-1.3 - Average

SOP Name:

Measured: Monday, October 22, 2018 2:56:20 PM

Sample Source & type:

Measured by: D3M966

Analysed: Monday, October 22, 2018 2:56:21 PM

Sample bulk lot ref:

Result Source: Averaged

Particle Name: Zirconia av

Accessory Name: Hydro 2000G (A)

Analysis model: General purpose

Sensitivity: Normal

Particle RI: 2.165

Absorption: 1

Size range: 0.020 to 2000.000 um

Obscuration: 11.89 %

Dispersant Name: Water

Dispersant RI: 1.330

Weighted Residual: 2.604 %

Result Emulation: Off

Concentration: 0.9823 %Vol

Span : 0.698

Uniformity: 0.218

Result units: Volume

Specific Surface Area: 0.011 m²/g

Surface Weighted Mean D[3,2]: 546.454 um

Vol. Weighted Mean D[4,3]: 585.815 um

d(0.1): 402.097 um **d(0.5):** 565.072 um **d(0.9):** 796.792 um

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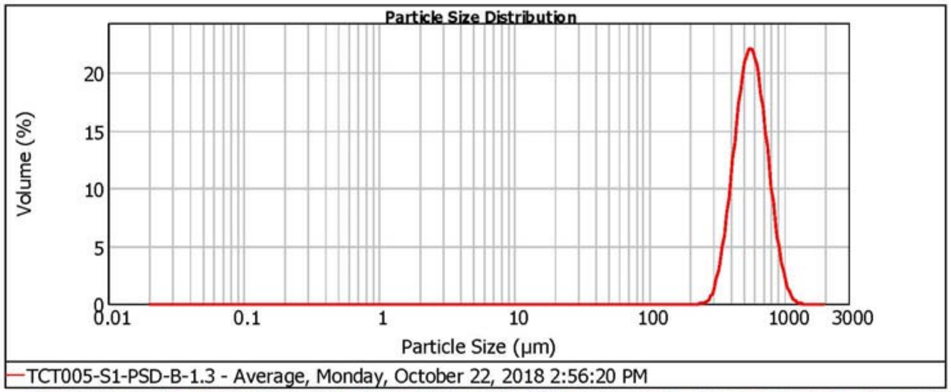

Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	0.00	355.656	5.85
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	0.00	399.052	9.96
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	63.246	0.00	447.744	13.89
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.00	70.963	0.00	502.377	16.34
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	0.00	563.677	16.34
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	0.00	632.456	13.96
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.00	100.237	0.00	709.627	10.01
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	0.00	796.214	6.00
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	0.00	893.367	2.84
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589	0.00	1002.374	1.00
0.063	0.00	0.448	0.00	3.170	0.00	22.440	0.00	158.866	0.00	1124.683	0.20
0.071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	0.00
0.080	0.00	0.564	0.00	3.991	0.00	28.251	0.00	200.000	0.00	1415.892	0.00
0.089	0.00	0.632	0.00	4.477	0.00	31.698	0.00	224.404	0.00	1588.656	0.00
0.100	0.00	0.710	0.00	5.024	0.00	35.566	0.00	251.785	0.09	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	0.00	282.508	0.82	2000.000	
0.126	0.00	0.893	0.00	6.325	0.00	44.774	0.00	316.979	2.70		
0.142		1.002		7.096		50.238		355.656			

Operator notes: *0.1 M NaOH + CST*

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Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 60
10/24/2018 1:42:49 PM

Figure A.6. Post-sonication, <25 mesh CST Lot 8056202-999, Duplicate

MASTERSIZER 2000

Result Analysis Report

Sample Name:
TCT005-CST-PSD-03-1.1 - Average

SOP Name:

Measured:
Monday, October 22, 2018 3:09:55 PM

Sample Source & type:

Measured by:
D3M966

Analysed:
Monday, October 22, 2018 3:09:57 PM

Sample bulk lot ref:

Result Source:
Averaged

Particle Name:
Zirconia av

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Normal

Particle RI:
2.165

Absorption:
1

Size range:
0.020 to 2000.000 um

Obscuration:
5.15 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
3.207 %

Result Emulation:
Off

Concentration:
0.4952 %Vol

Span :
0.907

Uniformity:
0.284

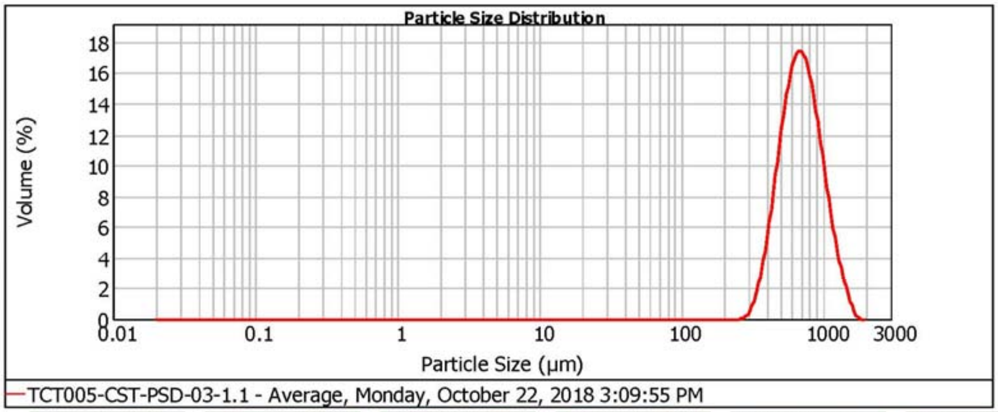
Result units:
Volume

Specific Surface Area:
0.00907 m²/g

Surface Weighted Mean D[3,2]:
661.272 um

Vol. Weighted Mean D[4,3]:
738.019 um

d(0.1): **454.052** **um**   **d(0.5):** **694.685** **um**   **d(0.9):** **1084.161** **um**



Size (µm)	Volume In %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	

Size (µm)	Volume In %
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.00
0.796	0.00
0.893	0.00
1.002	

Size (µm)	Volume In %
1.002	0.00
1.125	0.00
1.262	0.00
1.416	0.00
1.589	0.00
1.783	0.00
2.000	0.00
2.244	0.00
2.518	0.00
2.825	0.00
3.170	0.00
3.557	0.00
3.991	0.00
4.477	0.00
5.024	0.00
5.637	0.00
6.325	0.00
7.096	

Size (µm)	Volume In %
7.096	0.00
7.962	0.00
8.934	0.00
10.024	0.00
11.247	0.00
12.619	0.00
14.159	0.00
15.887	0.00
17.825	0.00
20.000	0.00
22.440	0.00
25.179	0.00
28.251	0.00
31.698	0.00
35.566	0.00
39.905	0.00
44.774	0.00
50.238	

Size (µm)	Volume In %
50.238	0.00
56.368	0.00
63.246	0.00
70.963	0.00
79.621	0.00
89.337	0.00
100.237	0.00
112.468	0.00
126.191	0.00
141.589	0.00
158.866	0.00
178.250	0.00
200.000	0.00
224.404	0.00
251.785	0.00
282.508	0.28
316.979	1.18
355.656	

Size (µm)	Volume In %
355.656	2.75
399.052	5.01
447.744	7.65
502.377	10.24
563.677	12.21
632.456	13.11
709.627	12.73
796.214	11.22
893.367	8.94
1002.374	6.48
1124.683	4.24
1261.915	2.51
1415.892	1.21
1588.656	0.24
1782.502	0.00
2000.000	

