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Scale-up of Caustic-Side Solvent Extraction Process for Removal of Cesium at Savannah River Site

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Abstract: The caustic-side solvent extraction process to remove radioactive cesium from Department of Energy salt waste was developed using small-scale annular centrifugal contactors. A scale-up factor of 750X is required. Testing with commercially available centrifugal contactors identified key design and operational parameters. Air flow is significant and the rotor bottom must remain covered to prevent surging flow. The Clean-in-Place feature was modified to allow hands-on maintenance. Flow rates and rotor speeds were optimized to reduce other-phase carryover. Startup, operation, and recovery methods were confirmed. Testing validated a Decontamination Factor >12 and a strip Concentration Factor of 12 to 15.

Keywords: Centrifugal contactor; CSSX; Solvent extraction

INTRODUCTION

In 2004, the Department of Energy (DOE) directed Westinghouse Savannah River Company (WSRC) to develop a Caustic-Side Solvent Extraction (CSSX) process at the Savannah River Site (SRS) capable of removing cesium from 1 million gallons a year of dissolved salt solution. This facility would provide interim processing for cesium containing salt solution until the Salt Waste Processing Facility (SWPF) comes on-line.

The DOE design inputs (1) were to utilize contactors similar in design to those to be used in the SWPF, assume class C waste with less than 0.5 Ci/gal Cs-137, achieve a Decontamination Factor (DF) greater than

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12, include the ability to clean the contactors in place, and assume an operating life of three years. The Modular Caustic-Side Solvent Extraction Unit (MCU) process salt solution flow rate should be 3.5 gallons per minute (gpm) to 8.5 gpm. WSRC embarked on a design, test, and build program to achieve these criteria as described in the following text. All DOE design criteria have been met or exceeded by WSRC.

PROCESS DEVELOPMENT

The initial development of the process was performed jointly at Argonne National Laboratory (ANL) and Oak Ridge National Laboratory (ORNL). Development of the solvent and the unique extractant was performed at ORNL and initial process flow sheet development and testing was performed at ANL. ANL used 2-cm centrifugal contactors (2-cm designates the rotor diameter of the contactor) for the initial testing (2), which was successful. An optimized solvent was subsequently developed by ORNL to decrease the probability of third-phase formation and allow an increase in the extractant concentration (3).

Further flowsheet testing was performed at the Savannah River National Laboratory (SRNL) using real waste from the SRS tank farms. The testing utilized 2-cm contactors; 16 extraction contactors, 2 scrub contactors, 16 strip contactors, and 2 wash contactors. Using real waste containing Cs-137, the process was operated in the SRNL Hot Cells. The results (4) demonstrated a DF $>40,000$ and a Concentration Factor (CF) of 12–15.

CONTACTOR SCALE-UP TESTING

Maximum salt solution flow during the Hot Cell testing at SRNL was 43 ml/min. Maximum salt flow for the MCU is 8.5 gpm, a factor of $\sim$750 times greater. The DOE directed WSRC to utilize technology similar to that being used for the SWPF. The SWPF is using CINC (Costner Industries Nevada Corporation) centrifugal contactors. WSRC made an exhaustive search of centrifugal contactor manufacturers and CINC was the only viable option. The SRS MCU process flow rates required to support DOE objectives are:

- Salt Solution 3.5–8.5 gpm
- Scrub 0.23–0.57 gpm
- Strip 0.23–0.57 gpm
- Wash 0.23–0.57 gpm
- Solvent 1.17–2.83 gpm

The models of CINC contactors chosen were based on the manufacturer's recommendations for throughput. Ten-inch-rotor contactors, model V-10 (Fig. 1), were selected for the salt solution bank (manufacturer specification of 30 gpm maximum flow) and five-inch-rotor contactors, model V-05 (6 gpm maximum), were selected for the scrub, strip and wash banks.

