

Fluidized Bed Steam Reforming Technology Demonstration for Conversion of Savannah River Tank 48 Waste to a Granular Carbonate Product – 10162¹

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ABSTRACT

Savannah River Remediation (SRR), formerly known as Washington Savannah River Company (WSRC), has selected the THOR[®] fluidized bed steam reforming (FBSR) technology (THOR[®] Process) to convert liquid Tank 48 High Level Waste (HLW) stored at the Savannah River Site (SRS) into a carbonate-based granular product. This granular product will be further processed, upon dissolution, by the Tank Farms and eventually sent to the Defense Waste Processing Facility (DWPF) to be incorporated into the borosilicate glass waste form.

The implementation of the THOR[®] Process for treatment of the Tank 48 HLW prior to further processing by the Tank Farm is necessary due to the presence of the legacy organic components residing in Tank 48. The tank's contents, a salt solution containing Cesium-137, are contaminated with tetraphenyl borate (TPB), which was added to Tank 48 in 1995 during a preliminary waste treatment effort. The addition of TPB resulted in the release of benzene vapor in the tank head space, necessitating the segregation of the solution pending further resolution. Additional species – nitrates, nitrites, and organic decomposition products – must also be eliminated to minimize potential downstream impacts on the vitrification process performed at DWPF.

The ability of the THOR[®] Process to effectively eliminate these detrimental species has been successfully proven using the Engineering Scale Technology Demonstration (ESTD) facility at the Hazen Research facility in Golden, Colorado on several occasions. Following the initial 2006 technology demonstration, three separate phases of validation testing for treating Tank 48 waste were performed from August 2008 to July 2009, each designed to demonstrate effective product conversion, and product handling systems and integrated system operability. The Phase 1 testing, performed in August of 2008, demonstrated the ability of the THOR[®] Process to create a granular carbonate product, while addressing open items remaining from the initial 2006 Tank 48 technology demonstration. Phase 2 testing, performed in May of 2009, included bench and full-scale testing and analyses aimed at verifying the operation of the product handling system portion of the process. Finally, the Phase 3 test, performed in June and July of 2009, integrated the FBSR and product handling systems, including dissolution of the carbonate product in water, to produce a solution representative of a waste stream compatible for return to the SRS tank farm and ultimate vitrification as HLW. The integrated Phase 3 system was an approximately one-third scale demonstration of the intended full-scale Tank 48 production facility.

Completion of the three phases of validation testing accomplished all defined test objectives, including safe and efficient process system functionality, operation within regulatory emissions standards, and process reliability. Knowledge attained from operation of the ESTD will be used to perform the detailed design of the full-scale production facility for treatment of the Tank 48 wastes.

INTRODUCTION

Liquid radioactive waste, a salt solution containing Cesium-137 among other radioisotopes, is currently stored in Tank 241-948H (Tank 48) at the Savannah River Site (SRS). The approximately 946.4 m³ (250,000 gallons) of HLW contains significant quantities of TPB as a result of a full-scale demonstration of the In-Tank Precipitation (ITP) process. As a result of the ITP process, benzene was released into the tank head space, thus actions were taken to isolate Tank 48 from tank farm operations [1].

Returning Tank 48 to service is critical to the SRR Tank Farm mission and to support the tank space management program. As such, it is imperative that the waste be treated to reduce or eliminate nitrates, nitrites, and sodium tetraphenyl borate (NaTPB) to minimize the adverse impacts of these species on the melting process [2,3]. After reviewing potential processes and independent technical reviews, the THOR[®] Process was selected as the primary technology capable of safely and cost-effectively treating the Tank 48 waste in a manner compatible with current

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SRS tank farm operational requirements. The THOR[®] Process produces a solid, water-soluble carbonate product and destroys any organics present in the waste stream.

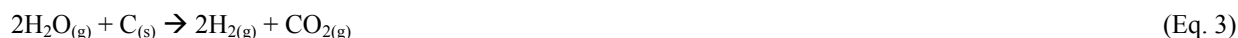
The steam reforming process has been tested using a Tank 48 simulant multiple times in the past, including a 2003 engineering-scale test performed at Science Applications International Corporation's Science and Technology Research Center in Idaho Falls, Idaho [4]. To further evaluate the process, identify potential issues, and to support the conceptual design and permitting determination for a full-scale steam reforming process, a follow-on test was completed in 2006 using the ESTD pilot plant located at the Hazen Research facility (Hazen) in Golden, Colorado [5]. While the 2006 test clearly demonstrated the capabilities of the THOR[®] Process, additional testing was warranted to address equipment operability issues. Subsequently, the Phase 1, 2, and 3 test programs [6,7] were developed to validate and verify individual equipment item functionality, as well as integrated system functionality. Results from the Phase 2 and Phase 3 tests are reported together.

PROCESS DESCRIPTION

The THOR[®] Process, a fully integrated system, is designed around two fluidized bed steam reformers. The first reformer, the Denitration and Mineralization Reformer (DMR), operating at ~650°C in a chemically reducing mode, evaporates liquids, volatilizes organics, converts nitrates and nitrites to nitrogen gas, and converts the nonvolatile constituents of the feed into a solid product. The reducing conditions in the DMR are created by the injection of fluidizing steam and granular coal, which react to produce small amounts of hydrogen, carbon monoxide, and carbon dioxide by the water gas and water gas shift reactions:



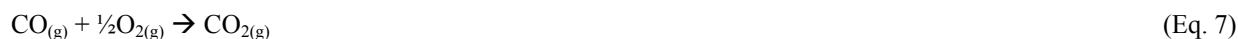
The net result of these two reactions is:



An additional important reaction in the bed is the reduction of alkali metal nitrates (NaNO_3 , KNO_3 , or CsNO_3) with reducing gases, coal particles and carbon dioxide to produce water, nitrogen and alkali metal carbonates. For example, the reaction of sodium nitrate with hydrogen and carbon dioxide:



The water gas and water gas shift reactions and evaporation of water are all endothermic processes. A small amount of oxygen is added to the bed to react exothermically with carbon, hydrogen, and carbon monoxide to maintain the bed temperature at ~ 650°C. These reactions are:



The solid product from the DMR is removed with an auger assembly and pneumatically transferred to the Off-Gas Filter (OGF). The process gas from the DMR, consisting mostly of water vapor, nitrogen, carbon dioxide, with small amounts of carbon monoxide, hydrogen, NO_x , short-chained organics, and acid gases is filtered through the High Temperature Filter (HTF). Approximately 25% to 35%, depending on vessel configuration, of the solid product produced in the pilot-scale DMR elutriates to the HTF as smaller particulate. The HTF removes the smaller product solids and coal fines that elutriate out of the DMR with the process gas. The filtered gas stream is then introduced into the bottom of the second steam reformer, the Carbon Reduction Reformer (CRR).

