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Single Stage Contactor Testing of the Next Generation Solvent Blend

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ABSTRACT

The Modular Caustic Side Solvent Extraction (CSSX) Unit (MCU) facility at the Savannah River Site (SRS) is actively pursuing the transition from the current BOBCalixC6 based solvent to the Next Generation Solvent (NGS)-MCU solvent to increase the cesium decontamination factor. To support this integration of NGS into the MCU facility the Savannah River National Laboratory (SRNL) performed testing of a blend of the NGS (MaxCalix based solvent) with the current solvent (BOBCalixC6 based solvent) for the removal of cesium (Cs) from the liquid salt waste stream. This testing utilized a blend of BOBCalixC6 based solvent and the NGS with the new extractant, MaxCalix, as well as a new suppressor, tris(3,7dimethyloctyl) guanidine.

Single stage tests were conducted using the full size V-05 and V-10 liquid-to-liquid centrifugal contactors installed at SRNL. These tests were designed to determine the mass transfer and hydraulic characteristics with the NGS solvent blended with the projected heel of the BOBCalixC6 based solvent that will exist in MCU at time of transition. The test program evaluated the amount of organic carryover and the droplet size of the organic carryover phases using several analytical methods.

The results indicate that hydraulically, the NGS solvent performed hydraulically similar to the current solvent which was expected. For the organic carryover 93% of the solvent is predicted to be recovered from the stripping operation and 96% from the extraction operation. As for the mass transfer, the NGS solvent significantly improved the cesium DF by at least an order of magnitude when extrapolating the One-stage results to actual Seven-stage extraction operation with a stage efficiency of 95%.

INTRODUCTION

A solvent extraction system for removal of cesium from alkaline solutions was developed utilizing a novel solvent developed at Oak Ridge National Laboratory (ORNL).[1], [2] This solvent consists of a calix[4]arene-crown-6 (calixarene) extractant dissolved in an inert hydrocarbon matrix. Modifier is added to the solvent to increase the solubility of the calixarene and to prevent the formation of a third phase. An additional additive, the suppressor, is used to improve stripping performance by mitigating, or suppressing, the effects of any surfactants present in the feed stream.[3] The process that deploys this solvent system is known as CSSX. The solvent system has been deployed at SRS in MCU since 2008.

From its radioactive start-up in April 2008 until the end of May 2013, MCU processed approximately 3.6 million gallons of high-level waste (HLW) solution for disposition. The decontaminated salt solution (DSS) is sent to the SRS Saltstone Facility as Low Activity Waste where it is stabilized in grout. The concentrated Cs strip effluent (SE) stream is transferred to the Defense Waste Processing Facility (DWPF) as HLW where it is included in the vitrification process.

MCU uses liquid-to-liquid centrifugal contactors from CINC[®] for cesium extraction (10 inch rotor or “V-10”) and for solvent scrub and solvent strip stages (5 inch rotor or “V-05”) to provide mechanical mixing and phase separation between solvent and aqueous waste solutions. The process involves two separations. The first separation extracts Cs from waste solutions into the solvent system; the second separation strips Cs from the solvent into an aqueous phase while providing a nominal Cs concentration factor (CF) of 15. The current solvent uses a strip solution of dilute nitric acid, but the NGS will use

boric acid. Between the two cesium transfer processes the solvent is “scrubbed” via contact with dilute nitric acid, too, but the NGS will use a mild caustic solution. The purpose is to remove competing cations (K^+ , etc.) and to adjust the pH, thereby making the acid strip process more effective. Additionally, the solvent stream is washed to remove impurities and solvent degradation products. Note that the wash was not performed during the testing described in this paper. The lack of a wash will have no impact on the results on the testing since the mass transfer tests were once-through.

Continued development efforts by ORNL have identified an improved solvent system that can raise the expected decontamination factor (DF) in MCU from ~200 to potentially more than 40,000[4]. The improved DF is attributed to an increased distribution ratio for cesium [D(Cs)] in extraction from ~15 to ~50 (at 50 mM extractant concentration), due to an increased solubility of the new extractant (MaxCalix) in the solvent from 0.007 M to ~0.050 M, and the use of boric acid (H_3BO_3) for stripping that yields D(Cs) values less than 0.01. Additionally, the changes incorporated into NGS are intended to reduce solvent entrainment. The NGS solvent contains four components:

- 0.050 M 1,3-alt-2S,27-Bis(3,7-dimethyloctyloxy)-calix[4]arene-benzocrown-6, also known as MaxCalix, is the extractant,
- 0.50 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, or Cs-7SB, is the Modifier,
- 0.003 M N,N',N''-Tris(3,7-dimethyloctyl)guanidine, or TiDG, is the suppressor, and
- C_{12} -isoparaffinic hydrocarbon, or Isopar™ L, is the diluent.

Based on ORNL recommendations and testing[5] showing similarly improved DFs, Savannah River Remediation (SRR) plans to initially blend the NGS with the existing BOBCalixC6 based solvent for use in MCU. Both the existing BOBCalixC6 based solvent and the NGS consist of extractant, modifier and suppressor dissolved in an Isopar™ L diluent. A concentrated NGS will be added to the existing solvent heel in MCU at time of transition to prepare blended solvent. This projected blend was used for the testing described in this paper. Over time at MCU as solvent is depleted, make-up material added will be the NGS components as part of a normal solvent addition cycle at MCU until all of the BOBCalixC6 and trioctylamine (TOA) is depleted leaving only NGS constituents.

MCU is actively pursuing the transition from the current BOBCalixC6 based solvent to the NGS solvent. To support this integration of NGS to MCU, SRR MCU-NGS Implementation Project requested that SRNL perform testing of the new solvent for the removal of Cs from the liquid salt waste stream. The new solvent has been shown to improve the decontamination of Cs from the liquid salt waste material; however, understanding of the hydraulic and mass transfer properties of this solvent is required at a larger scale prior to utilization of the material in the MCU process. Additionally, SRNL was tasked with characterizing performance of both a stripping coalescer (20 inch long, 10 micron pore size) and an extraction coalescer (40 inch long, 20 micron pore size). These objectives were achieved through the analysis of droplet size distributions upstream and downstream of the coalescer using standard analytical methods.

