IWTU

Sodium-Bearing Waste (SBW) Treatment Project

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IWTU Project

Presentation Outline

- *Project History*
- *Overview of steam reforming technology*
- *Bench scale tests and results*
- *Engineering scale tests and results*

SBW Project History

- *Spent nuclear fuel processing discontinued at INTEC in 1991, HLW ceased to be generated.*
- *Liquid, mixed transuranic waste/SBW has continued to accumulate in the TFF tanks from NWCF operations, decontamination, and other activities.*
- *Activities associated with the Idaho High-Level Waste and Facilities Disposition EIS (DOE/EIS-0287) evaluated over one hundred SBW treatment options. The FEIS narrowed the field to five technologies:*
  - *1) Direct Vitrification,*
  - *2) Cesium Ion Exchange with a grout waste form,*
  - *3) Calcination with Maximum Achievable Control Technology upgrades,*
  - *4) Direct Evaporation, and*
  - *5) Steam Reforming.*
- *A treatment technology evaluation report (INEEL/EXT-04-01692, Rev. 1) summarized the process development and conceptual design results for the five preferred treatment technologies in 2004.*
- *CH2M WG Idaho proposed steam reforming as the treatment technology for SBW and was awarded the ICP contract in 2005. The treatment technology decision was finalized by issuance of the EIS ROD (FR 44598 – August 3, 2005).*

Fluidized bed steam reforming

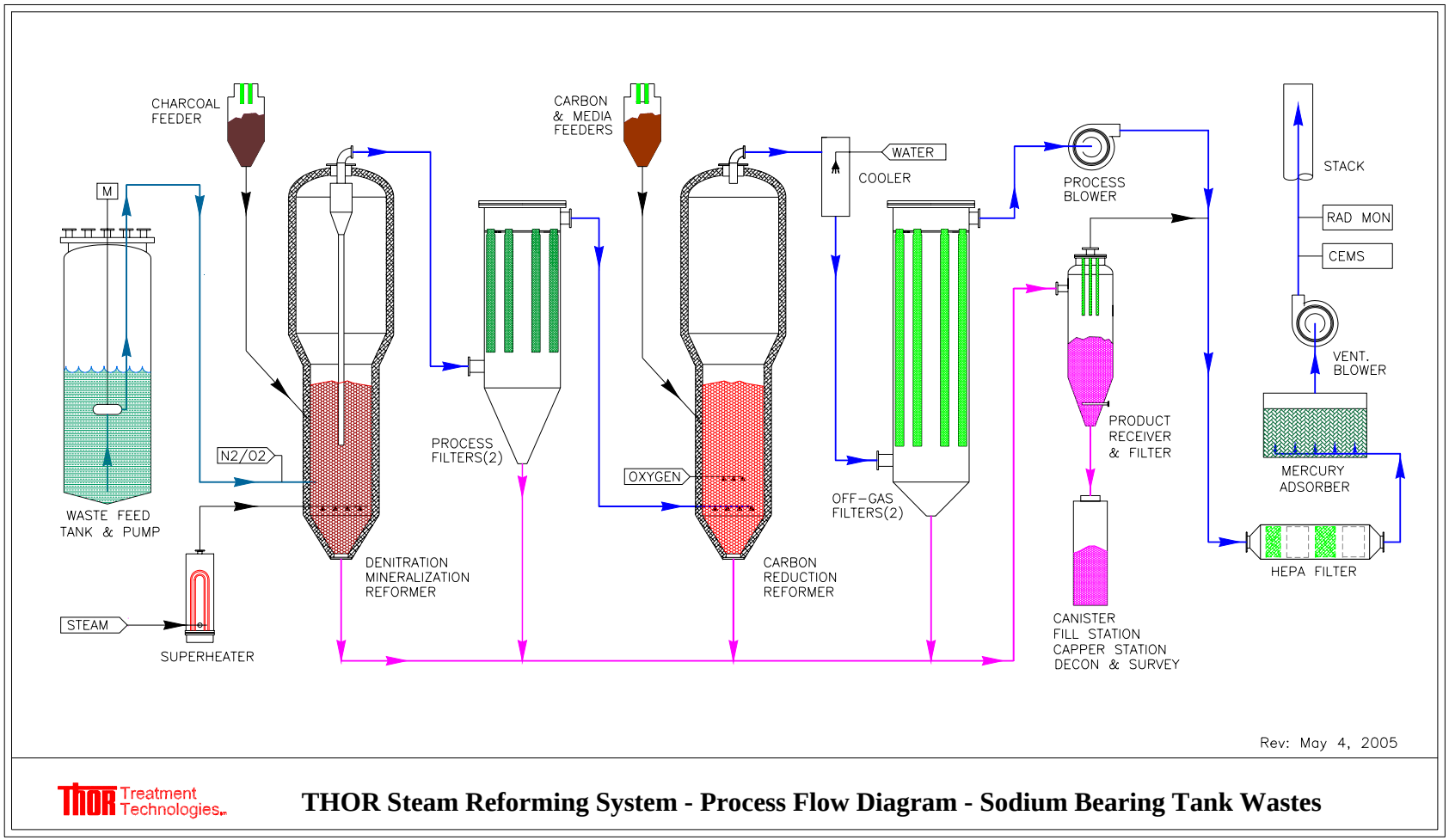
- *The DMR is fluidized with low pressure steam and operated at 625 to 740℃*
- *Process energy and reducing environment produced by carbonaceous reductant and sub-stoichiometric oxygen addition*
- *Waste atomized into the DMR fluidized bed*
- *Water is evaporated, organics and nitrates/nitrites converted to carbon dioxide and nitrogen gas*
- *Alkali metals and other inorganic constituents incorporated into granular solid product matrix*