Operator notes: *0.1 M NaOH + CST*

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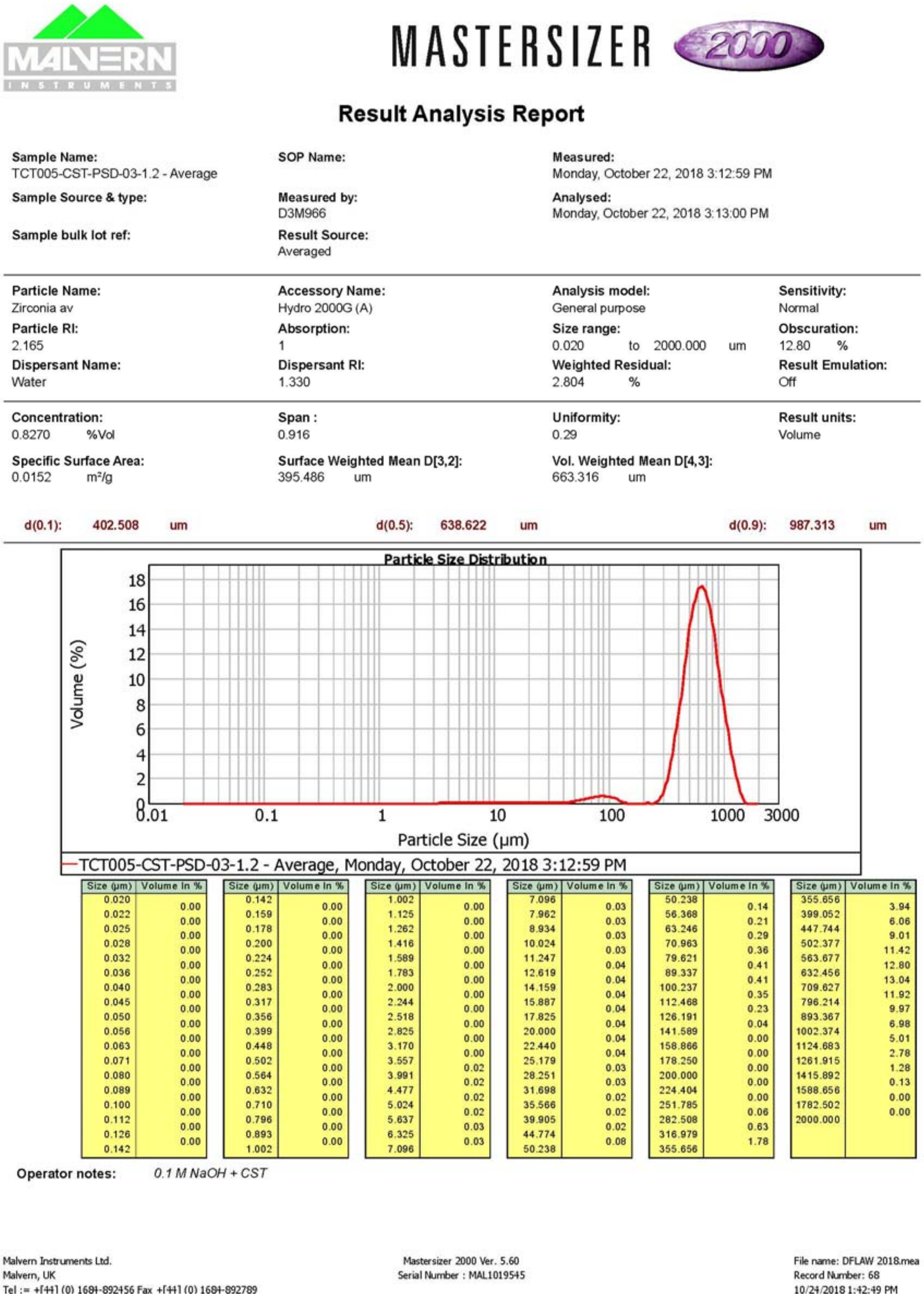
Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 64
10/24/2018 1:42:49 PM

Figure A.7. Pre-sonication, Full PSD CST Lot 8056202-999



Result Analysis Report

Sample Name: TCT005-CST-PSD-03-1.2 - Average
SOP Name:
Measured: Monday, October 22, 2018 3:12:59 PM
Sample Source & type:
Measured by: D3M966
Analysed: Monday, October 22, 2018 3:13:00 PM
Sample bulk lot ref:
Result Source: Averaged

Particle Name: Zirconia av
Accessory Name: Hydro 2000G (A)
Analysis model: General purpose
Sensitivity: Normal
Particle RI: 2.165
Absorption: 1
Size range: 0.020 to 2000.000 um
Obscuration: 12.80 %
Dispersant Name: Water
Dispersant RI: 1.330
Weighted Residual: 2.804 %
Result Emulation: Off

Concentration: 0.8270 %Vol
Span : 0.916
Uniformity: 0.29
Result units: Volume
Specific Surface Area: 0.0152 m²/g
Surface Weighted Mean D[3,2]: 395.486 um
Vol. Weighted Mean D[4,3]: 663.316 um

d(0.1): 402.508 um **d(0.5):** 638.622 um **d(0.9):** 987.313 um

Size (μm)	Volume In %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	

Size (μm)	Volume In %
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.00
0.796	0.00
0.893	0.00
1.002	

Size (μm)	Volume In %
1.002	0.00
1.125	0.00
1.262	0.00
1.416	0.00
1.589	0.00
1.783	0.00
2.000	0.00
2.244	0.00
2.518	0.00
2.825	0.00
3.170	0.00
3.557	0.02
3.991	0.02
4.477	0.02
5.024	0.02
5.637	0.03
6.325	0.03
7.096	

Size (μm)	Volume In %
7.096	0.03
7.962	0.03
8.934	0.03
10.024	0.03
11.247	0.04
12.619	0.04
14.159	0.04
15.887	0.04
17.825	0.04
20.000	0.04
22.440	0.04
25.179	0.03
28.251	0.03
31.698	0.02
35.566	0.02
39.905	0.02
44.774	0.08
50.238	

Size (μm)	Volume In %
50.238	0.14
56.368	0.21
63.246	0.29
70.963	0.36
79.621	0.41
89.337	0.41
100.237	0.35
112.468	0.23
126.191	0.04
141.589	0.00
158.866	0.00
178.250	0.00
200.000	0.00
224.404	0.00
251.785	0.06
282.508	0.63
316.979	1.78
355.656	

Size (μm)	Volume In %
355.656	3.94
399.052	6.06
447.744	9.01
502.377	11.42
563.677	12.80
632.456	13.04
709.627	11.92
796.214	9.97
893.367	6.98
1002.374	5.01
1124.683	2.78
1261.915	1.28
1415.892	0.13
1588.656	0.00
1782.502	0.00
2000.000	

Operator notes: *0.1 M NaOH + CST*

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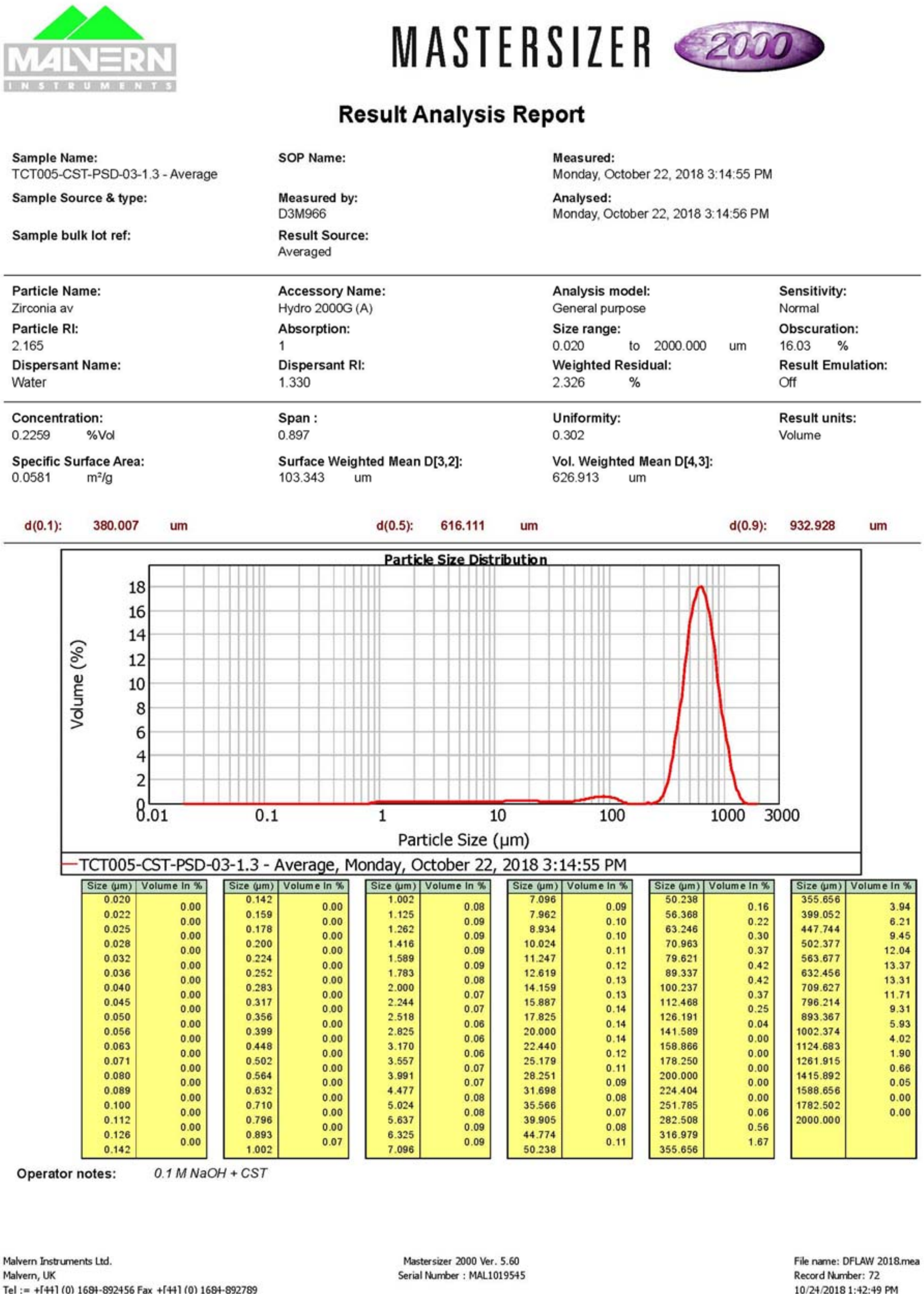
Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 68
10/24/2018 1:42:49 PM