An oxygen/nitrogen or autothermal gas (ATG) mixture is injected into the CRR through a set of gas nozzles positioned above the fluidizing gas distributors, through which the DMR process gases enter the CRR. The ATG injection nozzles supply sufficient oxygen to maintain a desired bed temperature and a set outlet gas free oxygen content. Propylene glycol is introduced into the CRR to provide the energy for heating the vessel.

The upper portion of the CRR bed and freeboard are operated in an oxidizing mode to oxidize the hydrogen, carbon monoxide, and organics in the gas stream to carbon dioxide and water. The CRR off-gas, now mostly nitrogen, oxygen, water, and carbon dioxide, is cooled in the Off-Gas Cooler (OGC), filtered in the OGF, and passed through the Granular Activated Carbon (GAC) Adsorber to remove mercury, when present. The off-gas is then monitored by the Continuous Emissions Monitoring System (CEMS), and discharged to the stack via two off-gas blowers.

The Product Handling System (PHS) is coupled with the DMR, HTF and OGF vessels. Solids are periodically transferred from the DMR and HTF to the OGF. Accumulated solids in the OGF are removed via an auger and transferred to a coal separator (CSEP) where oversize particles (>900 μm) are removed from the product solids. The oversize material, which includes predominantly oversize coal particles, is recycled back to the DMR, while the undersize product and coal particles are pneumatically transferred to a Product Dissolution Tank (PDT). In the PDT, the product solids are dissolved in water to make the product solution. A demister pad and packed bed column along with a vent blower/filter are used to control any dust that may be evolved during the pneumatic transfer and dissolution processes.

A simplified process flow diagram of the integrated THOR[®] Process is shown in Figure 1. Of the tests discussed here, only Phase 3 represents the fully integrated system (i.e., integrated FBSR and PDT systems). Detailed descriptions of the equipment for each test program can be found in the corresponding design bases [8-10].

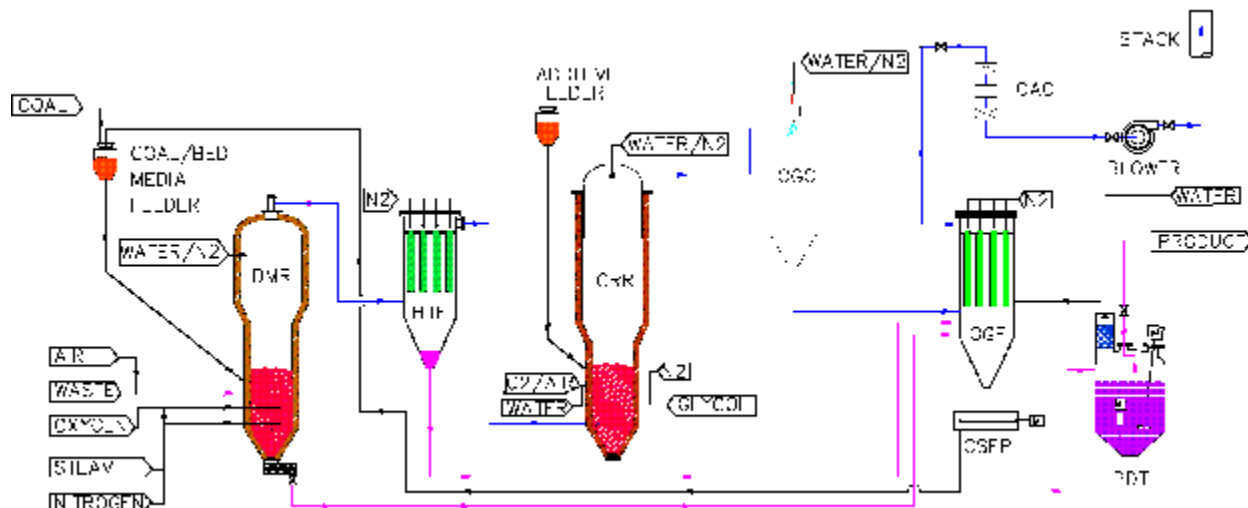


Fig. 1. Engineering Scale Technology Demonstration Process Flow Diagram.

EQUIPMENT

Liquid Simulant Preparation and Feed System

The Tank 48 simulant feed is made-up using reagent chemicals in the 6.8 m³ (1800 gallon) Waste Feed Make-Up Tank. It is transferred in batches to one of two Waste Feed Day Tanks. If applicable for a specific test, a heavy metal simulant is added to the Waste Feed Day Tanks. The Tank 48 simulant is pumped into the DMR and the flow rate is monitored by a magnetic flow meter. The simulant is injected into the DMR through one of two specially designed atomizing feed nozzles.

A Principal Organic Hazardous Constituent (POHC) is injected into the DMR feed line between the Waste Feed Day Tanks and the atomizing nozzles during selected tests to determine the Destructive Removal Efficiency (DRE) of the POHC in the process. The POHC used for this process was monochlorobenzene.

Denitration and Mineralization Reformer

The DMR is a 38 cm (15") inside diameter, refractory-lined steel vessel. The DMR was provided with a mechanical auger/grinder and a nitrogen jet eductor assembly to remove the hot bed product material from the DMR and pneumatically transfer it to the OGF during the integrated test. The bed media is fluidized with oxygen-enriched, superheated steam via distributors located near the bottom of the vessel. Tank 48 simulant is fed horizontally into the DMR through one of two feed nozzles located above the fluidizing gas distributor. Bed temperatures are monitored via thermocouples inserted strategically along the entirety of the vessel. Process gases flow from the DMR to the HTF. Granular coal is fed to the DMR via an automatic loss-in-weight screw auger feeder connected to an airlock/pressure "shot pot" that forces the coal into the active bed region.