DESCRIPTION

To measure the effectiveness of contactor and coalescer operations, testing was conducted in two key areas; mass transfer and hydraulic. During mass transfer testing, the test facility is operated in a once-through fashion of both solvent and aqueous streams during which timed samples are taken to measure the transfer of Cs. For hydraulic operation the organic and aqueous streams are circulated in closed loops and are operated in a continuous mode to demonstrate the pressure drop across the coalescer. Samples are

collected at the contactor outlet, and the inlet and outlet of the coalescer to understand the organic carryover into the aqueous streams.

Contactors

The CINC[®] contactor utilizes the centrifugal force generated by the rotation of a cylinder about a central axis.[6] By spinning two fluids of different densities within the cylinder, or rotor, the denser fluid (aqueous) is forced to the wall at the inside of the rotor while the less dense fluid (solvent) is forced toward the center of the rotor. As additional fluid is introduced to the rotor, the fluid within the rotor is forced upward to the rotor underflows and weirs. The less dense fluid flows toward the center of the rotor where it exits the rotor over the lighter phase weir through the lighter phase outlets. The more dense fluid continues up the rotor through the underflows, then exits over the heavy phase weir. Each fluid is collected in its own collector ring and then leaves the separator through the heavy and light phase outlets. The pilot-scale test facility contains a single full-scale V-10 contactor (10-inch diameter), a single full-scale V-05 contactor (5-inch diameter). The contactors are shown in Figure 1.

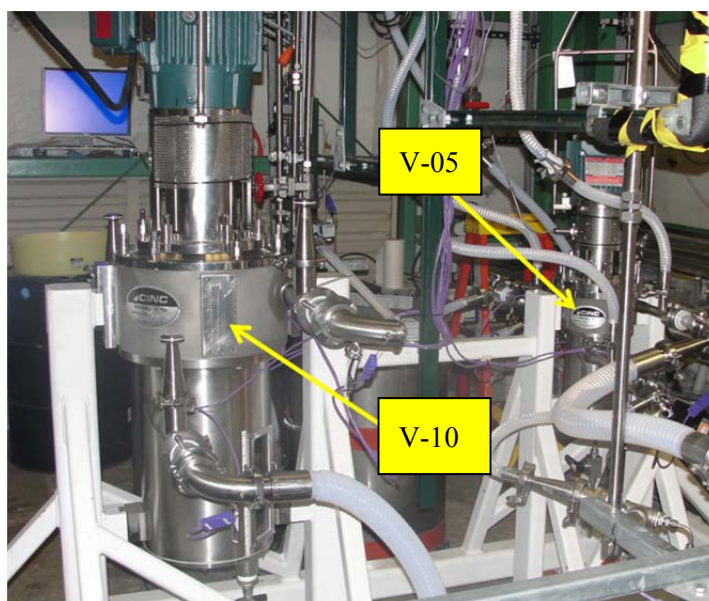


Figure 1. Full-Scale V-05 and V-10 Contactors in the Engineering Development Lab

Coalescer

The purpose of the coalescer is to combine the entrained solvent droplets and allow them to be collected in the decanter. Coalescence is a three step process. The first step is the collection or capture of droplets, the second step is the combining of several small droplets into larger droplets, and the third step is the rise or fall of the enlarged droplets by buoyancy or gravity. The test facility included a transparent coalescer housing that allows the use different sized coalescer elements, as required per the test matrix. This design permitted visual observations of solvent coalescence and proved invaluable in understanding some of the droplet size data and carryover data. The coalescers elements used in the test were supplied by Pall[®], constructed of polyphenylene sulfide, and met the MCU specifications. Testing sizes included a 20-inch long element with 10 micron nominal-sized pores and 40-inch long element with 20 micron nominal-sized pores.

Decanter

To provide solvent/aqueous phase disengagement, a 400-gallon decanter was used. The purpose of the decanter in plant operations is to allow the entrained solvent droplets to separate from the aqueous solution due to density difference and be recycled back into the process. The intent of the decanter during

testing was to be of sufficient diameter to minimize the superficial flow velocity of the bulk fluid, and consequently the flow velocity of buoyant solvent during hydraulic testing. As simulant enters the decanter, heavier aqueous solution moves to the bottom of the vertical vessel to be recirculated while most of the lighter solvent floats to the top where it is trapped to be recovered after testing. Any solvent that manages to leave the decanter through the bottom drain must be very small droplet size to be carried by the flow streamlines. Note that no effort was made in these tests to replicate MCU Strip Effluent or Decontaminated Salt Solution decanters design and operation.

Test Matrix

The matrix Table I is divided into two major sections; Mass Transfer (Tests 1, 2, and 3) and Hydraulic (Tests 4 and 5). The remaining tests (i.e., 0.9A & B) were performed to shakedown the overall operation of the test facility after it was cleaned with 1 M nitric acid and de-ionized (DI) water. These shakedown tests employed a previously used but filtered Isopar™ L solvent in the organic flow loop and the listed aqueous solution in the aqueous flow loop to prepare the test facility and evaluate the operation of all the test and measurement equipment.