Figure A.8. During-sonication, Full PSD CST Lot 8056202-999



MASTERSIZER 2000

Result Analysis Report

Sample Name: TCT005-CST-PSD-03-1.3 - Average	**SOP Name:**	**Measured:** Monday, October 22, 2018 3:14:55 PM	
Sample Source & type:	**Measured by:** D3M966	**Analysed:** Monday, October 22, 2018 3:14:56 PM	
Sample bulk lot ref:	**Result Source:** Averaged		
Particle Name: Zirconia av	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 2.165	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 16.03 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.326 %	**Result Emulation:** Off
Concentration: 0.2259 %Vol	**Span :** 0.897	**Uniformity:** 0.302	**Result units:** Volume
Specific Surface Area: 0.0581 m²/g	**Surface Weighted Mean D[3,2]:** 103.343 um	**Vol. Weighted Mean D[4,3]:** 626.913 um	

d(0.1): 380.007 um **d(0.5):** 616.111 um **d(0.9):** 932.928 um

Size (μm)	Volume In %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	

Size (μm)	Volume In %
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.00
0.796	0.00
0.893	0.07
1.002	

Size (μm)	Volume In %
1.002	0.08
1.125	0.09
1.262	0.09
1.416	0.09
1.589	0.09
1.783	0.08
2.000	0.07
2.244	0.07
2.518	0.06
2.825	0.06
3.170	0.06
3.557	0.07
3.991	0.07
4.477	0.08
5.024	0.08
5.637	0.09
6.325	0.09
7.096	

Size (μm)	Volume In %
7.096	0.09
7.962	0.10
8.934	0.10
10.024	0.11
11.247	0.12
12.619	0.13
14.159	0.13
15.887	0.14
17.825	0.14
20.000	0.14
22.440	0.12
25.179	0.11
28.251	0.09
31.698	0.08
35.566	0.07
39.905	0.08
44.774	0.11
50.238	

Size (μm)	Volume In %
50.238	0.16
56.368	0.22
63.246	0.30
70.963	0.37
79.621	0.42
89.337	0.42
100.237	0.37
112.468	0.25
126.191	0.04
141.589	0.00
158.866	0.00
178.250	0.00
200.000	0.00
224.404	0.00
251.785	0.06
282.508	0.56
316.979	1.67
355.656	

Size (μm)	Volume In %
355.656	3.94
399.052	6.21
447.744	9.45
502.377	12.04
563.677	13.37
632.456	13.31
709.627	11.71
796.214	9.31
893.367	5.93
1002.374	4.02
1124.683	1.90
1261.915	0.66
1415.892	0.05
1588.656	0.00
1782.502	0.00
2000.000	

Operator notes: *0.1 M NaOH + CST*

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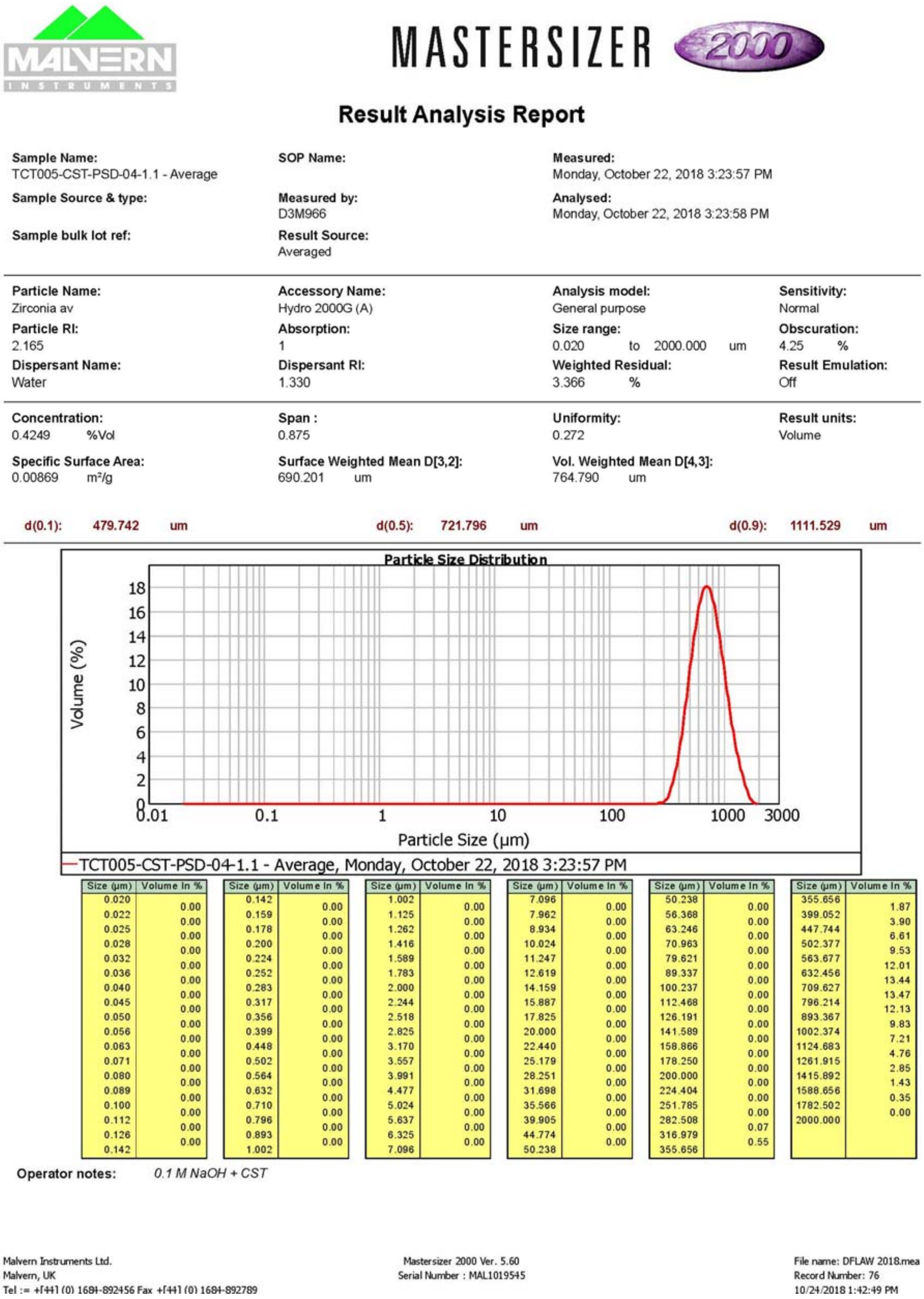
Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 72
10/24/2018 1:42:49 PM