High Temperature Filter

The process gas from the DMR flows to the HTF, a conical-bottom, cylindrical vessel. The top of the vessel is fitted with sintered metal filter elements. An automated nitrogen gas pulse-back manifold is used to clean the filter elements while on-line. A differential pressure instrument is provided to sense the pressure drop across the filters and automatically actuate the pulse-back function. External electrical heaters maintain the filter elements and vessel above 400°C during operation and ensure there is no condensation in the vessel. During the integrated test a product pump system conveys the filtered solids to the OGF.

Carbon Reduction Reformer

Process gas from the HTF flows to the fluidizing gas inlet distributors of the CRR located near the bottom of the vessel. The CRR is a refractory-lined vessel. The conical-bottom is equipped with a valve through which bed material can be removed, though this typically occurs only at the end of an operation as solid product does not accumulate in the CRR bed. Oxygen diluted with nitrogen is injected into the CRR above the process gas inlet distributors to convert CO, H₂, and hydrocarbons to CO₂ and water. Additional oxygen injected higher in the CRR controls the process outlet gas oxygen and CO concentrations. The semi-permanent bed media is composed primarily of ceramic media. Propylene glycol serves as the energy source for the CRR maintaining the operating temperature at ~950°C. As with the DMR, bed temperatures are monitored via thermocouples along the length of the vessel. Process pressures and differential pressures are monitored via nitrogen purged pressure taps.

Off-gas Cooler

An OGC, using direct contact water spray located downstream of the CRR, cools the CRR process gas from 950°C to ~200°C. The CRR process gases enter the OGC tangentially and flow downward contacting the water spray. The OGC is a cylindrical vessel with a conical bottom.

Off-gas Filter

The gases exiting the OGC contain minor amounts of particulate fines elutriated from the CRR. The OGF removes these particulates from the off-gas stream. In addition, the OGF received product solids pneumatically transferred from the DMR and HTF during the integrated test. An automated instrument air pulse-back manifold cleans the filter elements while on-line. A differential pressure instrument senses the pressure drop across the filters automatically actuating the pulse-back function. External electrical heaters maintain the filter elements and vessel above the gas dew point to prevent moisture condensation on the filter media during normal operations and during start-up and shutdown periods. The OGF also has a product draining auger to transfer solids from the OGF to the Coal Separator during integrated operations. Fluidizing pads in the bottom of the OGF prevent the fine solids from bridging and plugging the bottom outlet.

Mercury Absorber and Off-gas Blower

Just prior to discharge, the off-gas passes through the Mercury Absorber. This unit consists of three beds, two containing sulfur-impregnated Granular Activated Carbon, in series designed to remove mercury from the off-gas stream. The unit can be bypassed for process start-up or during tests that do not involve mercury. The off-gas blower maintains system gas flows and pressures as they exit through the stack.

Coal Separator

The integrated tests use a CSEP unit designed to sieve the product solids for removal of material larger than 900 µm from the product. The oversize solids, which consist primarily of coal, are collected and transferred manually to the DMR via the shot pot under recycle test conditions. The particles that are less than 900 µm diameter are collected and batch transferred via a product pump to the PDT to be dissolved into the final product solution. Over the course of testing, two different types of devices were implemented, a “wagging bar” type separator, and a Sweco sieve unit.

Product Dissolution Tank

The product solids that are transferred from the CSEP are deposited into the PDT. Here, the solids are dissolved in water to form the final product solution. The PDT is equipped with a mixer, level indicator/transmitter, density transmitter, recirculation pump, heat exchanger, pH inline analyzer, and vent line. The recirculation pump continually recirculates the product solution and transfers the product solution to totes when the dissolution is complete. The heat exchanger removes heat of dissolution to maintain the solution temperature below 35°C. The PDT is equipped with a weigh scale to determine the weight of the product solids and water transferred to the vessel.

A vent blower/filter is used to maintain a vacuum on the tank and to capture fine solids during the transfer and dissolution processes. A water scrubber removes solids from the vent gas before it flows to the blower/filter.

Process and System Off-gas Measurement

Process and system off-gas streams are continuously monitored at three locations. The first measurement point is just downstream of the HTF. Here, the Continuous Process Monitoring System (CPMS) monitors the filtered DMR process gas stream for H₂, O₂, CO, CO₂, total hydrocarbons (THC), NO, NO₂, and total NO_x. The H₂ concentration is a key parameter for operational control of the DMR. It is used to control the carbon concentration in the DMR bed and hence the reducing environment in the DMR, which in turn is essential to NO_x control. The second measurement point is just downstream of the CRR, where O₂ concentration in the process gas leaving the CRR is monitored. This is important to ensure that there is adequate O₂ in the stream so that CO levels are low in the final off-gas. The final measurement point is at the stack where the CEMS monitors for O₂, CO, CO₂, THC, NO, NO₂, total NO_x, and SO₂.

In addition to the continuous monitoring, manual samples are obtained from ports in the stack during testing. These samples are pulled and analyzed by independent subcontractors in accordance with formal Environmental Protection Agency (EPA) methods.

TEST SPECIFIC OBJECTIVES AND RESULTS

The demonstration of the suitability of the THOR[®] Process for treating Tank 48 waste was performed in four distinct testing campaigns: an initial technology demonstration in 2006 followed by three separate phases of validation testing from August 2008 to June 2009. Each of the production tests utilized a liquid waste simulant that included a salt solution, a sodium tetraphenyl borate solution, a PUREX sludge simulant, a monosodium titanate slurry, a metals salt solution, and miscellaneous organic compounds [11, 12]. Each test built on lessons learned from previous tests, developing the necessary technical data to support the design of a full-scale production facility. Summaries, recommendations, and results from the test programs follow.

2006 ESTD Test

Pilot-plant testing of the THOR[®] Process for Tank 48 waste was conducted in 2006 at Hazen using all unit operations planned for the full-scale production facility. The test consisted of a two-phase demonstration program designed to develop operating conditions, evaluate potential alternate reductants, and to demonstrate operation of the pilot plant for extended periods. The test was designed to demonstrate destruction of the principal chemical constituents including TPB ions, nitrates, nitrites, biphenyls, benzene, and other species, while converting insoluble minerals and heavy metals to solid product. In addition, the test focused on a detailed evaluation of the off-gas stream. A full discussion of the 2006 ESTD Test results has been reported to SRR [13]. A process flow diagram similar to Figure 1 was used for this test. The optimization and production test series, conducted during September and October 2006, consisted of a matrix of variable operating conditions that included feed composition, feed rate, DMR temperature, and reductant in the DMR and CRR [5]. During these tests, 12.5 m³ (3,310 gal) of Tank 48 simulant were processed into 3135.2 kg (6,912 lb) of granular solid product during 310 hr of “feed-on” operation. These tests confirmed operating parameters needed to design and operate the Tank 48 production systems and overall demonstrated that the THOR[®] steam reforming process is a viable and effective process to treat the Tank 48 waste. Specific recommendations resulting from the test program are described below and were incorporated into the follow-on test programs to improve and refine the system and to address additional design considerations.