TABLE I. Test Matrix for Testing from 02-27-2013 to 04-18-2013

Test #	Description	Test Duration	Contactors*	Contactors	Aqueous Simulant	Organic Flowrate	Aqueous Flowrate	Contactors Speed	Solution Temp.	Contactor Residence Times, ms			
		minutes	Turnover Volumes	Name	Concentration	GPM	GPM	RPM	°C	6 CRT	7 CRT	8 CRT	10 CRT
0.9A	Shakedown/Strip Hydraulic Testing w/Isopar-L (V-05)	cont.	N/A	V-05	0.01 M H ₃ BO ₃	various	various	various	33	N/A	N/A	N/A	N/A
0.9B	Shakedown/Extraction Hydraulic Testing w/Isopar-L (V-10)	cont.	N/A	V-10	5.6 M Salt	various	various	various	23	N/A	N/A	N/A	N/A
1A	Extraction (low flow)	9.6	8	V-10	5.6 M Salt	1	4	1200	23	0:07:12	0:08:24	0:09:36	N/A
1B	Extraction (medium flow)	4.8	8	V-10	5.6 M Salt	2	8	1700	23	0:03:36	0:04:12	0:04:48	N/A
1C	Extraction (high flow)	3.2	8	V-10	5.6 M Salt	3	12	1700	23	0:02:24	0:02:48	0:03:12	N/A
2A-1	Scrub Solvent (low flow)	50	N/A	V-05	0.025 M NaOH	1	0.27	1800	23	0:02:51	0:03:19	0:03:47	0:04:44
2A-2	Scrub Solvent (low flow)	50	N/A	V-05	0.025 M NaOH	1	0.27	1800	23	0:02:51	0:03:19	0:03:47	0:04:44
2B-1	Scrub Solvent (medium flow)	25	N/A	V-05	0.025 M NaOH	2	0.53	2100	23	0:01:25	0:01:39	0:01:54	0:02:22
2B-2	Scrub Solvent (medium flow)	25	N/A	V-05	0.025 M NaOH	2	0.53	2100	23	0:01:25	0:01:39	0:01:54	0:02:22
2C-1	Scrub Solvent (high flow)	17	N/A	V-05	0.025 M NaOH	3	0.80	2100	23	0:00:57	0:01:06	0:01:16	0:01:35
2C-2	Scrub Solvent (high flow)	17	N/A	V-05	0.025 M NaOH	3	0.80	2100	23	0:00:57	0:01:06	0:01:16	0:01:35
3A	Strip (low flow)	3.8	8	V-05	0.01 M H ₃ BO ₃	1	0.27	1800	33	0:02:51	N/A	0:03:47	0:04:44
3B	Strip (medium flow)	1.9	8	V-05	0.01 M H ₃ BO ₃	2	0.53	2100	33	0:01:25	N/A	0:01:54	0:02:22
3C	Strip (high flow)	1.3	8	V-05	0.01 M H ₃ BO ₃	3	0.80	2100	33	0:00:57	N/A	0:01:16	0:01:35
4A	Strip Hydraulics w/Coalescer (low flow) [20", 10 micron rating]	cont.	N/A	V-5	0.01 M H ₃ BO ₃	1	0.27	1800	33				
4B	Strip Hydraulics w/Coalescer (medium flow) [20", 10 micron rating]	cont.	N/A	V-05	0.01 M H ₃ BO ₃	2	0.53	2100	33				
4C	Strip Hydraulics w/Coalescer (high flow) [20", 10 micron rating]	cont.	N/A	V-05	0.01 M H ₃ BO ₃	3	0.80	2100	33				
5A	Extraction Hydraulics w/ Coalescer (low flow) [40", 20 micron rating]	cont.	N/A	V-10	5.6 M Salt	1	4	1200	23				
5B	Extraction Hydraulics w/ Coalescer (medium flow) [40", 20 micron rating]	cont.	N/A	V-10	5.6 M Salt	2	8	1700	23				
5C	Extraction Hydraulics w/ Coalescer (high flow) [40", 20 micron rating]	cont.	N/A	V-10	5.6 M Salt	3	12	1700	23				

*Note: V-10 Internal Volume ~ 6 gallons and V-05 Internal Volume ~ 0.6 gallon

To mimic plant operation each of the test sessions were subdivided into the extraction, scrub and strip (tests 1, 2 and 3 respectively). During extraction, the organic solvent separates cesium from the caustic 5.6 M Na salt solution simulant, which is a surrogate waste stream. The scrub uses a dilute caustic

solution to remove competing extraction ions and reducing the aqueous flow loop's high pH to prepare for the next process. Stripping is where a dilute acid solution removes the cesium from the organic solvent.

Each of the flow processes were further subdivided into low, medium, and high flows (designated A, B and C respectively) to evaluate the effect of flow rate on the decontamination efficiency. The contactor rotor speeds were varied based on the total flow through the contactor. The tests were conducted at the normal MCU operation temperatures, 23 °C for extraction and scrub with 33 °C for strip. In all cases the Organic to Aqueous ratio (O:A), was maintained at 1:4 for the extraction process and 3.75:1 for the scrub and strip processes matching the ratios currently run in MCU.

The medium flow rates in the test matrix, Table I, were chosen using the current MCU flow rates for the respective stream (extraction, scrub, or strip). The low-flow rate was chosen to be 50% of the medium-flow value, and the high-flow rate was selected at 150% of the medium-flow value. Per the test matrix, SRNL performed four extraction tests (three for mass transfer and one for hydraulic).

The mass-transfer tests processed the organic solvent and aqueous streams in an open-loop once-through operation. That is, a solvent or an aqueous solution left a feed tank, fed through a contactor, and ended up in a receipt tank. This approach was necessary to analytically measure the effectiveness of each process. Because the aqueous solutions were sampled for both cesium and organic carryover at the end of each test the coalescer and the decanter were not used in the mass transfer tests. Furthermore, between each process the aqueous flow loop had to be thoroughly rinsed with first water and then the next aqueous solution (i.e., Salt Simulant (with 75 mg/L Cs), sodium hydroxide [NaOH], or H₃BO₃), to ensure it was not contaminated with the previous solution. To minimize waste the aqueous feed tank was only filled with just enough solution to complete the low, medium, and high flow rate tests.

The hydraulic tests were conducted as closed-loop continuous operation; the feed tanks of the aqueous and solvent solutions were also the receipt tanks. For these tests, the coalescer and the 400-gallon decanter tank were employed. Here the effectiveness of the coalescer was evaluated and the decanter was used to help separate the organic from the aqueous solutions. After the strip hydraulic tests, which used boric acid, were completed, the aqueous flow loop was thoroughly flushed with water and then with the salt simulant to help minimize the formation of precipitated solids that would affect the overall results.