Figure A.9. Post-sonication, Full PSD CST Lot 8056202-999



Result Analysis Report

Sample Name:
TCT005-CST-PSD-04-1.1 - Average

SOP Name:

Measured:
Monday, October 22, 2018 3:23:57 PM

Sample Source & type:

Measured by:
D3M966

Analysed:
Monday, October 22, 2018 3:23:58 PM

Sample bulk lot ref:

Result Source:
Averaged

Particle Name:
Zirconia av

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Normal

Particle RI:
2.165

Absorption:
1

Size range:
0.020 to 2000.000 um

Obscuration:
4.25 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
3.366 %

Result Emulation:
Off

Concentration:
0.4249 %Vol

Span :
0.875

Uniformity:
0.272

Result units:
Volume

Specific Surface Area:
0.00869 m²/g

Surface Weighted Mean D[3,2]:
690.201 um

Vol. Weighted Mean D[4,3]:
764.790 um

d(0.1): **479.742** **um** **d(0.5):** **721.796** **um** **d(0.9):** **1111.529** **um**

Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	0.00	355.656	1.87
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	0.00	399.052	3.90
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	63.246	0.00	447.744	6.61
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.00	70.963	0.00	502.377	9.53
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	0.00	563.677	12.01
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	0.00	632.456	13.44
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.00	100.237	0.00	709.627	13.47
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	0.00	796.214	12.13
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	0.00	893.367	9.83
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589	0.00	1002.374	7.21
0.063	0.00	0.448	0.00	3.170	0.00	22.440	0.00	158.866	0.00	1124.683	4.76
0.071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	2.85
0.080	0.00	0.564	0.00	3.991	0.00	28.251	0.00	200.000	0.00	1415.892	1.43
0.089	0.00	0.632	0.00	4.477	0.00	31.698	0.00	224.404	0.00	1588.656	0.35
0.100	0.00	0.710	0.00	5.024	0.00	35.566	0.00	251.785	0.00	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	0.00	282.508	0.07	2000.000	
0.126	0.00	0.893	0.00	6.325	0.00	44.774	0.00	316.979	0.55		
0.142		1.002		7.096		50.238		355.656			

Operator notes: *0.1 M NaOH + CST*

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Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 76
10/24/2018 1:42:49 PM

Figure A.10. Pre-sonication, Full PSD CST Lot 8056202-999, Duplicate

MASTERSIZER 2000

Result Analysis Report

Sample Name:
TCT005-CST-PSD-04-1.2 - Average

SOP Name:

Measured:
Monday, October 22, 2018 3:26:34 PM

Sample Source & type:

Measured by:
D3M966

Analysed:
Monday, October 22, 2018 3:26:36 PM

Sample bulk lot ref:

Result Source:
Averaged

Particle Name:
Zirconia av

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Normal

Particle RI:
2.165

Absorption:
1

Size range:
0.020 to 2000.000 um

Obscuration:
10.69 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
3.045 %

Result Emulation:
Off

Concentration:
0.7471 %Vol

Span :
0.929

Uniformity:
0.3

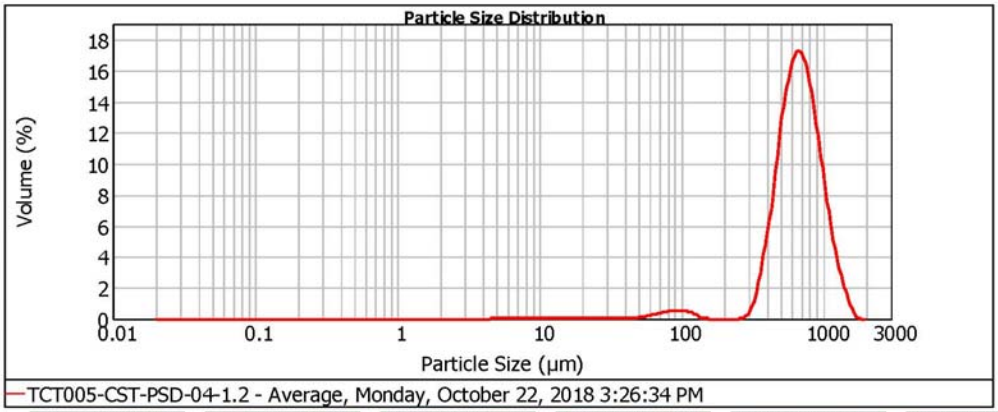
Result units:
Volume

Specific Surface Area:
0.0134 m²/g

Surface Weighted Mean D[3,2]:
446.821 um

Vol. Weighted Mean D[4,3]:
703.175 um

d(0.1): 425.119 um **d(0.5): 671.520 um** **d(0.9): 1048.714 um**



Size (µm)	Volume In %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	

Size (µm)	Volume In %
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.00
0.796	0.00
0.893	0.00
1.002	

Size (µm)	Volume In %
1.002	0.00
1.125	0.00
1.262	0.00
1.416	0.00
1.589	0.00
1.783	0.00
2.000	0.00
2.244	0.00
2.518	0.00
2.825	0.00
3.170	0.00
3.557	0.00
3.991	0.00
4.477	0.01
5.024	0.02
5.637	0.02
6.325	0.02
7.096	

Size (µm)	Volume In %
7.096	0.02
7.962	0.03
8.934	0.03
10.024	0.03
11.247	0.03
12.619	0.04
14.159	0.04
15.887	0.04
17.825	0.04
20.000	0.04
22.440	0.04
25.179	0.03
28.251	0.03
31.698	0.02
35.566	0.02
39.905	0.02
44.774	0.04
50.238	

Size (µm)	Volume In %
50.238	0.09
56.368	0.16
63.246	0.24
70.963	0.32
79.621	0.38
89.337	0.41
100.237	0.38
112.468	0.29
126.191	0.10
141.589	0.00
158.866	0.00
178.250	0.00
200.000	0.00
224.404	0.00
251.785	0.01
282.508	0.29
316.979	1.14
355.656	

Size (µm)	Volume In %
355.656	3.05
399.052	4.97
447.744	7.93
502.377	10.55
563.677	12.31
632.456	13.04
709.627	12.38
796.214	10.62
893.367	8.21
1002.374	5.75
1124.683	3.62
1261.915	2.09
1415.892	0.93
1588.656	0.15
1782.502	0.00
2000.000	

Operator notes: *0.1 M NaOH + CST*

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Mastersizer 2000 Ver. 5.60
Serial Number : MAL1019545

File name: DFLAW 2018.mea
Record Number: 80
10/24/2018 1:42:49 PM

Figure A.11. During-sonication, Full PSD CST Lot 8056202-999, Duplicate

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name: TCT005-CST-PSD-04-1.3 - Average	**SOP Name:**	**Measured:** Monday, October 22, 2018 3:28:36 PM
Sample Source & type:	**Measured by:** D3M966	**Analysed:** Monday, October 22, 2018 3:28:37 PM
Sample bulk lot ref:	**Result Source:** Averaged	

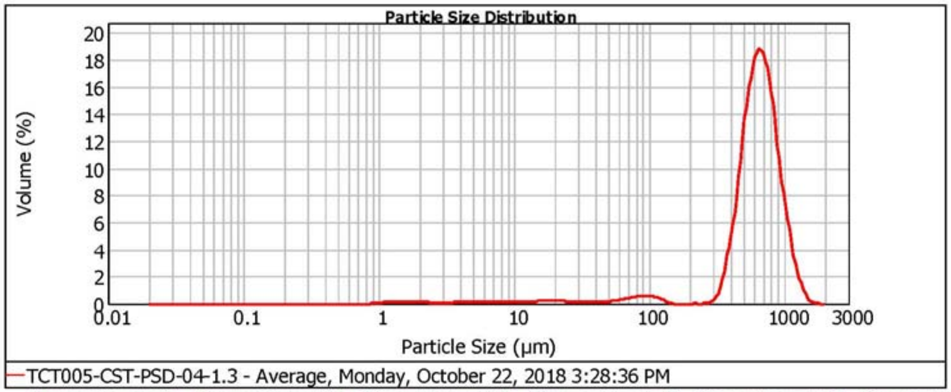
Particle Name: Zirconia av	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 2.165	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 13.86 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.454 %	**Result Emulation:** Off