- The test evaluated alternative organic reductants, including liquid propylene glycol, solid polyethylene plastic beads, and a sugar solution. It was found that granular coal was the preferable reductant for the DMR.
- It was determined that the initial DMR design should be modified to either improve the cyclone downcomer pulse jet clearing capability or eliminate the cyclone and enlarge the DMR freeboard.
- To control DMR bed HMPD particle growth, follow-on tests should include the capability for addition of ceramic material as seed particles.
- The 2006 test concluded that a mechanical coal separation unit, should be evaluated for incorporation into the full-scale production facility.

- The limited size and design of the test HTF vessel, along with the cohesive nature of the fine carbonate product, resulted in minor bridging between the filter elements during the demonstration program. Design modifications to the HTF and an increase in the nitrogen pulse pressure were recommended to better clean the HTF unit on subsequent test runs.
- Solid carbon and propylene glycol (glycol) were evaluated as energy sources for the CRR unit. The glycol resulted in a significant reduction in fine carbon solids and was, therefore, recommended as the preferred energy source for subsequent runs.
- Due to the slow loss of CRR bed material from the CRR (due to limited vessel height and gas flow velocity), larger, harder bed media was recommended for subsequent tests to minimize elutriation rates.

2008 Phase 1 Test

The Phase 1 Validation Test was performed at Hazen during August 2008. The main purpose of this phase of testing was to evaluate additional design considerations and extend the data developed during the 2006 ESTD test. The test also focused on a detailed evaluation of the product chemistry [6]. Full discussion of the events of the test has been reported in a final test report to SRR [14]. A total of 13.8 m³ (3643 gallons) of simulant were processed, 8.1 m³ (2136 gallons) of which were processed during the 168 hours (“feed-on”) parametric tests, producing 1825 kg (4024 pounds) of solid product. The remaining 5.7 m³ (1507 gallons) were processed during the 122.6 hour (“feed-on”) verification test, producing 1231 kg (2713 pounds) of solid product. In addition to accomplishing the general test objectives described below in the Common Test Objectives and Results section, the test incorporated many of the equipment and process control recommendations from the 2006 test program. Successful findings from the 2008 program included:

- Modifications to the fluidizing gas distribution system, the elimination of the cyclone, and an additional 5 foot taller DMR freeboard section resulted in a significant improvement in fines disengagement. The final product to fines ratio was approximately 2.2, and transport disengagement height calculations showed that additional improvements were possible with increased vessel height.
- Adjustments to the atomizing air flow, waste feed rate, and periodic addition of seed particles demonstrated excellent bed particle size control as measured by the harmonic mean particle diameter (HMPD). The HMPD varied from 450 to 600 μm during parametric tests and from 400 to 550 μm during verification test.
- As with the 2006 test, HTF operations were controlled with an increased pulse-jet nitrogen pressure as well as the pulse duration and frequency. An auger was also added to the collection hopper to facilitate removal of large solids, should they form. The test program also demonstrated the successful removal of carbonate filter cake from the filter elements through water dissolution at 80°C and agitation through nitrogen bubbling.
- CRR elutriation was addressed by lowering the superficial space velocity of the process gas through the vessel and using sintered ceramic as starting bed material, as it was a tougher mineral with a higher density and rounded, as opposed to angular, surfaces as shown in Figure 3.
- Analytical results provided by the Savannah River National Laboratory (SRNL) and Air Pollution Testing supported the findings that all goals for the test were achieved. Detailed chemical analysis of the feed, product, and off-gas all support the findings listed above. In depth discussion of analytical results was presented by the test team [14] and by Williams, et. al.[15].

2009 Phase 2/3 Test

The Phase 2/3 testing program consisted of Phase 2, the individual PHS component and sub-system test, and Phase 3, the integrated test. Phase 2 testing was performed in May 2009 at Hazen. The purpose was to assemble and demonstrate the operation of the proposed PHS. Phase 2 included a bench-top product dissolution test followed by an engineering-scale test, based on the bench-top results. The data from Phase 2 were used as input for the final design and operation of the Phase 3 ESTD integrated process system tests. A detailed report discussing the results was developed and issued to the client [16].

Phase 2 had four specific test objectives. The first was to demonstrate the separation of >900 μm coal, including the transfer of the oversize particles to a collection drum. Achieving this objective required the incorporation of the CSEP on the outlet of the OGF to remove the oversize particles. The undersize particles were transferred via a product pump to the PDT for dissolution. Analysis of the particle sizes at the CSEP outlet fines collection hopper

confirmed that approximately 1.5 wt% of the particles were greater than 900 μm , well under the 5 wt% acceptance criteria. Phase 3 tests later demonstrated that, due to the cohesive nature of the product, the “wagging bar” separator, as currently designed, would be incapable of separating the product produced for the Tank 48 project. A dry Sweco sieving unit was installed and proved to be a superior option under test conditions.

The second objective, demonstration of on-line particle size determination of DMR product solids, was also achieved. A Particle Size Analyzer (PSA) was incorporated into the system such that DMR particle sizes could be periodically measured during the Phase 3 test. During the phase 2 test, the unit was tested with material of a known particle size to evaluate the accuracy of the PSA. The on-line operation achieved greater than 90% agreement with the manual particle size determination methods. Later during the Phase 3, this objective was revisited using three separate DMR sampling configurations. The third configuration, a specialty sampling pot collected bed material, directed the particles to the analyzer, returned the sampled material to the process, and successfully demonstrated on-line sampling with two different PSA devices.