A vendor was chosen to build, and test the 18-stage contactor process. The first step in the process was to individually test the V-05 and V-10 contactors. These tests determined the optimum rotor speed and weir size to minimize solvent carryover and maximize throughput. The tests also allowed observation of general hydraulic behavior and to identify any areas for improvement.

To facilitate the individual contactor testing, a test stand capable of holding both contactors was constructed. The test stand also provided a stable foundation to evaluate contactor vibration. It also allowed cold

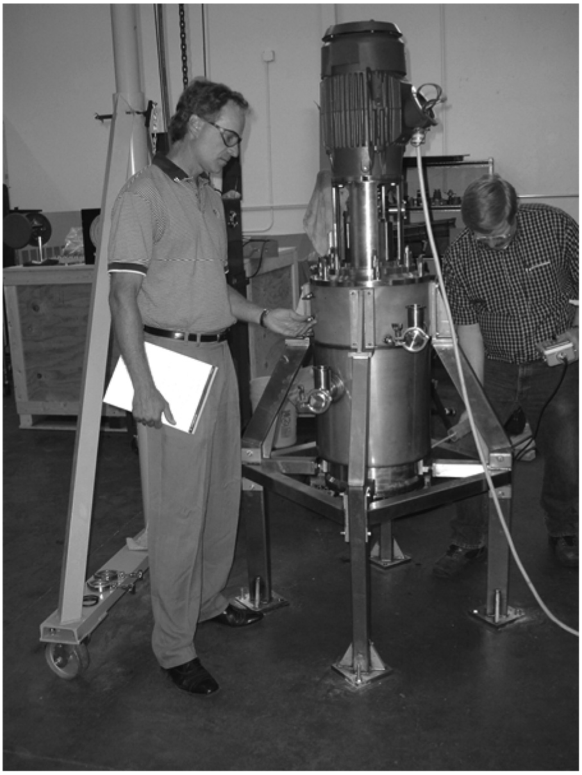

Figure 1. CINC V-10 contactor with motor.

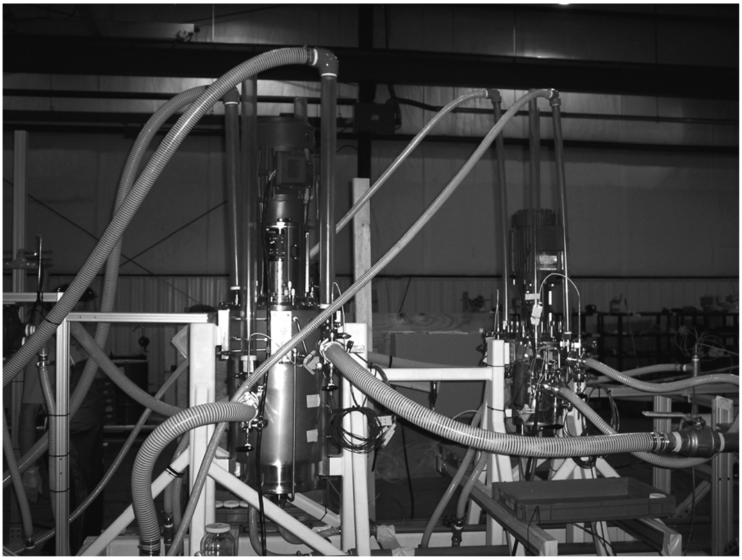

Figure 2. V-10 and V-05 contactors mounted on test stand.

feeds to be centrally located and easily accessible. The contactors mounted on the test stand are shown in Fig. 2.

RESULTS AND DISCUSSION

The most significant hydraulic issue that arose during Hot Cell testing with the 2-cm contactors was flow between stages. Due to the low flow rate, the slope of the interstage lines was critical to obtain adequate flow. The interstage fluid inertial forces far exceed surface tension forces in five- and ten-inch rotor contactors, so obtaining adequate interstage line slope between contactors was not an issue.