---

Concentration: 0.2188 %Vol	**Span :** 0.874	**Uniformity:** 0.289	**Result units:** Volume
Specific Surface Area: 0.0519 m²/g	**Surface Weighted Mean D[3,2]:** 115.574 um	**Vol. Weighted Mean D[4,3]:** 661.448 um	

d(0.1): 407.930 um **d(0.5):** 650.448 um **d(0.9):** 976.243 um

---



Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %	Size (μm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.07	7.096	0.09	50.238	0.13	355.656	2.60
0.022	0.00	0.159	0.00	1.125	0.09	7.962	0.09	56.368	0.19	399.052	4.56
0.025	0.00	0.178	0.00	1.262	0.09	8.934	0.10	63.246	0.27	447.744	8.01
0.028	0.00	0.200	0.00	1.416	0.09	10.024	0.10	70.963	0.34	502.377	11.25
0.032	0.00	0.224	0.00	1.589	0.08	11.247	0.11	79.621	0.40	563.677	13.46
0.036	0.00	0.252	0.00	1.783	0.08	12.619	0.12	89.337	0.42	632.456	14.19
0.040	0.00	0.283	0.00	2.000	0.07	14.159	0.13	100.237	0.40	709.627	13.04
0.045	0.00	0.317	0.00	2.244	0.06	15.887	0.13	112.468	0.31	796.214	10.67
0.050	0.00	0.356	0.00	2.518	0.06	17.825	0.14	126.191	0.11	893.367	6.97
0.056	0.00	0.399	0.00	2.825	0.06	20.000	0.14	141.589	0.00	1002.374	4.78
0.063	0.00	0.448	0.00	3.170	0.06	22.440	0.13	158.866	0.00	1124.683	2.40
0.071	0.00	0.502	0.00	3.557	0.06	25.179	0.11	178.250	0.00	1261.915	1.14
0.080	0.00	0.564	0.00	3.991	0.07	28.251	0.10	200.000	0.00	1415.892	0.25
0.089	0.00	0.632	0.00	4.477	0.07	31.698	0.08	224.404	0.00	1588.656	0.04
0.100	0.00	0.710	0.00	5.024	0.08	35.566	0.07	251.785	0.01	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.08	39.905	0.07	282.508	0.19	2000.000	
0.126	0.00	0.893	0.02	6.325	0.08	44.774	0.09	316.979	0.80		
0.142		1.002		7.096		50.238		355.656			

Operator notes: *0.1 M NaOH + CST*

Figure A.12. Post-sonication, Full PSD CST Lot 8056202-999, Duplicate

Appendix B

Medium Column Test Results

Appendix B

Medium Column Test Results

This appendix provides the raw data results for each of the medium column process tests. A cross-reference of column color and process conditions is provided in Table B.1. Results are provided in Table B.2 and Table B.3.

Table B.1. Cross-Reference of Column Color Code and Process Conditions

Test Color Code	Feed Material	Flowrate, BV/h	Superficial Velocity, cm/min	Process Temp., °C
Red	5.6 M Na Simulant	1.83	0.82	20
Yellow	5.6 M Na Simulant	11.4	5.13	20
Green	5.6 M Na Simulant	15.0	6.76	20
Pink	5.6 M Simulant	1.93	0.87	35
Purple	5.6 M Na Simulant with Added Organics	1.86	0.84	20
White	6.0 M Na Simulant	1.88	0.85	20

Table B.2. Red, Yellow, and Green Column Data

Red			Yellow			Green		
BV	µCi ^{137}Cs/ mL	% C/C_0	BV	µCi ^{137}Cs/ mL	% C/C_0	BV	µCi ^{137}Cs/ mL	% C/C_0
14	3.53E-5	0.58	5.7	7.70E-7	0.013	6.6	9.59E-7	0.016
40	3.57E-5	0.58	15.9	2.33E-6	0.039	25	5.35E-6	0.089
78	3.95E-6	0.065	52.3	2.37E-5	0.392	70	9.90E-5	1.65
112	1.65E-6	0.027	84.3	9.19E-5	1.52	119	2.79E-4	4.66
151	4.49E-6	0.073	154	3.43E-4	5.68	217	7.00E-4	11.7
201	2.20E-6	0.036	234	7.52E-4	12.4	319	1.36E-3	22.7
232	5.22E-6	0.085	302	1.07E-3	17.7	406	1.72E-3	28.7
279	1.91E-5	0.31	361	1.28E-3	21.2	483	2.29E-3	38.2
327	4.85E-5	0.79	426	1.71E-3	28.3	573	2.48E-3	41.5
370	1.05E-4	1.72	510	2.03E-3	33.5	689	2.95E-3	49.2
414	1.90E-4	3.11	564	2.34E-3	38.8	764	3.23E-3	54.0
458	2.71E-4	4.43	622	2.44E-3	40.4	826	3.46E-3	57.8
516	4.55E-4	7.45	681	2.64E-3	43.6			
550	6.27E-4	10.26	736	2.82E-3	46.7			
596	7.90E-4	12.92	793	2.87E-3	47.5			
640	1.06E-3	17.27	848	3.24E-3	53.7			
688	1.32E-3	21.58						
730	1.51E-3	24.74						
775	1.86E-3	30.51						
825	2.00E-3	32.73						
866	2.20E-3	35.96						
918	2.54E-3	41.49						
967	2.89E-3	47.31						

Feeds: Red 6.11E-3 µCi/mL ^{137}Cs; Yellow 6.04E-3 µCi/mL ^{137}Cs; Green 5.99E-3 µCi/mL ^{137}Cs.

Table B.3. Pink, Purple, and White Column Data

Pink			Purple			White		
BV	µCi ^{137}Cs/ mL	% C/C$_0$	BV	µCi ^{137}Cs/ mL	% C/C$_0$	BV	µCi ^{137}Cs/ mL	% C/C$_0$
7	2.20E-6	0.035	6	4.10E-5	0.69	5	1.16E-6	0.021
45	5.21E-7	0.008	46	2.86E-7	0.005	41	7.23E-7	0.013
89	5.20E-7	0.008	92	2.68E-7	0.005	86	2.01E-7	0.004
141	2.16E-6	0.035	142	9.47E-7	0.016	135	5.28E-7	0.010
190	2.56E-5	0.41	186	3.68E-6	0.062	179	3.20E-6	0.059
239	8.99E-5	1.43	229	1.02E-5	0.17	222	1.08E-5	0.20
284	2.17E-4	3.46	277	2.58E-5	0.44	269	3.09E-5	0.57
331	4.81E-4	7.66	322	5.99E-5	1.01	315	6.27E-5	1.16
378	8.78E-4	14.0	370	1.02E-4	1.71	361	1.28E-4	2.36
439	1.38E-3	22.0	414	1.79E-4	3.02	406	2.02E-4	3.72
473	1.65E-3	26.3	460	2.49E-4	4.19	451	2.94E-4	5.42
522	2.20E-3	35.1	501	2.75E-4	4.64	507	4.20E-4	7.75
566	2.81E-3	44.8	501	2.32E-4	3.91	541	5.87E-4	10.8
616	3.34E-3	53.3	531	3.84E-4	6.48	587	7.83E-4	14.4
656	3.88E-3	61.9				634	9.51E-4	17.5
705	4.21E-3	67.2				678	1.14E-3	21.0
						724	1.39E-3	25.7
						775	1.57E-3	29.0
						820	1.79E-3	33.1
						859	2.17E-3	40.0
						903	2.36E-3	43.5
						948	2.54E-3	46.9
						989	2.63E-3	48.5
						Feed displacement		
						991	2.00E-4	3.69
						993	3.88E-5	0.71
						995	2.89E-5	0.53
						Water rinse		
						997	1.95E-5	0.36
						1000	2.17E-5	0.40
						1002	1.37E-5	0.25
						1004	1.25E-5	0.23
						1006	1.04E-5	0.19
						1008	8.48E-6	0.16

Feeds: Pink 6.27E-3 µCi/mL ^{137}Cs; Purple 5.93E-3 µCi/mL ^{137}Cs; White 5.42E-3 µCi/mL ^{137}Cs.