Phase 2 testing also sought to demonstrate carbonate-based product dissolution. This objective involved two separate sets of tests, bench-scale and functional. Bench-scale dissolution tests were conducted to determine the amount of consolidated Phase 1 test product that could be dissolved in water, while precluding the post-dissolution precipitation of sodium carbonate. The bench-scale dissolution tests also sought to determine if additives, such as sodium hydroxide, would enhance the dissolution process or were necessary to maintain a final solution pH of greater than 9.5. The bench-scale dissolution tests showed: 1) the maximum achievable concentration of Phase 1 product that remained in solution at 10°C was 22.5 wt%, 2) addition of sodium hydroxide to the dissolution water decreased the amount of Phase 1 product that dissolved, and 3) sodium hydroxide was not required to ensure a slurry pH of at least 9.5. Based on these bench-scale results, a functional testing procedure was developed outlining target slurry concentration, specific gravity, and expected weights and flow rates associated with the target values.

Pilot scale functional dissolution testing during Phase 2 followed the bench-scale tests. These tests included three separate batch dissolutions, the results of which are shown below in Table I. In all three dissolution tests the final slurry temperature remained below 35°C and the final pH was above 9.5. While testing demonstrated the effectiveness of the heat exchanger, the unit was not needed to cool the slurry as it was generated, and supplemental NaOH was not needed to ensure the pH of the final solution was greater than 9.5.

Table I. Functional Dissolution Test Results.

Dissolution Test	1	2	3
Solids, kg	168	231	240
Water, kg	771	816	862
Waste Loading %	17.9	22.1	21.8
Final Solution pH	12	12	11.4
ΔT , °C	14	18	14
Final Specific Gravity	1.17	1.14	--
Crystallization Temp, °C	2	--	--

Phase 3 testing, performed in June and July of 2009 at Hazen, was designed to demonstrate the integrated THOR[®] Process and its capabilities. Integrated testing of the FBSR and PHS processes was accomplished in multiple segments, including parametric and verification phases, following preliminary equipment testing and final component checkout and functional testing. A breakdown of the various verification tests and their objectives is shown in Table II.

The primary Phase 3 objective was to confirm the capability of the steam reforming process to convert simulated Tank 48 waste into a carbonate soluble solid product and to then dissolve the solids product in water at the desired concentration, in a safe and efficient manner. A corollary objective was the demonstration of long-term process

operability and key components by performing a five-day minimum continuous operation test of the integrated system. Successful demonstration of the integrated system included generating a solid product free of coal particles >900 μm (<5%) and generating a final product slurry of carbonate salts. The ESTD facility was an approximately one-third scale demonstration of the full-scale production facility.

During the Phase 3 test, the ESTD facility was successfully operated for a total elapsed “feed-on” time of nearly 315 hours. Manual recycle of coal and product particles +20 mesh and above (>841 μm) sieved from the consolidated OGF product was also accomplished. Four separate coal recycle tests were performed covering a range of recycle-to-virgin coal ratios. DMR operations continued under each recycle condition, including a two-hour period where it was successfully operated exclusively on recycled coal. Integrated operations also effectively confirmed product conveyance through the use of dense phase product pumps. The PDT dissolution process successfully produced aqueous solutions with initial solids loadings of ~22.5 wt% with no observed precipitation or the need for additional required additives.

Table II. Operating Conditions for Verification Tests ^{(a)(b)}.

Test Number	Duration (Hours)	Reductant	Off-gas Testing Methods	Test Purpose
T48-I-4A	33.33	Coal	CPMS, CEMS, EPA Manual Sampling	Fully integrated, extended-duration test
T48-I-4B	21.63	Coal	CPMS, CEMS, EPA Manual Sampling	Fully integrated, extended-duration test
T48-I-4	120.25	Coal	CPMS, CEMS, EPA Manual Sampling	Fully integrated, extended-duration test
T48-I-3A	1.75	Recycled Coal	CPMS, CEMS, EPA Manual Sampling	First coal recycle test
T48-I-3B	2.00	Recycled Coal	CPMS, CEMS, EPA Manual Sampling	Second coal recycle test
T48-I-3C	0.85	Recycled Coal	CPMS, CEMS, EPA Manual Sampling	Third coal recycle test
T48-I-3D	2.17	Recycled Coal	CPMS, CEMS, EPA Manual Sampling	Fourth coal recycle test

a. Off gas testing: CPMS, CEMS, EAP Manual Sampling (Included EPA method 18, 29, 31)

b. Included full simulant feed @ 0.2 gpm, screened starting bed, and 950°C CRR and 650°C DMR temperatures.

The Phase 3 verification test experienced some minor operational interruptions. These were due to test facility complications such as utility service interruptions, erratic simulant feed rate, and low gas flow capacity of the HTF filter elements. On one occasion, a combination of a spike in simulant feed rate and the low capacity of the HTF filter element resulted in a spike in the pressure inside the DMR, which in turn, caused failure of the DMR rupture disk. This resulted in the activation of the Emergency Shutdown System (ESS). The ESS functioned as designed by shutting off simulant feed, switching fluidizing steam to nitrogen, and shutting off all oxygen flows. The rupture disk was replaced, system operating conditions were restored, and simulant feed was resumed after only 10 hours of down time. Process safety was demonstrated with no injuries or unplanned environmental releases throughout the test.

The verification test was successfully completed with a continuous 120-hour extended duration run that had a “feed on” efficiency of 98.2% and an average simulant feed flow rate of 0.76 L/min (0.20 gpm). See Figure 2 for a timeline of this run. Over the extended duration test, 5.3 m³ (1410 gallons) of simulant were processed into 1123 kg (2475 lbs) of product. All automatically and manually logged data was as expected aside from higher-than-expected pressure differentials across the HTF, likely a result of material build-up in the filter elements due to usage over several pilot plant runs. As shown in Figure 2, the average DMR bed temperature was 650°C. The average DMR freeboard temperature was 640°C throughout the extended duration test. Figure 2 also illustrates bed particle size data as measured by the HMPD, which was shown to be consistent and controllable throughout the test. Figure 3 illustrates the appearance of typical DMR and CRR bed material.

The extended duration test run also successfully demonstrated that the operational and conceptual design parameters critical to the process were adequately developed and suitable for implementation. Measurement of this objective was successfully achieved through the monitoring of critical operating parameters such as temperatures, pressure, feed rates, gas flow rates, mass of input and output streams, DMR process gas composition, and CRR off-gas composition.

Phase 3 integrated testing also served to evaluate benzene fate within the process system. This included both normal and off-normal operating conditions. In addition, the feed was spiked with a POHC and is shown on Figure 2 below. Over the course of Phase 3, benzene was not detected in the PDT headspace. Off-gas sampling results will be discussed below in the Common Test Objectives and Results section.