Next Generation Solvent

The solvent used in this testing was comprised of the six components that make up the blend that will be employed at MCU. It is comprised of: 0.0465 M MaxCalix, 0.500 M Cs-7SB (Modifier), 0.0035 M BOBCalixC6, 0.003 M TiDG, and 0.0015 M TOA with the balance being Isopar™ L (~74 wt %). The solvent used for this testing was blended by SRNL.

Aqueous Streams

To support the MCU contactor and coalescer testing, SRNL, with SRR approval, developed a 5.6 M Na Simulant Salt Solution recipe. The manufacture of the salt solution simulant was contracted to Harrell Industries, Inc. The strip solution was 0.010 M H₃BO₃ in DI water and the scrub solution was 0.025 M NaOH in DI water both prepared by SRNL.

Sampling Protocols

During the mass transfer tests, samples were pulled from two distinct sets of sample points, one from the organic stream and one from the aqueous stream. Portions of these samples were removed and sent for ICPMS analysis. Before each test a sample was taken from the organic and aqueous feed tanks and this organic sample was also used to measure its density. At the end of each test, samples were taken from the organic and aqueous receipt tanks.

The sample age was considered a critical factor in droplet size analysis. Organic material entrained in the aqueous phase will quickly coalesce and rise to the top. To minimize data skew associated with this behavior, a sample time protocol was developed for all droplet size analysis. The time from the taking of a sample to the time the sample was placed into the MicroTrac™ S3500 was controlled to 5 minutes. When a sample was taken, a stop watch was started, and the sample was placed into the MicroTrac™ S3500 at exactly 5 minutes after the sample draw. The timing of sampling was developed testing to balance the removal of entrained air.

For the hydraulic tests, samples were collected downstream of the contactor aqueous effluent, and upstream of the coalescer, and finally, downstream of the coalescer. Samples were collected in clean glass jars with Teflon™ lids.

DISCUSSION

Contactor Test Results

The extraction and strip tests were each operated individually in a single step; the exception was the scrub test, which was performed in two steps for each test to mimic two-stage operation that is prototypic of plant operation. SRNL examined the effects of the contactor speed and flow rate on the Cs distribution ratio in primarily three extraction, six scrub, and three strip tests.

The mass transfer results were obtained from the aqueous and organic samples that were analyzed by ICPMS for Cs (mass 133). Those results are shown in Table II, and Table III. For each row that contains a “0” for the contactor volume (CV), in the second column of each table, indicates the feed solution concentration. In those same second columns, the timed results are shown in the rows that indicate 6, 7, 8, or 10 CVs. The tables list the results in Cs concentration by volume as well as the Cs concentration ratio [D(Cs)] by dividing the Cs concentration for the organic phase by the Cs concentration in the aqueous phase.

The extraction results in Table II show that the NGS effectively extracted cesium from simulated waste stream, the 5.6 M Na aqueous solution. The initial Cs concentration in the simulated wasted dropped from between a high of 84 mg/L pre-extraction to a final low concentration of 3.3 mg/L post-extraction. Another way to look at this is the cesium distribution ratio ranged from 30.1 to 66.0 indicating good extraction.

TABLE II. Extraction Mass-Transfer Test Results

Extraction V-10 Contactor Test No.	# of Contactor Volumes Processed When Sampled	Org.	Aq.	D(Cs)
		Cs	Cs	Org/Aq
		mg/L	mg/L	-
1A	0	1.4	83.7	-
1A	6	245.5	4.5	53.4
1A	7	260.5	4.3	61.0
1A	8	270.6	4.1	66.0
1B	0	0.6	72.1	-
1B	6	188.2	5.2	31.3
1B	7	213.4	4.8	38.6
1B	8	311.6	5.0	46.5
1C	0	3.9	69.0	-
1C	6	210.4	3.3	38.5
1C	7	260.5	3.6	43.6
1C	8	166.3	3.3	30.1

The D(Cs) values shown are temperature corrected to reflect deviations from the desired (23 or 33 °C) operational temperatures. The temperature correction coefficients are the same ones used for pure NGS.[7] At this time there are no experimentally determined temperature correction coefficients for the blend solvent.

After the NGS extracts Cs from the waste stream, the Cs needs to be stripped back into the aqueous solution for ultimate disposition. To prepare the NGS to strip the captured Cs it is first “scrubbed” to remove the competing ions. Furthermore, it is also important to buffer the organic NGS with a mild caustic solution in preparation for contacting with the acidic stripping solution that will remove the captured Cs. The distribution ratio for the scrubbing is an order of magnitude smaller than for the extraction process. The D(Cs) is consistent with the recent NGS Extraction, Scrub, and Strip (ESS) tests.[8]

With the NGS scrubbed, it was then ready to release its captured Cs by using a dilute acid, 0.01 M H₃BO₃, in the stripping process. The results of the strip tests are listed in Table III.

TABLE III. Strip Mass Transfer Test Results

Strip V-05 Contactor	# of Contactor Volumes Processed	Org.	Aq.	D(Cs)
		Cs	Cs	Org/Aq
Test No.	When Sampled	mg/L	mg/L	-
3A	0	333.5	0.003	-
3A	6	33.2	358.6	0.0833
3A	8	30.9	361.6	0.0770
3A	10	31.4	405.2	0.0698
3B	0	152 ⁽²⁾	0.013	-
3B	6	32.5	338.4	0.0926
3B	8	24.7	368.7	0.0646
3B	10	24.8	389.5	0.0613
3C	0	137.8	1.460	-
3C	6	24.4	309.1	0.0467
3C	8	19.1	331.2	0.0341
3C	10	20.1	338.8	0.0351

In general, the process shows good performance under the tested range of conditions.