Appendix C

Full Height Column Test Results

Appendix C

Full Height Column Test Results

This appendix provides the results for each of the full height column process tests. A cross-reference of column color and process conditions is provided in Table C.1. Results are provided in Table C.2 and Table C.3.

Table C.1. Cross-Reference of Column Color Code and Process Conditions

Test Color Code	Feed Material	Flowrate, BV/h	Superficial Velocity, cm/min	Process Temp., °C
Orange	5.6 M Na Simulant	1.30	4.88	20
Blue	5.6 M Na Simulant	1.82	6.94	20

Table C.2. Orange Column Data

Column 1			Column 2			Column 3			Column 4		
BV	µCi ^{137}Cs/ mL	% C/C_0	BV	µCi ^{137}Cs/ mL	% C/C_0	BV	µCi ^{137}Cs/ mL	% C/C_0	BV	µCi ^{137}Cs/ mL	% C/C_0
8	1.50E-7	0.02	32	<1.2E-8	<1.2E-3	73	<1.2E-8	<1.3E-3	32	<1.1E-8	<1.2E-3
32	5.83E-7	0.06	73	<1.4E-8	<1.4E-3	128	<1.9E-8	<2.0E-3	73	<1.1E-8	<1.2E-3
73	9.56E-7	0.10	128	<1.2E-8	<1.2E-3	186	<2.8E-8	<2.9E-3	128	<2.0E-8	<2.1E-3
129	1.29E-5	1.36	186	2.87E-8	3.01E-3	227	<2.5E-8	<2.6E-3	186	<3.7E-8	<3.8E-3
186	5.79E-5	6.09	227	2.13E-7	0.02	317	<1.6E-8	<1.7E-3	227	<2.0E-8	<2.1E-3
227	1.05E-4	11.06	288	1.58E-6	0.17	440	1.48E-7	0.016	288	<1.9E-8	<2.0E-3
317	2.50E-4	26.25	317	3.44E-6	0.36	537	1.21E-6	0.13	317	<1.8E-8	<1.9E-3
440	4.64E-4	48.74	382	1.20E-5	1.26	630	5.49E-6	0.58	382	<1.7E-8	<1.8E-3
537	6.32E-4	66.44	440	2.91E-5	3.06	742	1.91E-5	2.00	440	<1.5E-8	<1.6E-3
591	7.19E-4	75.51	467	3.86E-5	4.06	843	4.78E-5	5.02	467	<1.9E-8	<2.0 E-3
742	7.72E-4	81.08	537	7.71E-5	8.10	951	8.28E-5	8.70	537	<2.0E-8	<2.1E-3
843	8.64E-4	90.80	591	1.09E-4	11.5				591	<2.7E-8	<2.8E-3
951	8.33E-4	87.55	630	1.65E-4	17.3				629	2.68E-8	2.82E-3
			683	1.92E-4	20.1				683	1.05E-7	0.011
			742	2.20E-4	23.1				742	2.93E-7	0.031
			783	2.73E-4	28.7				783	5.57E-7	0.059
			844	3.27E-4	34.4				843	1.48E-6	0.16
			866	4.27E-4	44.9				866	2.81E-6	0.30
			951	4.55E-4	47.9				951	4.77E-6	0.50
									Feed Displacement		
									952.2	4.97E-6	5.23E-1
									953.5	3.19E-7	3.35E-2
									954.6	<3.93E-8	<4.13E-3
									955.7	<2.90E-8	<3.05E-3
									957.0	3.19E-8	3.35E-3
									957.9	<2.16E-8	<2.27E-3

Column 1			Column 2			Column 3			Column 4		
BV	μCi ^{137}Cs/ mL	% C/C_0	BV	μCi ^{137}Cs/ mL	% C/C_0	BV	μCi ^{137}Cs/ mL	% C/C_0	BV	μCi ^{137}Cs/ mL	% C/C_0
									Water Rinse		
									960.3	2.33E-8	2.45E-3
									961.5	2.73E-7	0.029
									964.0	9.86E-7	0.10
									966.2	1.03E-6	0.11
									967.3	3.51E-6	0.37
									968.2	1.54E-6	0.16

Feed contained 9.52E-4 μCi ^{137}Cs/ mL.

Table C.3. Blue Column Data

Column 1			Column 2			Column 3			Column 4		
BV	μCi ^{137}Cs/ mL	% C/C$_0$	BV	μCi ^{137}Cs/ mL	% C/C$_0$	BV	μCi ^{137}Cs/ mL	% C/C$_0$	BV	μCi ^{137}Cs/ mL	% C/C$_0$
11	3.08E-7	0.024	49	6.73E-6	0.52	95	1.17E-6	9.12E-2	95	<1.9E-8	<1.5E-3
49	4.35E-7	0.034	96	2.18E-8	0.0017	186	1.65E-8	1.29E-3	186	<2.0E-8	<1.5E-3
96	1.01E-5	0.79	142	4.25E-8	0.0033	276	<1.9E-8	<1.5E-3	276	<1.8E-8	<1.4E-3
142	4.68E-5	3.65	186	2.12E-7	0.0165	356	7.32E-8	5.71E-3	356	<1.9E-8	<1.5E-3
187	9.93E-5	7.74	229	1.03E-6	0.080	431	4.14E-7	3.23E-2	431	<2.1E-8	<1.7E-3
229	1.83E-4	14.24	276	3.80E-6	0.30	471	4.62E-7	3.60E-2	471	<1.6E-8	<1.3E-3
276	2.75E-4	21.42	318	8.46E-6	0.66	544	2.86E-6	2.23E-1	544	<3.4E-8	<2.6E-3
356	4.11E-4	32.03	356	1.53E-5	1.19	630	1.06E-5	8.23E-1	630	1.23E-7	9.57E-3
432	5.08E-4	39.56	395	2.57E-5	2.00	723	2.57E-5	2.00E+0	723	6.60E-7	5.15E-2
471	5.10E-4	39.74	432	3.41E-5	2.66	858	8.15E-5	6.35E+0	813	2.60E-6	2.03E-1
544	7.33E-4	57.09	466	4.56E-5	3.55	894	9.78E-5	7.62E+0	858	4.60E-6	3.58E-1
631	8.81E-4	68.66	471	4.02E-5	3.13				894	6.53E-6	5.09E-1
723	1.06E-3	82.88	498	6.98E-5	5.44				Feed Displacement		
859	1.17E-3	91.42	544	1.08E-4	8.44				895.6	6.62E-6	5.16E-1
895	1.06E-3	82.89	588	1.42E-4	11.0				896.5	5.70E-7	4.44E-2
			631	1.94E-4	15.1				897.6	1.30E-7	1.02E-2
			680	2.47E-4	19.3				898.5	6.97E-8	5.43E-3
			724	2.68E-4	20.9				899.6	4.24E-8	3.31E-3
			761	3.39E-4	26.4				900.7	5.35E-8	4.17E-3
			814	4.01E-4	31.3				Water Rinse		
			859	4.43E-4	34.5				903	7.44E-8	5.80E-3
			895	4.69E-4	36.5				905	2.86E-7	2.23E-2
									906	8.86E-7	6.91E-2
									908	1.09E-6	8.49E-2
									910	1.00E-6	7.81E-2
									911	9.41E-7	7.33E-2

Feed contained 1.28E-3 μCi ^{137}Cs/ mL.

Appendix D

Gamma Scan Results from Orange Column

Appendix D

Gamma Scan Results from Orange Column

This appendix provides the gamma count results from scanning each of the four columns associated with the Orange column test process run. Results are provided in Table D.1. The column location represents the result from top to bottom for each individual column. The continuous location column in Table D.1 adds column 1 bed depth to column 2 bed depth, then column 3 bed depth to the revised column 2 bed depth and the column 4 bed depth to the revised column 3 bed depth.