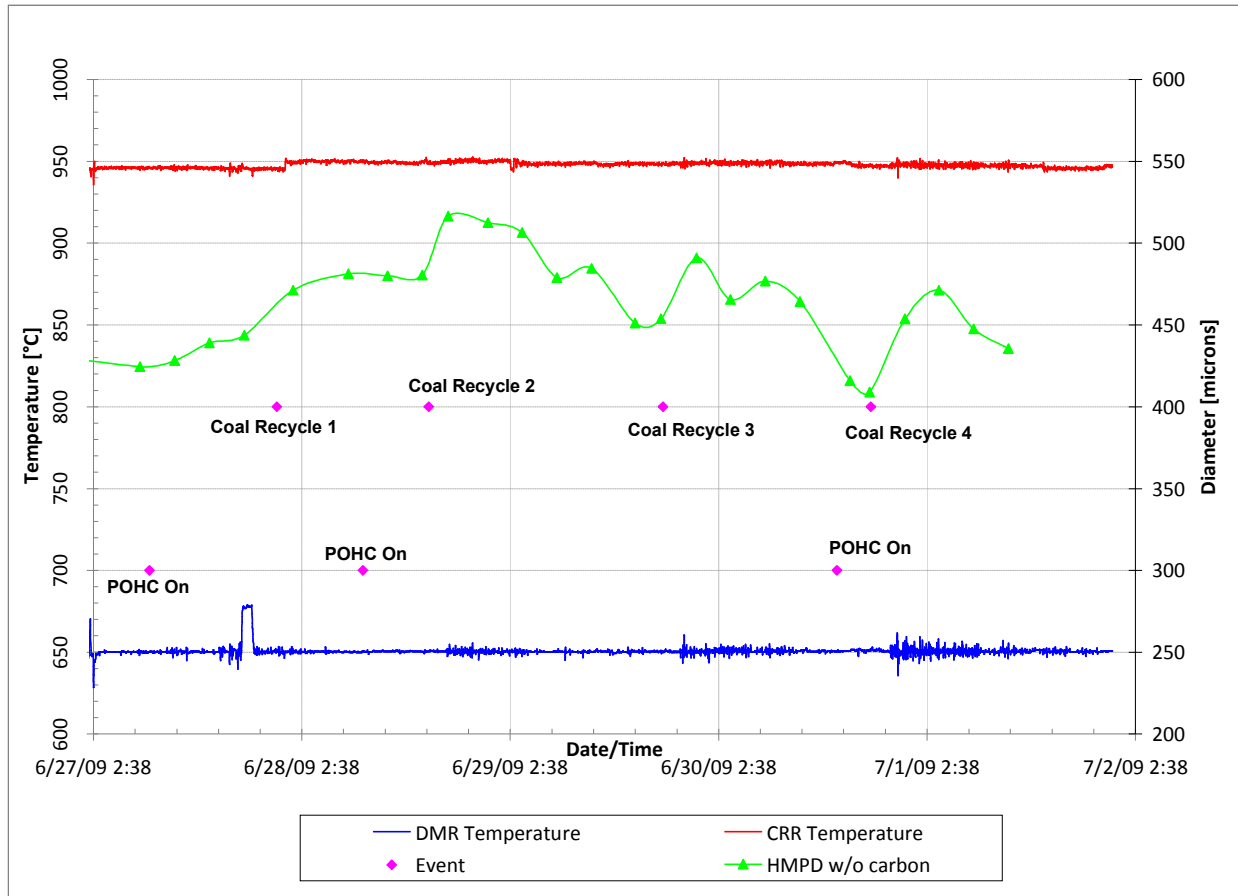


Fig. 2. Phase 3 Verification Testing Timeline.

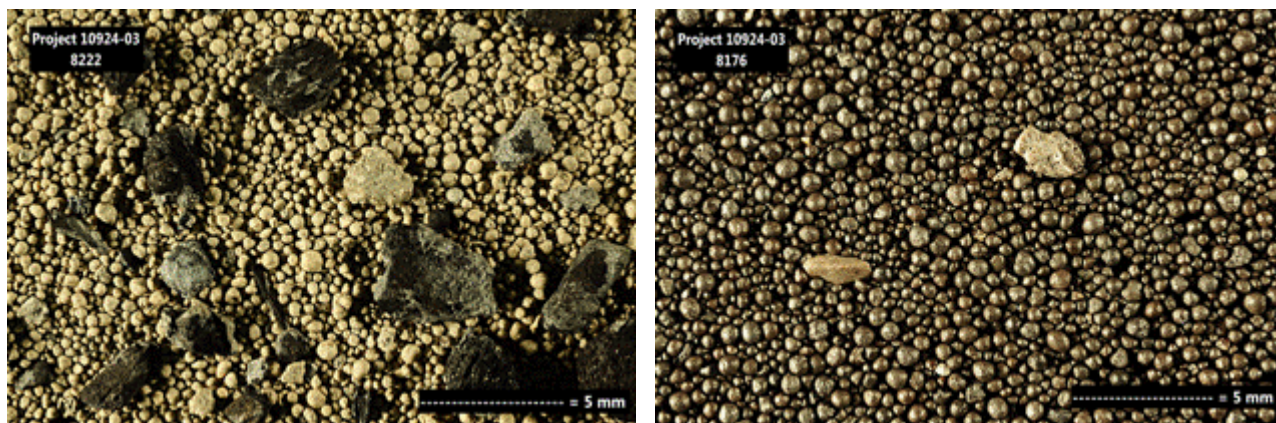


Fig. 3. Macro-scale photos of DMR product material (Sample 8222) and CRR bed material (Sample 8176).

Phase 3 testing also sought to minimize unreacted additives in the output product stream. Measurement of this objective was verified through acceptance criteria of less than 4 wt% alumina and less than 10 wt% unreacted coal in the consolidated OGF product. This objective was demonstrated by maintaining the operating parameters of the DMR in a defined range so as to maximize the oxidation of coal, maintain a reducing environment, and minimize elutriation of product fines and unreacted coal from the DMR. Additionally, the CRR operated in an oxidizing environment to maximize destruction of organics and CO, as well as minimize elutriation of particulate material. This objective was considered partially achieved at the end of Phase 3. The average alumina concentration measured in the consolidated OGF product was 3.5 wt%. However, the unreacted coal content of the OGF product transferred to the PDT averaged from 11 to 13 wt% following separation of the $>841\mu\text{m}$ product material by a dry sieving separation. This issue prompted production facility design changes to reduce the content to target levels.