The individual contactor testing involved selecting weir sizes and rotor speeds that minimized organic carryover. Salt simulant representing average SRS feed, which had been used for all previous CSSX testing, was utilized. Solvent without the extractant (hydraulically insignificant) was used as the organic phase. Organic carryover >1000 ppm was obtained from both units, which was well above the design criteria. Further investigation revealed that the organic weir diameter in the V-05 was incorrectly specified. Using the correct organic weir diameter, a more appropriate heavy phase weir size was selected and organic carryover was reduced.

Hands-on maintenance is a criterion due to the short three-year operating life. CINC contactors have a Clean-in-Place (CIP) system as a standard feature; however, it focused on cleaning the internal rotor and heavy phase underflow regions. At SRS Cs-137 is the primary radionuclide of concern from a worker dose standpoint, so it was important to modify the contactors so that all wetted areas within the contactor would be cleaned. The standard CINC CIP includes perforations in the rotor shaft plenum through which cleaning solution is sprayed onto the rotor internal surface, and nozzles in the underflow region. SRS added spray ball nozzles in the annular region, 90 degrees apart, and two spray nozzles in each collector ring, 180 degrees apart. To test the system, all internal components were coated with yellow food dye (Fig. 3) and the system was run. The CIP system was able to remove all food dye (Fig. 4) and considered to be acceptable for decontamination during hot operations to reduce the dose rate.

Both inlets and both outlets on CINC contactors are vented. In past tests on the contactors anomalies in air flow through the vents were observed. The goal was to minimize air flow to the bottom of the rotor. The rotor would then be "sealed" so no air flow could bypass the annular region and directly enter the rotor. That would allow the fluids in the annular region to mix more thoroughly and to prevent surges in flow as the rotor bottom covers then uncovers. Figure 5 displays typical air flow through each of the inlet and outlet vents.

A comprehensive test plan was developed to explore the effect of a number of contactor variables and modify those that would accomplish the goal of efficient operation. The purpose of the testing was to:

Figure 3. Rotor before clean-in-place.

Figure 4. Rotor after clean-in-place.

1. Identify differences between the standard CINC "TA" rotors (with bearings at the top and bottom of the rotor) and the new "TAH" or "hanging" rotor purchased for the MCU
2. Increase the probability of successful mass transfer testing by investigating methods to increase the liquid height in the mixing zone (annulus)

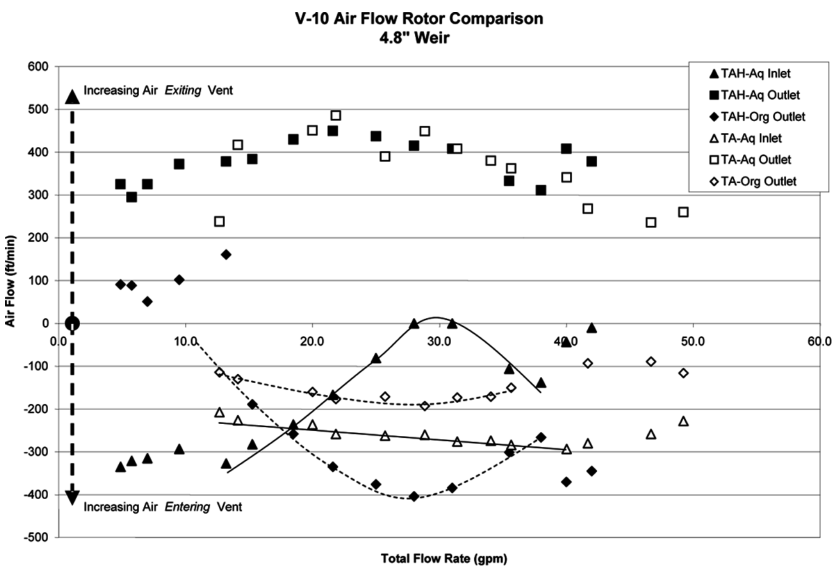

Figure 5. Typical vent air flow (TAH-"hanging" rotor, bearings only at top of rotor; TA-bearings at top and bottom of rotor).

3. Recommend preferred contactor configurations for the V-05s and V-10 s based on the testing.

The parameters investigated are (5).