Table D.1. Orange Column Gamma Scan Data Summary

Orange Column #	Column Location, cm	Continuous Location, cm	Live Time, seconds	Net Peak Area, counts	Net Peak Rate, cps
1	3	3	1200	19285	16.07
1	13	13	1200	19278	16.07
1	23	23	1200	18849	15.71
1	33	33	1200	18487	15.41
1	43	43	1200	18172	15.14
1	53	53	1200	17676	14.73
1	63	63	1800	26194	14.55
1	73	73	1800	25201	14.00
1	83	83	1800	24532	13.63
1	93	93	1800	23911	13.28
1	103	103	1800	22439	12.47
1	112	112	1800	21850	12.14
2	0	113	1800	21605	12.00
2	13	126	1816	22942	12.63
2	23	136	2700	31953	11.83
2	33	146	2705	30536	11.29
2	43	156	2700	27983	10.36
2	53	166	3600	35463	9.85
2	63	176	2700	24445	9.05
2	73	186	3600	29094	8.08
2	83	196	3600	26495	7.36
2	93	206	3600	22992	6.39
2	103	216	3600	19626	5.45
2	112	225	43200	214693	4.97
3	2	228	43200	233326	5.40
3	31	257	43200	154153	3.57
3	52	278	43200	120897	2.80
3	72	298	43200	77579	1.80
3	91	317	54000	70551	1.31
3	112	338	72000	58689	0.82
4	1	340	61200	49770	0.81
4	28	367	43200	19340	0.45
4	38	377	43200	15391	0.36
4	57	396	72000	13485	0.19
4	89	428	61200	5618	0.09
4	113	452	61200	1067	0.02

The region of interest for the ^{137}Cs peak was channel 433 to 521 out of 1024 channels in the spectrum. Count live times varied in order to obtain <2% uncertainty in the net peak area results. Column location is relative to the bottom of the 3 mm collimator (e.g., column location = 100 cm is ‘seeing’ a column slice from ~100 to 100.3 cm).

Appendix E

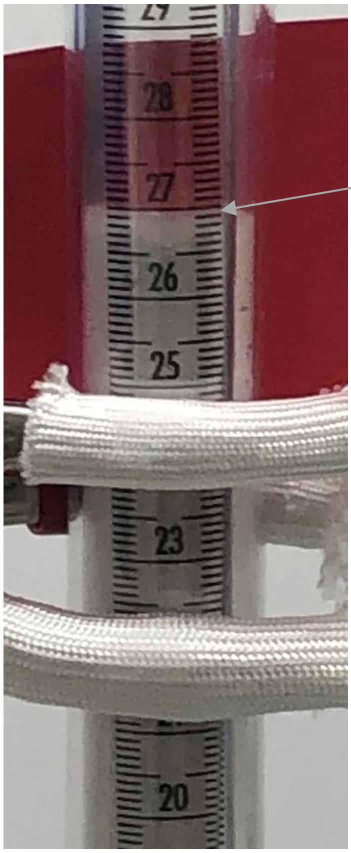
Analysis of Colloid Solids Suspended in 5.6 M Na Simulant with Added Organics

Appendix E

Analysis of Colloid Solids Suspended in 5.6 M Na Simulant with Added Organics

This appendix provides the phase identification results for the colloidal solids suspended in the Purple coded column feed solution (5.6 M Na simulant with added organics) and the non-crystalline silicotitanate (CST) solids collected from the top of the Purple column CST bed.

A total of 531 bed volumes (BVs) of the 5.6 M Na simulant with added organics were processed over 335 h inclusive of a ~17-h stopflow condition. The flowrate slowed from 1.95 BV/h to 1.37 BV/h after processing 460 BVs of feed. The CST column plugged after processing and an additional 41 BVs of feed. The CST bed was backflushed with 0.1 M NaOH (without fluidizing) in an effort to release the plug. Processing commenced for another 30 BVs before the CST bed plugged again, at which point processing was discontinued. Colloidal solids were observed in a feed sample that was collected from the fluid that bypassed the column after activating the pressure relief valve; a sample was collected for analysis (sample identification TCT004P-feed). A thin white later of solids was observed at the top of the CST bed (see Figure E.1). A sample of these solids was removed from the top of the column with a plastic transfer pipet for analysis (sample identification TCT004P-solids).



White solids
on top of
CST bed

Figure E.1. Thin White Solids Layer on Top of Purple Column CST Bed

E.1 Experimental

The samples TCT004P-solids and TCT004P-feed were transferred from the solution/slurry vials onto carbon-coated copper transmission electron microscopy (TEM) grids. This technique enabled the high salt solution to wash away rapidly from the suspended solids. If the solution was left to dry, salts would precipitate and occlude observations of the phases of interest. The samples were analyzed under backscattered electron (BSE) and secondary electron imaging (SEI) using an FEI (Thermo Fisher Scientific, Inc., Hillsboro, OR, USA) Quanta™ 250FEG scanning electron microscope (SEM). The SEM was equipped with an X-ray energy dispersive spectrometer (EDS) (EDAX™, Mahwah, NJ, USA) for elemental analysis and mapping. To image the morphology of the particles, the beam energy was lowered to 5-10 keV and a lower beam current was used.

The *in situ* experiments on the aqueous phase associated with the TCT004P-solids were conducted by pipetting 6 µL of the contact solution into a QX-202 WetSEM sample cell (QuantomiX, Rehovot, Israel) (Buck et al. 2018). These cells enable observation of the suspended particles in solution in the electron microscope. These were examined at 15 keV and a low beam current to avoid rupturing the cells during observation.

E.2 Results and Discussion

This section describes the particle analysis results for the two samples: TCT004P-solids and TCT004P-feed.[1]

E.2.1 TCT004P-solids

Sample TCT004P-solids was examined using the SEM and two major phases were observed. A sodium phosphate phase consisting of crystals ~100 to 200 µm long and ~40 µm wide was found along with an agglomerated phase, consisting of micrometer-sized particles (see Figure E.2). The images in Figure E.2A-B were obtained under a range of magnification and imaging conditions to provide an overview of the particle agglomerates and morphology. The grid bars observed were from the Cu-grid that supports a carbon film. The highest magnification image (Figure E.2C-D) shows the morphology of the alumino-silicate phase that is typical of cancrinite. EDS mapping of the sample showed the two phases. In Figure E.3, the phosphate phase is present as the large particles and the alumino-silicate phase is dispersed but sometimes attached to the phosphate.

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[1] Results are provided as FIO because the data did not undergo the technical review rigor as normally applied to the project, the staff performing the analysis had not been trained to the project QA procedures, and the system setup and data acquisition were conducted per discussion and not a project approved test instruction.

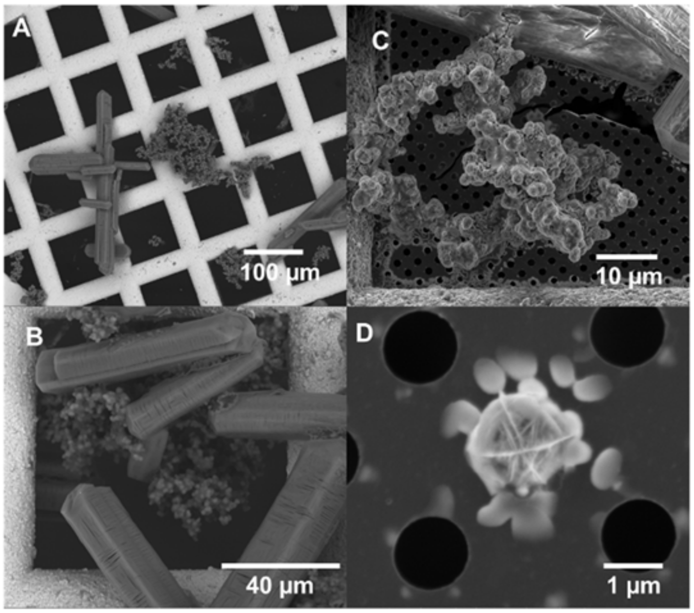

Figure E.2. Low Magnification View of the Two Major Phases in the TCT004P-Solids (FIO)

Figure notes: (A) BSE imaging showing the large, elongated phosphate crystals and the agglomerate of aluminum silicate. (B) Slightly higher magnification image shows the rigid crystallinity of the phosphate phase. (C) Using SEI, the surface morphology of the aluminum silicate agglomerate is better visualized. (D) At low energy SEI, the "balls of twine" morphology characteristic of cancrinite is shown (Buck and McNamara 2004).