- *Key in-bed reactions*
  - $C + O_2 \leftrightarrow CO_2$
  - $C_xH_yO_z \leftrightarrow C + CH_4 + CO + H_2$
  - $H_2O + C \leftrightarrow H_2 + CO$
  - $CO + H_2O \leftrightarrow CO_2 + H_2$
  - $2NO_3 + 3C \leftrightarrow N_2 + 3CO_2$
  - $2NO_3 + 6H_2 \leftrightarrow N_2 + 6H_2O$
  - $2NaNO_3 + 4C \leftrightarrow Na_2CO_3 + 3CO + N_2$
  - $2NaNO_3 + Al_2O_3{\cdot}2SiO_2 \cdot 2H_2O + 5H_2 \leftrightarrow Na_2Al_2Si_2O_8 + 7H_2O + N_2$

Fluidized bed steam reforming (cont.)

- *High temperature process gas filter removes fines elutriated from DMR*
- *CRR fluidized with process gas from DMR, operated at 950 - 1000℃*
  - *Reducing mode in very bottom section of reformer to increase NOx destruction*
  - *Oxidizing mode in remainder of reformer to convert gas to nitrogen, carbon dioxide, and water vapor.*
- *Off-gas cooler*
- *Off-gas filter to remove elutriated fines from the CRR*
- *Sulfur impregnated, granular activated carbon bed to remove vaporized mercury*
- *Gas discharged to environment is compliant with HWC MACT emission standards.*