- Rotor inlet size
- Bottom vane shape (curved vs. straight)
- Major vane diameter
- Vane-to-rotor gap height

A V-05 and a V-10 were procured from the vendor that had removable bottom plates, adjustable rotor inlets, and windows on the housing that allowed the height of fluid in the annular region to be observed.

After varying the size of the rotor inlet it was discovered that this was not a viable parameter to increase the fluid height in the annulus. Increases in the rotor inlet diameter resulted in a step jump in fluid height for the V-10. One larger diameter showed no increase, then the third and fourth diameter increases resulted in a step jump to the top of the window. The standard rotor allowed the contactor to operate in the fully pumping mode, then an increase in rotor inlet diameter put it into the partially pumping mode. This parameter was deemed too sensitive to consider for increasing fluid height.

The standard CINC design incorporates curved vanes on the bottom plate (Fig. 6). DOE designed contactors have always had straight vanes.

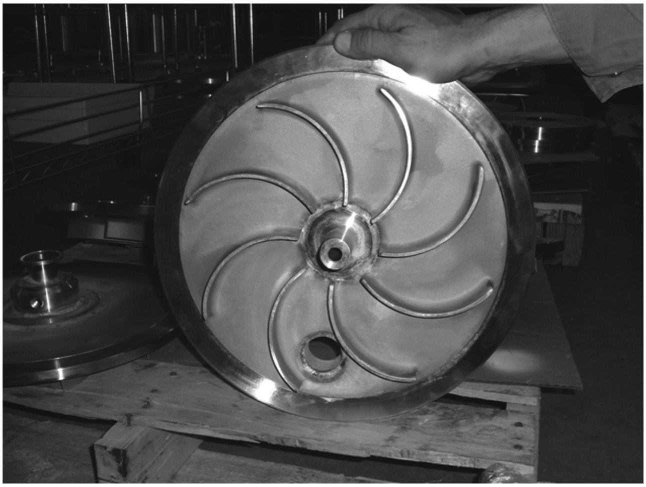

Figure 6. Curved vane bottom plate.

A series of tests was conducted using both styles of vanes to evaluate the effect on fluid height in the annulus.

A number of vane diameters were tested with curved and straight vanes. The only vane configuration that demonstrated any appreciable difference in annulus fluid height was curved vanes in the V-05. Those vanes were of slightly less diameter than the base case vanes.

Increasing the vane-to-rotor gap reduced the pumping efficiency of the rotor and therefore raised the fluid level in the annulus. The effects were not as significant as those observed with changes in the vane diameter. Most of the increase in annulus height was seen only at the higher flow rates for the V-05. The V-10 showed only a small increase in annulus height over the MCU flow range.

Varying the V-05 rotor inlet diameter had no appreciable affect on the annulus height. Increasing the gap between the rotor bottom and the top of the curved vanes and decreasing the major vane diameter the results were an increased annulus height with the vane diameter having a slight advantage over the MCU flow range. Testing with straight vanes typically showed larger annulus heights than curved vanes, but the air flow was not reduced by the increasing liquid height. Therefore, the major vane diameter on the V-05 contactors was reduced to 5.17" from 5.5", with no change to any other parameters.

Varying the V-10 rotor inlet did not cause a gradual increase in annulus height, but resulted in a step change in height that flooded the contactor. Decreasing the major diameter of the curved vanes resulted in an increase in annulus height up to the point the contactor was no longer able to pump. Testing with different straight vane diameters the contactor lost pumping ability with a much smaller diameter change than with the curved vanes. Increasing the vane-to-rotor gap also increased the annulus level, but to a lesser extent than the vane diameter changes. None of the parameter changes showed any improvement in the air flow through the contactor. No changes were made to the V-10 contactors.

INDIVIDUAL CONTACTOR MASS TRANSFER TESTING

The extraction V-10 contactor was tested using a salt simulant and an actual solvent containing extractant. The strip V-05 contactor was tested using strip solution and solvent. "Cold" Cs-133 was used in place of radioactive Cs-137. This testing was completed to assure that individual stage efficiency was high enough to allow the design DF and CF to be obtained.