A follow-on objective from the functional dissolution tests in Phase 2 was the demonstration of the dissolution process in the integrated system. Full functionality involved incorporation of the CSEP and PDT into the process flowsheet to effectively demonstrate the batch dissolution process of product solids derived from the combined DMR, HTF, and OGF solids. Over the entirety of Phase 3, eleven batch dissolutions of sieved OGF product were successfully conducted. Chemical and physical analysis confirmed the slurries were within acceptable ranges. The results of these analyses for the extended duration test batches are shown below in Table III. It was during the integrated testing of the dissolution process that the “wagging bar” CSEP, as designed, was found to be sub-optimal as a separation device for the Tank 48 product. It was replaced with a dry Sweco sieving-type separator for the duration of the test.

Table III. Integrated Dissolution Test Results.

PDT Batch	7	8	9	10	11	
Solids, kg	259	218	231	231	225	
Water, kg	884	714	797	795	454	
Max Temp, °C	51	44	45	52	40	
Waste Loading %	23	23	22	23	33	
Sample Number	8165 A1	8189 A1	8211 A1	8247 A1	8249 A1	Avg ^(b)
pH ^(a)	--	12.7	12.8	12.9	--	12.8
Density, kg/m ³ ^(a)	--	1180	1200	1210	--	1200
Viscosity, Pa·s ^(a)	--	0.0027	0.003	0.0033	--	0.003
wt% solids	0.1	5.5	5.2	2.8	9.7	4.5
Crystallization Temp, °C	<10	<10	<10	<10	<10	<10
wt% Carbon in PDT UDS [SRNL] ^(e)		17.10	12.26	9.29		12.89
wt% Carbon in OGF [SRNL] ^(e)			20.25 (Sample 8192)	2.33 (Sample 8237)		11.29

- Data provided by SRNL was performed on the non-archived sample [15].
- The average values listed here exclude values obtained for PDT Batches 7 and 11.
- The carbon content of the PDT Batches reported here is based on Loss on Ignition (LOI) analysis techniques performed at 530°C as to inhibit release of inorganic carbon. The LOI technique reports the total mass of evolved carbon atoms plus any minor constituents (i.e. hydrogen and volatiles).
- The TIC/TOC analytical technique reports the total mass of only carbon atoms in the sample.
- Values reported are on a 60°C dry basis or similar basis as OGF and prior 2006/2008 samples.

COMMON TEST OBJECTIVES AND RESULTS

The tests conducted in support of the Savannah River Tank 48 Project (2006 Test, Phase 1 Test, and the Phase 2/3 Test) have had several test objectives in common. This section outlines the eleven objectives the three tests had in common, as well as the test findings.

Nitrate and Nitrite Destruction

The test programs were required to demonstrate the ability of the process to destroy >99% of the nitrates and nitrites in the simulant feed and to maximize conversion of these species to nitrogen gas, significantly reducing NO_x emissions. As a means of determining the destruction of nitrates and nitrites, the mass balance of nitrates and nitrites in the solid products and the mass balance of gas-phase NO_x were compared to nitrates and nitrites in the simulant feed. Nitrate and nitrite results are listed in Table IV below and the NO_x results are listed in Table V [15].

Organic Removal

The process had to demonstrate the removal of >99% of the organics in the simulant feed, converting them to carbon dioxide and water. This was determined via measurements of organics in the solid products, and measurement of THC and organic species in the stack gas. This objective was met for all the tests. Complete off-gas data was collected only for the 2006 test. These results are shown in Table IV below and the solids results for all the tests are listed in Table IV.

Retention of Feed Elements

Another objective of the test programs was the retention of fluorides, chlorides, aluminum, and other elements from the simulant feed in the solid waste products. This was determined via measurements of emissions in stack gas via EPA-designated methods using both CEMS and manual extractive sampling. The findings from the 2006 test run are shown in Table V. The full spectrum of off-gas analyses for metals, halides, particulates, and specific organic compounds, normally obtained by extractive sampling of the off-gas stream and off-site laboratory analysis, were not performed as part of the 2008 or 2009 tests, since compliance to off-gas emission limits for these constituents was adequately demonstrated in 2006.

No Liquids in Solid Products

Operation of the THOR[®] Process must be conducted such that no liquid appears in the solid waste product streams. Determination was based on direct visual observations of products. No liquids were observed in the solid products in 2006, 2008, or 2009.

Compliant Off-Gas Emissions

Measurement of emissions in the stack gas was determined via EPA-designated methods using both CEMS and manual extractive sampling. Compliance with applicable environmental regulations was demonstrated for each test. The pertinent data for the 2006 test is provided in Table V.

Material Balance Closure

The demonstration of acceptable material balance closure for major and minor constituents was also a key SOW requirement. A material balance using feed sample make-up, solid product samples, and off-gas emissions was prepared for each test phase following its completion. The overall mass balance closure values are shown in Table IV. A full component mass balance was performed on the 2006 data. While a complete component mass balance was not performed for the 2009 test, key species (C, H₂, O₂, N₂) were evaluated, as these components represent more than 90% of the total mass processed by the ESTD. The component balance closure for these species ranged from good to excellent, with variances ranging from -3.2 to +19.5% between feeds and discharges. The component balance uncertainties arise from the determination of weight fractions of each component in the various streams.

Table IV. Product Summary for Tank 48 2006, Phase 1 (2008), and Phase 2/3 (2009) Testing Programs.

Category	2006 Test Results	2008 Test Results	2009 Test Results
Nitrate Destruction	> 98.5% in solid product	> 99% in solid product	> 99% in solid product
Nitrite Destruction	75% to 98%	> 98% for all solids	> 98% for all solids
Solid Di-, Tri- and TPB Concentration	Not detectable	Not detectable	Not detectable
No Liquids Present	No liquids present	No liquids present	No liquids present
Mass Balance Closure	Overall: 97-104%	Overall: 99.7%	Overall: 93.6%
Extended Verification Operations	> 96 hr of integrated but non-continuous operations.	~ 300 hours of safe process operations, including approximately 123 hours of sustained “feed-on” verification operations.	> 120 hours of sustained “feed-on” operations

Integrated Operations

All the ESTD tests, to various extents, were designed to demonstrate integrated operation of the entire Tank 48 treatment system and confirm system operability with respect to process chemistry, material flows, mass and energy balance, equipment durability, and particle size control. Collectively, the tests developed an operating envelope within which the integrated process could be operated without trends that would lead to shutdown.