Equilibrium Sample Results

To evaluate the efficiency of the ion exchange that occurs during the very short time the solvent and aqueous streams intermingle in the contactors it is important to know what the exchange would be if the streams were in intimate contact for a long enough time that further exchange is not possible, i.e., when the streams are in chemical equilibrium with each other. Therefore, the samples that were regularly pulled from the organic and aqueous streams at the end of Tests 1A (extraction), 2A (scrub), and 3A (strip) were used to both measure the cesium concentration at the time pulled and to measure equilibrium concentrations. That is, each solvent and aqueous sample taken was split so one part was used to measure the instantaneous cesium concentration and one part was stored. Later the stored solvent and aqueous samples that were taken at exactly the same time were contacted in the appropriate proportions. From the samples, eleven contact tests were performed. For the extraction tests, the stored sampled from Test 1A, 1B and 1C were contacted in a 1:4 O:A volume ratio. For the scrub and strip tests only the low flow test samples were used (2A-8CV and 3A-8CV, respectively). These utilized organic and aqueous phases from Test 2A and 3A in a 3.75:1 O:A volume ratio. The samples were agitated by vigorous hand shaking for 30 seconds and then allowed to sit for several days. By allowing the samples to contact for an extended

period of time, the final equilibrium point for the phases were determined. At the end of that time, samples from each phase from each vial were sent for ICPMS for Cs analysis. The organic samples required digestion before analysis. The results are reported in Table IV.

TABLE IV. Mass Transfer Equilibrium Concentrations

Test ID	Temperature (°C)	Process Stream	Aqueous Cs-133 (mg/L) (1)	Organic Cs-133 (mg/L) (1)	D(Cs)	D(Cs) Temp Corrected	Instantaneous D(Cs) from Tables I&II
1A-6CV	17.5	Extract	1.8	161	79.6	58.3	53.4
1A-7CV	17.5	Extract	1.8	249	136.6	68.3	61.0
1A-8CV	17.5	Extract	1.8	229	127.4	63.7	66.0
1B-6CV	17.5	Extract	2.0	280	142.0	71.0	31.3
1B-7CV	17.5	Extract	2.0	199	100.5	50.3	38.6
1B-8CV	17.5	Extract	1.9	152	79.2	39.6	46.5
1C-6CV	17.5	Extract	1.7	191	115.6	57.8	38.5
1C-7CV	17.5	Extract	1.6	223	137.9	69.0	43.6
1C-8CV	17.5	Extract	0.8	123	152.5	76.3	30.1
2A-8CV	21	Scrub	39	165	4.2	2.63	3.35
3A-8CV	21	Strip	327	37	0.12	0.01	0.08

(1) Analytical measurement uncertainty = 20%

Except for the 1C-8CV test the equilibrium aqueous results show a high degree of consistency between the 6, 7, and 8 CV results, the equilibrium organic results vary to a much higher degree. This is the same trend noted in the instantaneous mass transfer results. Given the variation in the organic results there are no obvious trend in the 6-7-8 CV series for each test.

D(Cs) is the ratio of the solvent to aqueous cesium concentrations, i.e., for extraction the Cs ion is moving from the aqueous to the solvent, which means that the larger D(Cs) becomes the better the efficiency. For the scrub process the exact opposite occurs, the smaller the D(Cs) become the better the efficiency. The scrub process does not significantly affect Cs therefore D(Cs) should be basically unaffected.

For extraction, the equilibrium sample D(Cs) values are always higher than the equivalent instantaneous values for the extraction samples. This is an indication that the instantaneous extraction samples were not fully at equilibrium. The D(Cs) for the 2A-8CV (scrub) instantaneous and equilibrium results were essentially the same, as expected. For the strip samples (3A-8CV), the D(Cs) equaled 0.077 and the equilibrium value D(Cs) was 0.0112, indicating equilibrium was not reached. The 10CV for test 3A did see a slight drop in the instantaneous D(Cs) to 0.0698. However, when considering measurement uncertainty, the difference is only slightly significant; therefore, like the extraction results the short time that the solutions inhabited the contactors the ion exchange did not reach a state of equilibrium.

Stage Efficiencies

Stage efficiency was calculated using the Murphree stage efficiency calculation.[9] The results are presented in Table V. The Murphree stage efficiency is calculated by dividing the difference between the initial and instantaneous Cs concentrations for a test by the difference between the initial and temperature-corrected equilibrium Cs concentrations. A temperature correction was necessary because the equilibrium tests were run at a temperature that is not at the test temperature and results are significantly dependent on temperature. Calculations are based on the stage being depleted of Cs, which is the aqueous stream for extraction and the organic stream for stripping.

TABLE V. Stage Efficiency

Test ID	Rotor Speed (rpm)	Aqueous Flow (gpm)	Organic Flow (gpm)	Contactor Volumes When Sampled	Stage Efficiency (%)
1A	1200	4.0	1.0	6	98.7
				7	99.2
				8	99.3
				average	99.1
1B	1700	8.0	2.0	6	97.0
				7	97.7
				8	97.1
				average	97.3
1C	1700	12.0	3.0	6	96.9
				7	96.1
				8	96.1
				average	96.4
3A	2100	0.27	1.0	8	82.7
Stage efficiency values shown are temperature corrected					

The data show good efficiencies for the extraction, Tests 1A-1C, ranging from 96.1% to 99.3%. The Test 3A, 1 gpm organic and 0.27 gpm aqueous, strip efficiency was calculated to be 82.7%.

The calculated efficiencies were used as the basis for input into SASSE^a to predict the total DF of a multistage system, in this case, 7 extraction, 2 scrub, and 7 strip contactor stages. Three different sets of stage efficiencies were assumed, 90% and 80% for each all stages, as well as a final case assuming 95% extraction efficiency and 80% scrub and strip efficiency. All three stage efficiency cases used as input, the operating conditions and results of the tests performed in this study (flow rates, DF, etc.). The DF values and concentration factor (CF) are shown in Table VI.