FBSR Process Flow Diagram



FBSR Demonstrations

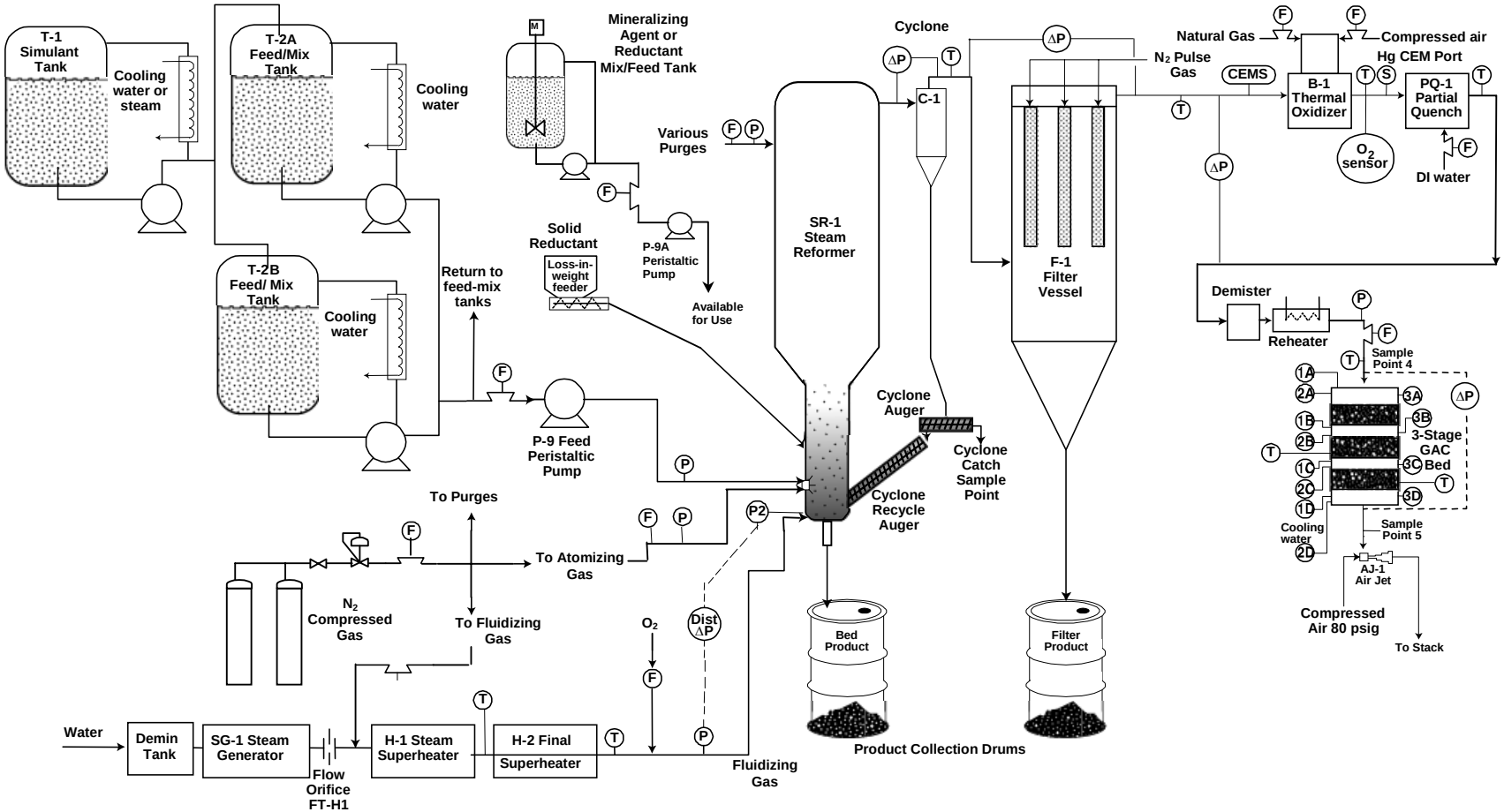
- ***Early development***
  - ***a) Hazen Research Inc/Studsvik – 1997***
    - ***6" Fluidized Bed, Hanford 5.2 $NaNO_3$ surrogate, carbonate product***
    - ***15" Fluidized Bed, ion exchange resins, oils, solvents***
  - ***b) Hazen Bechtel/Studsvik – 2001 (6" Fluidized Bed, LAW surrogate, carbonate and NAS products)***
  - ***c) LMITCO INEEL – 2002 (3" Fluidized Bed, SBW surrogate)***
- ***Bench scale at SAIC STAR Center, 6" Fluidized Bed***
  - ***a) Jan. 2003 - SBW surrogate, carbonate product (Phase 1)***
  - ***b) July 2003 - SRS Tank 48H surrogate, carbonate product***
  - ***c) Nov. 2003 - SBW surrogate, carbonate and NAS product (Phase 2)***
  - ***d) Aug. 2004 - LAW surrogate, NAS product (Phase 3)***
  - ***e) July and Sept. 2004 - SBW surrogate, NAS product (Phase 3)***
- ***Engineering Scale Test & Demo at Hazen Research Inc.***
  - ***a) Nov. 2005 through June 2006 (15" Fluidized Bed, SBW surrogate, carbonate product)***
  - ***b) Sept. 2006 through Oct. 2006 (15" Fluidized Bed, SRS Tank 48H surrogate, carbonate product)***
  - ***c) Oct. through Dec. 2006 (15" Fluidized Bed, SBW surrogate, NAS mineralized product)***