The contactors were tested at the various design flow rates and rotor speeds. Efficiencies greater than 80% were obtained, which validated the assumption that the CINC contactors were able to meet the design criteria.

VENDOR FULL SCALE TESTING

When the specifications for the contactors had been finalized, testing of the assembled full bank of 18 contactors (Fig. 7) commenced at a vendor facility. A tank farm to supply feeds to the process was constructed and the full process was tested.

The purpose of the vendor full scale test was to observe the hydraulics, to demonstrate a decontamination factor (DF) ≥ 12, and to demonstrate a concentration factor (CF) ≥ 12. All seven V-10 contactors and all eleven V-05 contactors were assembled as they would be in the MCU. The operating conditions were selected based on the results of the Individual Contact test and Mass Transfer test. This was the first test of the MCU flow sheet at full scale. If the objectives are successfully met this will then conclude contactor testing until Cold Chemical Runs at SRS.

Testing included (6):

- Mass Transfer Test (using "cold" Cs-133)
- Durability Test (ability to run continuously for 96 hours)

Figure 7. Contactor assembly at vendor facility.

- Upset/Transient Conditions Testing
- Transient Condition Testing involved stopping certain unit operations or feed streams in order to see how the contactors responded. The events tested were in order, as follows:
  - Loss of Process Vessel Vent (PVV) system
  - Loss of Temperature Control (tepid water) system
  - Loss of solvent feed flow
  - Loss of salt solution feed flow
  - Loss of scrub feed flow
  - Loss of strip feed flow

  The hydraulic impacts of each of the events were observed, and samples for carryover (both aqueous and organic) were collected.
- Clean-In-Place Test

Integrated testing provided a vast amount of information pertinent to the operation of the contactors in MCU:

- Due to a control system programming error, the skid experienced an "uncontrolled shutdown." A procedure was developed that successfully recovered the unit to an operable condition without having to drain the contactors.
- The MCU is capable of achieving a cesium Decontamination Factor at least an order of magnitude greater than the design specification.
- The MCU can meet and exceed the target concentration factor of 12 for cesium in the strip effluent, effectively minimizing the impact on DWPF cycle time due to boiling off excess water.
- Small variances in strip flow rate (2%) will have a noticeable impact on the concentration factor. Accurate and precise control of process streams is needed to assure process requirements are met.
- Solvent carryover from the full bank of contactors is within the capability of the MCU coalescers and decanters to meet the output requirement of 50 ppm Isopar. Results are best at low to mid salt solution feed rates.
- Foaming occurs during flow rate changes; however, the foam never reaches the vent header or causes process upsets. Foaming is less prevalent at low to mid salt solution feed rates. MCU should select a flow rate based on ARP process rates to avoid changes during operation.
- Due to pH changes, the Caustic Wash Tank must either be replenished at much shorter intervals than originally anticipated, or a feed-and-bleed system must be incorporated into the design.

- Operating parameters for the Caustic Wash contactors should be evaluated to minimize the aqueous carryover and avoid a volume decrease in the Caustic Wash Tank.
- The CIP system appears to be effective in wetting all parts of the contactor rotor and housing. This should significantly reduce the radiation hazards associated with hands-on maintenance of the contactors.
- Process fluids are present in the "crud trap" of the bearing isolators/seals. The seals were effective in protecting the bearings, but the material in the trap may pose a radiation hazard during maintenance. Further investigation demonstrated that the radiation rates will be manageable.

SUMMARY

The Caustic-Side Solvent Extraction flowsheet was successfully scaled-up 750X. Testing of individual contactors provided the relevant data needed to modify commercially available contactors for specific use. Full-scale, integrated testing of all the contactors in the actual configuration for radioactive service validated system performance. The design goals of the cesium Decontamination Factor, the cesium Concentration Factor, and the organic carryover were all met.

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