TABLE VI. SASSE Calculated DF Values for MCU Stages

Case #	Organic Flow Rate (gpm)	Extraction		Strip		Stage Efficiency	DF	CF
		Flow Rate (gpm)	D(Cs)*	Flow Rate (gpm)	D(Cs)*	%		
1	1	4	60.1	0.27	0.077	80	3359	14.8
2	2	8	38.8	0.54	0.073	80	2021	15.1
3	3	12	37.4	0.8	0.039	80	3637	15.0
4	1	4	60.1	0.27	0.077	90	18,822	14.8
5	2	8	38.8	0.54	0.073	90	12,466	15.1
6	3	12	37.4	0.8	0.039	90	45,939	15.0
7	1	4	60.1	0.27	0.077	95 extraction 80 scrub/strip	4870	14.8
8	2	8	38.8	0.54	0.073	95 extraction 80 scrub/strip	3503	15.1
9	3	12	37.4	0.8	0.039	95 extraction 80 scrub/strip	21,089	15.0
* Average from the 6, 7 and 8 CV samples								

To be conservative, the 80% stage efficiency is currently assumed when SASSE is run to support MCU operation. The 90% case was run to show the improvement expected by an increase in stage efficiencies. The 95% extraction with the 80% scrub and strip assumed efficiencies more closely represents the efficiencies from testing. Therefore, the results of the tests performed would predict DF in excess of 3500. At lower flow rates, the organic phase becomes limiting and excessive air can enter the contactor

^a SASSE= Spreadsheet Algorithm for Stagewise Solvent Extraction

chamber causing deteriorating performance. MCU operates near the lower hydraulic capacity for the contactors. The high flow rate of this test (e.g., 12 gpm aqueous) is well within the normal hydraulic capacity of the equipment and far from the maximum operating flow rate. Hence, one anticipates slightly poorer performance for the low flow rates.

Hydraulic Performance

After the completion of the mass transfer tests, the system was adapted for hydraulic testing. This included setting the valves from once-through operation to recirculate both the aqueous and organic streams. On the aqueous side, the coalescer and decanter were valved into the system. Thus the discharge of the aqueous feed pump now went to the coalescer and from the coalescer to the decanter prior to being fed to the contactor. Since the system already contained strip solution, the stripping hydraulic tests were conducted prior to the extraction hydraulic tests.

The sampling sequence started after the system obtained relatively steady flows. The first sample was taken at the contactor outlet. A time count was initiated with a stop watch once the sample was pulled. The sample was sent for MicroTrac™ analysis that was to be started exactly 5 minutes after the sample was pulled. The next sample was pulled from the coalescer inlet sample port 30 minutes after the previous sample. The time between samples was dictated by the time required to run the initial sample and prepare for the next sample. Therefore, the time interval was set by the amount of time required for the MicroTrac™ to perform the analysis and set up for the next analysis.

The third sample was pulled from the coalescer outlet 30 minutes after the coalescer inlet sample. After the third sample was pulled, three samples were pulled simultaneously from the three sample ports. These samples were for potential SVOA and HPLC analyses. Once the coalescer outlet sample was obtained, the next sample would start the sample sequence all over again. Hence, 30 minutes later a sample was pulled from the contactor outlet for MicroTrac™ analysis.

Overall, the operation of the strip hydraulic testing, Tests 4A, 4B and 4C, proceeded without incident. The system behaved well and showed no signs of instability.

The organic stream was visually cloudy but did not have significant aqueous carryover observed as a separate layer in the sample. The pre-coalescer aqueous sample was also cloudy and did not have a distinct organic layer indicating significant carryover. The post-coalescer sample was clearer than the pre-coalescer sample, as was expected.

TABLE VII. Hydraulic Strip Solvent Carryover to Aqueous Stream Test Results

Flow Rates O & A (gpm)	Test Identifier	Isopar SVOA (mg/L) (1)	Modifier SVOA (mg/L) (1)	Modifier HPLC (mg/L) (1)
1 & 0.27	4A_AQ_POST_Contactor	25	25	39
1 & 0.27	4A_AQ_PRE_Coalescer	12	34	39
1 & 0.27	4A_AQ_POST_Coalescer	<10	14	18
2 & 0.53	4B_AQ_POST_Contactor	67	45	56
2 & 0.53	4B_AQ_PRE_Coalescer	69	52	58
2 & 0.53	4B_AQ_POST_Coalescer	<10	17	22
3 & 0.8	4C_AQ_POST_Contactor	39	47	39
3 & 0.8	4C_AQ_PRE_Coalescer	29	32	49
3 & 0.8	4C_AQ_POST_Coalescer	<10	15	20
Analytical measurement uncertainty = 20%				

A trend for the impact of increasing the strip flow rates on carryover is not evident from the available data. Though the lowest flow rate has the lowest carryover number, the middle flow rate has the highest

carryover and the highest flow rate carryover number is between the two. However, carryover may be low enough at all these flows to be essentially the same.

As described in the methodology section, samples were obtained for particle (droplet) size analysis. The results show that the post-contactor and pre-coalescer droplet means are very similar. The post-coalescer samples have significantly higher mean values. The Test 4A data illustrates a greater spread in the data results than either Test 4B or Test 4C. This is probably due to the lower flow rate and the sampling location.

For all three tests, the post-contactor samples have significantly higher mean diameters. This trend indicates that the coalescer is performing well.

At the end of the extraction testing, a full set of samples was taken simultaneously from the three sample ports. This final set of samples was sent for analysis to determine the amount of solvent carryover. The results of the analyses are presented in Table VIII.