Extended Operations

The final common test objective was the demonstration of extended (96 hr or greater) integrated operation of the process system. All three tests included extended verification operations, with the durations listed in Table IV.

Table V. Emissions Summary for Tank 48 2006, Phase 1 (2008), and Phase 2/3 (2009) Testing Programs.

Pollutant	MACT Limit of Pollutant Corrected to 7% O ₂	Concentration Corrected to 7% O ₂	% of MACT Limit	Results and Comments
Radioactive Surrogates (Cs)	N/A	<0.59 µg/dscm	N/A	No Cs was detected in the off-gas during the 2006 and Phase 3 testing programs. No High Efficiency Particulate Air (HEPA) filters were installed.
Mercury	8.1 µg/dscm	2.29 µg/dscm (avg. for 2006 and 2009)	28%	Hg System Removal Efficiency averaged 99.8% in 2006 and Phase 3 testing programs.
Low-volatile Metals (As, Be, Cr)	23 µg/dscm	2.48 µg/dscm (2006) 4.95 µg/dscm (2009) 3.7 µg/dscm (Avg)	16%	No As or Be in simulant.
Semi-volatile Metals (Cd, Zn, Pb)	10 µg/dscm	5.3 µg/dscm (2006) 8.3 µg/dscm (2009) 6.8 µg/dscm (Avg)	68%	Met Maximum Achievable Control Technology (MACT) standard of 10 µg/dscm. Pb Removal Efficiency = 99.997% Cd Removal Efficiency = 99.994%.
HCl + Cl ₂ (as HCl)	21 ppmvd	3.3 ppmvd (2006)	16%	Met MACT standard of 21 ppmvd. Average HCl + Cl ₂ removal efficiency = 98.1% in 2006.
Particulate Matter	3.4 mg/dscm	3.92 mg/dscm (2006)	115%	No HEPA filters were installed. Would easily pass the MACT standard with HEPA filters.
Dioxins/furans	0.11 ng/dscm	0.013 – 0.014 ng/dscm (2006)	<13 %	Met MACT standard of 0.11 ng/dscm.
PCBs	DRE = 99.9999 %	12 – 17 ng/dscm (2006)	N/A	Most PCB congeners not detected in 2006 test. No dioxin-like coplanar PCBs detected at detection limits of 0.7 ng/dscm (2006)
VOCs (chlorobenzene)	DRE = 99.99 %	N/A	N/A	Met MACT standard of four nines DRE. Benzene DRE, based on conversion of all benzene precursors to benzene, equaled 99.991% and 99.998% during the Phase 3 Extended Duration Run to average 99.994%. Benzene DRE equaled 99.9996% and 99.9989% to average 99.9993 % (Phase 3) Benzene DRE during the 2006 test was >99.998%.
SVOCs	N/A	Mostly non-detectable	N/A	Two SVOCs detected in 2006, each only once near the detection limit.
NO _x	N/A	<181 ppmv dry (2006) <304 ppmv dry (2008) <391 ppmv dry (2009)	N/A	Destruction averaged 92% (2006) Destruction averaged 98% (2008) Destruction averaged 95% (2009)
THC	10 ppmvd	<1.5 ppmv dry (2006) <2.9 ppmv dry (2008) <1.4 ppmv dry (2009)	<29 %	Met MACT limit of 10 ppmvd at 7% O ₂
CO	100 ppmvd	<13 ppmv dry (2006) <8.7 ppmv dry (2008) <44 ppmv dry (2009)	9 – 44 %	Met MACT limit of 100 ppmvd at 7% O ₂
SO _x	N/A	<14.9 ppmv dry (2006) <23.4 ppmv dry (2008) <75 ppmv dry (2009)	N/A	Met test plan objective of <100 ppmv dry for all 2006 and Phase 1, and 2/3 (extended duration) testing programs.

CONCLUSIONS

Pilot plant tests have shown the THOR[®] Process to be effective for the treatment of SRS Tank 48 waste simulants, producing a product suitable for introduction into the DWPF vitrification process, after coal removal techniques are optimized. Operation of the integrated system complies with regulatory emissions standards and produces no secondary waste streams. In addition to the successful implementation of the overall FBSR system, the various test programs demonstrated important and critical compliance with the various major test objectives. The 2006 test demonstrated regulatory compliance for the process off-gas system, the 2008 test program demonstrated the capture of critical target feed species into the solid product streams, and the 2009 test program demonstrated the successful dissolution of the solid stream and important integration of all process unit operations.

The completion of the test programs described herein have been invaluable in preparing for the design of the full-scale production facility to be installed at the Savannah River Site in Aiken, SC. Completion of these test programs have resulted in the compilation of a significant body of Lessons Learned, which are discussed in detail in the Tank 48 Project-Validation Testing; Phase 2 and 3 Final Test Report [16]. In addition to gaining experimental verification of the process, performance, scale-up factors, and recommendations, these Lessons Learned include operational parameters which will increase product facility performance and reduce operational downtime, as well as providing input to the design process to effectively address potential process-related issues. Examples of some Lessons Learned include the modification of the fluidizing gas distributor nozzle and operational requirements to prevent in-bed agglomeration, the addition of DMR freeboard cooling to prevent solids build-up in the process gas outlet line, implementation of on-line particle size analysis for real-time analysis, and implementation/inclusion of the coal separator in the production facility baseline process. Several other lessons learned relate to the process conditions and operational requirements for the production facility. These include start-up and shut-down requirements, off-normal shut-down conditions, process control logic and interlocks, alarm conditions, user interface and data tracking optimization considerations, and information that will be incorporated into the operational and maintenance procedures for the production facility.

Many of the actions required to implement and incorporate the Lessons Learned into the baseline THOR[®] Process for Tank 48 waste treatment have already been accomplished. Further evaluation and implementation will be accomplished through engineering design studies, mock-up testing, and fabrication acceptance testing of individuation unit operations and equipment. It is the desire of THOR Treatment Technologies to provide SRR with the most reliable, cost-effective waste treatment facility available to help them meet the stringent waste acceptance criteria at DWPF and to help the Department of Energy maintain their environmental cleanup mission.

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