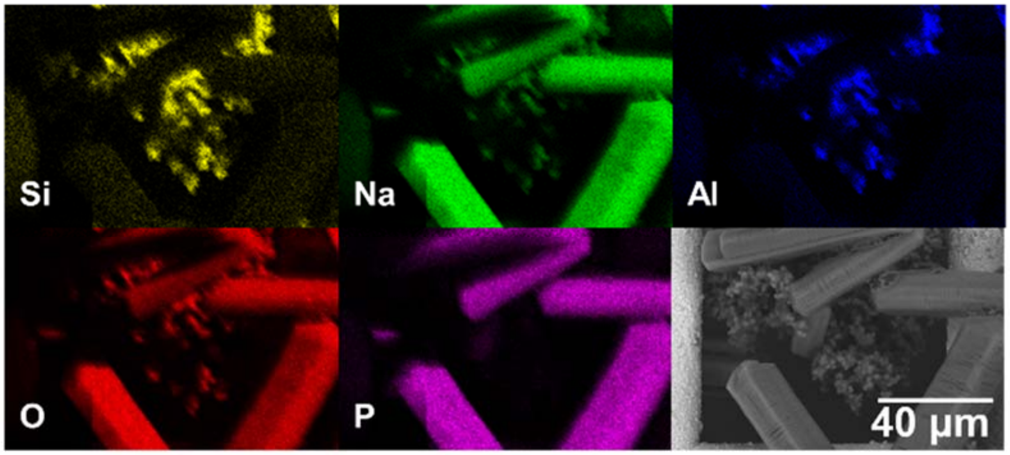

Figure E.3. Elemental Map Showing the Two Phases (Aluminum-silicate [Cancrinite] and Sodium Phosphate) in the TCT004P-Solids (FIO)

EDS analysis indicated that these were sodium-potassium aluminum silicate particles (Figure E.4). When compared to an ideal cancrinite composition, the EDS analysis from the sample had lower Al and Si contents than expected. The reason for this may be the form of the particles and possible interference; however, further analysis would be needed to confirm the composition. Nevertheless, the Al:Si ratio and the morphology do suggest cancrinite. The cancrinite in Hanford tank waste appears to be modified by the presence of excess sodium and nitrate compared to those reported in nature.

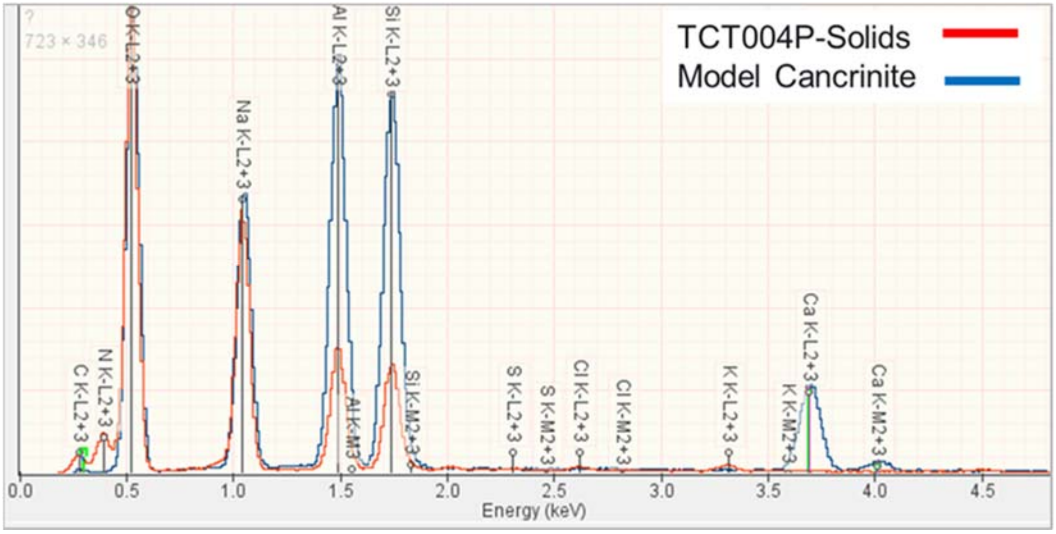

Figure E.4. EDS Analysis of Cancrinite Observed in TCT004P-Solids and a Simulation of Cancrinite with Composition [Na_6Ca_2 [$(CO_3)_2(Al_6Si_6)_{24}$]•$2H_2O$] (FIO)

With environmental cells available today, it is possible to image particles in solution. Although the resolution of imaging is greatly reduced when imaging in solutions, important information can be obtained on the nature of the particles. In Figure E.5, small, micrometer-sized individual particles appear to indicate that the cancrinite phase is partially separated in solution and that observation of the agglomerates in the dried state may be a consequence of the process to pipette these solutions on to the carbon film.

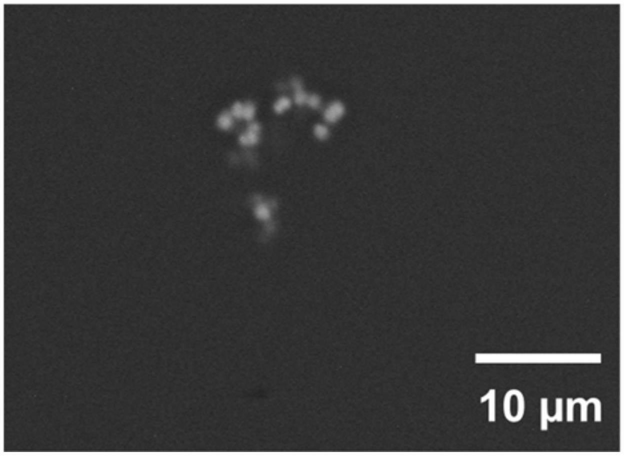

Figure E.5. Round Particles Consistent with the Cancrinite Phase on the order of a Micrometer in Diameter Are Shown to be Freely Floating in the Solution and Not Agglomerated (FIO)

E.2.2 TCT004P-Feed

Analysis of the TCT004P-feed specimen indicated only the occurrence of the sodium phosphate phase (see Figure E.6). These elongated particles appeared to be similar to particles observed by Reynolds and Herting (2016).

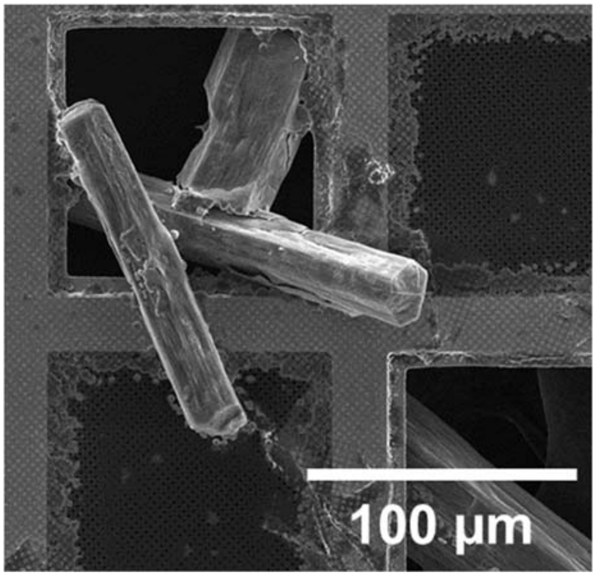

Figure E.6. SEM Image of Sodium Phosphate Phase in TCT004P-Feed Specimen Indicating only a Single Phase of Sodium Phosphate (FIO)

E.2.3 Discussion

The exact identity of the phosphate phase remains questionable, as does the exact nature of the alumino-silicate phase. Further analysis in the transmission electron microscope may be warranted to better elucidate the phase characteristics. Sodium phosphate dodecahydrate [$Na_3PO_4 \bullet 12H_2O \bullet (0.25)NaOH$] is known to form a gel during processes, whereas the natrophosphate $Na_7F(PO_4)_2 \cdot 19H_2O$ phase, which typically crystallizes as large acicular particles (Herting and Reynolds 2016), can also cause filtering (and hence column plugging) issues.

E.3 References

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