Table VIII. SVOA and HPLC Analysis of Aqueous Samples during Extraction Hydraulic Testing

Flow Rates O:A (gpm)	Test Identifier	Isopar by SVOA (mg/L)	Modifier by SVOA (mg/L)	Modifier by HPLC (mg/L)
1/4	5A_AQ_POST_CONT	370	81	106
1/4	5A_AQ_PRE_COAL	279	51	81
1/4	5A_AQ_POST_COAL	<10	<10	<10
1/4	5AR_AQ_POST_CONT	370	35	182
1/4	5AR_AQ_PRE_COAL	410	37	192
1/4	5AR_AQ_POST_COAL	39	32	12
2/8	5B_AQ_POST_CONT	450	58	217
2/8	5B_AQ_PRE_COAL	400	49	151
2/8	5B_AQ_POST_COAL	19	<10	10
3/12	5C_AQ_POST_CONT	480	71	222
3/12	5C_AQ_PRE_COAL	480	60	177
3/12	5C_AQ_POST_COAL	44	<10	22

Table VIII presents the analyses for Isopar™ L and Modifier by SVOA and HPLC for samples taken during the extraction process. Generally, SVOA is considered to have a lower uncertainty for Isopar™ L than for Modifier and the HPLC a lower uncertainty for Modifier. The data show that the impact of the feed tank and centrifugal pump between the contactor outlet and the coalescer inlet is small on the carryover numbers as the values at the two sample points show no consistent trend. The values for solvent concentration in the aqueous stream at the contactor discharge and the coalescer inlet are similar. This implies that the entrained droplets being sampled have insufficient time to coalesce in the 80-gallon feed tank, which sits between the contactor discharge and the coalescer inlet. As a reminder, the contactor discharge returns to the top of the feed tank and the pump suction is on the bottom of the feed tank. The relatively large diameter of the tank reduces the superficial velocity giving the solvent the opportunity to separate and not reach the pump suction.

The analysis shows that there is an increase in the amount of Isopar™ L and Modifier carryover as flow rates increase, though with the analytical uncertainty it does not appear to be significant. There is a significant drop, an order of magnitude, in the amount of Isopar™ L (by SVOA) and Modifier (by HPLC) after passing through the coalescer. The post-coalescer data presented here were used as input to the ARES Corporation’s decanter model and will be discussed later in this paper.

In addition to the amount of carryover, droplet size was also measured. Due to the density difference between the solvent and aqueous streams, large droplets float to the top of the flow stream. With the post-coalescer sample location near the center of the flow field, the largest droplets are not collected in the sample. With the test configuration design, the feed tank acts as a settling tank. Large droplets would be expected to separate from the solution and not return to the system. As the flow rates increased, it was expected that the carryover would also increase since this would reduce the amount of time for the solvent to separate. Furthermore, the increased velocity through the coalescer is expected to reduce coalescence. Additionally, the higher velocity tends to increase the disengagement of the Solvent from the coalescer media. However, for each test flow rate, the post-contactor and pre-coalescer sample means were consistently near 10 μm . There was a slight increase in the post-coalescer mean value for each test which was approximately 4 μm for Test 5A, 6 μm for Test 5B and 8 μm for Test 5C. The exception to this pattern was the first pre-coalescer sample in the Test 5C. This value was inconsistently high, but was measured high in all three sample analyses.

Decanter Modeling - Coalescer Calculations

ARES Corporation designed the coalescer-decanter currently installed in the MCU that is downstream of the Pall coalescer. The coalescer-decanter system was not included in the SRNL test stand and its performance is therefore predicted using the model that was used in its design. To design the coalescer-decanter, they developed a spreadsheet to calculate the coalescence of MCU solvent droplets as a function of droplet size distribution and the rise of droplets in the decanter. The results of the droplet size analysis were used as input to the ARES model. The model predicts a fraction in a particle size range that will be recovered by the decanter.

During testing, samples were obtained from the three sample points; post-contactor, pre-coalescer, and post-coalescer. The post-contactor sample was obtained immediately after discharge from the contactor. The pre-coalescer sample was obtained just prior to the coalescer and the post-coalescer sample at the coalescer outlet. To flow from the post-contactor to the pre-coalescer sample ports, the solution passes through the 80-gallon feed tank and centrifugal pump. Therefore, some differences in these samples are expected.

Table IX shows the average of the calculated fraction of droplets recovered by the coalescer-decanter corresponding to each of the tests. The calculations predict the DSS coalescer-decanter should recover a larger fraction of the BOBCalixC6 solvent than NGS. With the SE coalescer-decanter, in some cases the baseline solvent was predicted to be recovered better, while in others the NGS was predicted to be recovered better.

Table IX. Fraction of Droplets Calculated to be Recovered by the Coalescer Decanter

Stream	Aq. Flow Rate (gpm)	Test	Not Recovered (average of samples)	Recovered (average of samples)
DSS	4	5A-Extraction	0.3%	99.7%
DSS	8	5B-Extraction	52.6%	47.4%
DSS	12	5C-Extraction	43.2%	56.8%
SE	0.27	4A-Strip	8.5%	91.5%
SE	0.54	4B-Strip	23.3%	76.7%
SE	0.8	4C-Strip	18.0%	82.0%

During NGS testing, large masses of organic material were observed in the aqueous stream following passage through the coalescer. Analytical results showed the concentration of Isopar™ L in samples collected downstream of the coalescer to be significantly less than the concentration measured in samples collected at the inlet of the coalescer. Visual observation shows that a large fraction of the solvent has coalesced and has floated to the top of the coalescer housing. Since the sample point is mid-stream, this material would not be captured by the sampler. However, since this material has already coalesced and

separated, it would be easily recovered in the MCU decanters. Table X shows the solvent that would be recovered in the decanter from the coalescer in the test stand from the measurements of the solvent carryover into the coalescer, the amount of solvent carryover in the post coalescer sample, and calculating the amount of solvent carryover that would be recovered based on the organic droplet size measured in the post coalescer sample.

Table X. Solvent Recovery from Coalescer during Testing

Flow Rates O/A (gpm)		SVOA	Isopar™ L	Isopar™ L
	Sample ID	Isopar™ L (mg/L)	Relative Conc.	Recovery
STRIP				
1/0.27	4A_AQ_POST_CONT	25	1.00	0%
	4A_AQ_PRE_COAL	12	0.48	52%
	4A_AQ_POST_COAL	<10	0.40	≥60%
2/0.53	4B_AQ_POST_CONT	67	1.00	0%
	4B_AQ_PRE_COAL	69	1.03	-3%
	4B_AQ_POST_COAL	<10	0.15	≥85%
3/0.8	4C_AQ_POST_CONT	39	1.00	0%
	4C_AQ_PRE_COAL	29	0.74	26%
	4C_AQ_POST_COAL	<10	0.26	≥74%
EXTRACTION				
1/4	5A_AQ_POST_CONT	370	1.00	0%
	5A_AQ_PRE_COAL	279	0.75	25%
	5A_AQ_POST_COAL	<10	0.03	≥97%
2/8	5B_AQ_POST_CONT	450	1.00	0%
	5B_AQ_PRE_COAL	400	0.89	11%
	5B_AQ_POST_COAL	19	0.04	96%
3/12	5C_AQ_POST_CONT	480	1.00	0%
	5C_AQ_PRE_COAL	480	1.00	0%
	5C_AQ_POST_COAL	44	0.09	91%

Combining the data from Table IX and Table X allows us to predict the overall recovery of NGS by both the coalescer and the coalescer-decanter for the DSS and SE streams. Table XI shows more than 90% of the solvent is predicted to be recovered by both the coalescer and the coalescer decanter.

The testing occurred at 4, 8 and 12 gpm. However it should be noted that the ARES model is designed for 9.07 gpm. Since increased velocity decreases coalescence, using the model to predict the results of a lower flow would result in better performance than the model prediction. Therefore, the 4 gpm results are expected to under predict the amount of solvent recovered. Consequently, the 12 gpm model prediction is expected to over predict the amount of solvent recovered.

Table XI. Predicted Overall Recovery of NGS

Stream	Test	Aqueous Flow Rate (gpm)	Recovered from Decanter Inlet Coalescer (average of samples)	Recovered from In-line Coalescer(1) (average of samples)	Recovered Total (average of samples)	Post-Decanter Isopar (ppm) (average of samples)
DSS	5A-Extraction	4	100%	97%	100%	0.033
DSS	5B-Extraction	8	47%	96%	98%	9.5
DSS	5C-Extraction	12	57%	91%	96%	18.7
SE	4A-Strip	0.27	92%	60%	97%	0.85
SE	4B-Strip	0.54	77%	85%	97%	2.3
SE	4C-Strip	0.8	82%	74%	95%	1.8
(1) Pall Coalescer						

More than 96% of the DSS droplets have coalesced to a large enough size (70 micron) to be removed in the decanter based on a design flow rate of 9.07 gpm. If the flow rate is increased above 9 gpm, the removal of droplets in the decanter must be reassessed. The higher flow rate reduces the residence time in the decanter, causing reduced recovery. In addition, at a flow rate of 12 – 15 gpm, the flow in the inlet to the coalescer-decanter would become turbulent. The energy and shear from turbulence could cause some shearing of the droplets and the formation of droplets that are too small to be removed in the decanter.

More than 93% of the SE droplets have coalesced to a large enough size (40 micron) to be removed in the SE decanter based on a design flow rate of 0.6 gpm. If the flow rate is increased above 0.6 gpm, the removal of droplets in the decanter must be reassessed. The higher flow rate reduces the residence time in the decanter, causing a decrease in recovery of droplets. Increasing the flow rate increases the Reynolds number in the inlet, which may move the flow field out of the laminar flow regime needed for efficient coalescence.

CONCLUSIONS

SRNL conducted single-stage pilot-scale testing utilizing full-scale strip/scrub (V-05) and extraction (V-10) contactors. Testing utilized a solvent blend of NGS components and the solvent currently in operation at MCU. The tests concluded that the blend solvent in the expected O:A ratio of 1:4 extraction and 3.75:1 strip produced no hydraulic issues at the tested flow rates. The extraction flow rates tested were 4 gpm, 8 gpm and 12 gpm (aqueous). The strip flow rates tested were 0.27 gpm, 0.54 gpm and 0.8 gpm (aqueous).

Increasing the flow rates had little effect on the performance of the solvent. Stage efficiency and mass distribution ratios were determined using Cs mass transfer measurements. The nominal D(Cs) measured was approximately 37-60. The data indicate that equilibrium is achieved rapidly and maintained throughout sampling. The data showed greater than 95% stage efficiency for extraction. No statistically-significant differences were noted for operations at 12 gpm aqueous flow when compared with either 4 gpm or 8 gpm of aqueous flow.

The first scrub test yielded an average D(Cs) value of 3.33 to 5.20, and the second scrub test produced an average value of 1.82 to 2.25. For stripping behavior, the D(Cs) values ranged from 0.039 to 0.077. The stage efficiency of the low flow (0.27 gpm aqueous) strip was calculated to be 82.7%.

The concentrations of Isopar™ L and Modifier were measured using SVOA and HPLC to determine the amount of solvent carryover. For low-flow conditions in stripping, Isopar™ L concentration measured 25 mg/L. For moderate-flow conditions, Isopar™ L was ~69 mg/L. For high-flow conditions, Isopar™ L was 39 mg/L.

In extraction, the quantity of pre-coalescer Isopar™ L carryover was ~280-410 mg/L at low flow, ~400-450 mg/L at moderate flow, and ~480 mg/L at high flow. The amount of post-coalescer (pre-decanter) Isopar™ L carryover was less than 45 mg/L for all flow rates.

Droplet-size data obtained by MicroTrac™ S3400 analyzer consistently shows that the droplet size post-coalescer is significantly greater than the post-contactor or pre-coalescer samples during strip hydraulic testing. Increased flow rates did not show a consistent impact on the droplet size results. For the extraction testing, droplet size analysis showed that the post-contactor and pre-coalescer samples were essentially the same. The post-coalescer droplet mean diameters were slightly less than the pre-coalescer samples with a very slight upward trend in mean as the flow rate was increased.

The carryover results and droplet size measurements were used for the analysis of the decanter performance. Results show that over 93% of the solvent carryover from stripping is predicted to be recovered and over 96% solvent carryover from extraction is predicted to be recovered.

In general, the results of the testing show that NGS is expected to have a higher Cs removal than the current solvent. This benefit will have a greater impact as SRS moves to higher Cs salt feeds. In addition, it is expected that NGS will have less carryover than the current solvent and thus less organic will be passed on to the downstream facilities.

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