Demonstration (2001) Of The Processing Of LAW Under Contract With Bechtel National Inc

- *Hanford AN-107 LAW simulant was used in the 6-in diameter system; non-radioactive Cs and Re (as surrogates for ^{137}Cs and ^{99}Tc) were added to the waste simulant. Used carbon and sugar as reductants and an iron oxide as catalyst. Also used a clay additive for some of the operations. The system was operated at ~725°C.*
- *Produced a mineralized alkali aluminosilicate product, predominantly nosean and nepheline, using a clay additive. Produced a carbonate product without the clay.*
- *Provided the product for study by SRNL (Jantzen – WSRC-TR-2002-00317, Rev. 0) and PNNL (McGrail – PNNL-14414). Also was basis for risk assessment of initial selection of supplemental LAW process technology.*

Small Scale Testing at STAR Center

STAR Center Flow Diagram



Phase 1 (Jan 2003) Demonstration Of The Processing Of SBW

- *Scoping tests to determine the viability of fluidized bed steam reforming technology to process SBW. 6-inch diameter system operated at 675°C to 725°C*
- *Sugar and carbon reductants were employed in varying ratios. Iron oxide catalyst was also used. Achieved ~ 98% NOx destruction.*
- *Non-radioactive Cs and Re (as surrogates for ^{137}Cs and ^{99}Tc) were added to the waste simulant. Successfully produced a granular carbonate product. Greater than 99% of surrogate radioactive elements and non-volatile heavy metals were captured in the solid waste product.*
- *Hg was captured in a GAC bed in the off-gas system.*
- *Results documented in detail in report INEEL/EXT-03-00437.*

Demonstration (July 2003) Of The Treatment Of SRS Tank 48H Waste Solution.

- *Test program to evaluate the viability of FBSR processing of Tank 48H solution. Funded by SRS.*
- *Initial tests showed that steam reforming in the 6-inch diameter system using a silica bed at ~ 650°C was not satisfactory. Silica bed particles tended to agglomerate due to adhesive effects causing bed defluidization.*
- *Satisfactory steam reforming of the T48H simulant was accomplished using alumina bed particles. The feed products tended to adhere to the alumina particles, causing individual particle growth but not agglomeration.*
- *Produced sodium carbonate solid waste form suitable for vitrification in Defense Waste Processing Facility (DWPF).*
- *Feed denitration efficiency was high, ranging between 99.6-99.9%. No TPB or TPB decomposition products were detected in the solid products, making the destruction greater that 99.98%.*
- *Results documented in detail in report INEEL/EXT-03-01118.*

Phase 2 (Nov 2003) Demonstration Of The Processing Of SBW

- *Integrated demonstration of the upgraded equipment postulated to implement FBSR for processing SBW. Used different solid carbon and sugar reductants in varying ratios to each other and to the simulant feed rate in the 6-inch diameter system.*
- *Operated at ~670°C without a clay additive to generate a carbonate product. Operated at ~725°C to generate an alkali aluminosilicate product with the clay.*
- *NOx destruction averaged ~93% for the carbonate flow sheet and ~74% for the mineralizing flow sheet. Various types and quantities of iron catalysts were used, including none. NOx destruction without the iron catalyst was demonstrated.*
- *Greater than 99% of radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste product. Hg was captured with >99.9% efficiency in a granular activated carbon bed in the off-gas system.*
- *Results documented in detail in report INEEL/EXT-04-01493.*

Phase 3 (Aug 2004) Demonstration Of The Processing Of LAW Into A Mineralized Alkali Aluminosilicate Product

- *Funded by DOE-HQ*
- *Carbon and clay additives and addition ratios were specified through collaborative experimental work at SRNL. Temperature was ~725°C in the 6-inch diameter system.*
- *Successfully produced a granular alkali aluminosilicate product, predominately Nosean, Carnegieite/sodium aluminosilicates, and Nepheline*
- *These were desired mineral phases and the same as those produced in the Hazen demonstration in 2001. Greater than 99% of radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste product.*
- *NOx destruction stabilized at >96%, without an iron catalyst.*
- *Hg was captured with >99.9% efficiency in a GAC bed in the off-gas system.*
- *Results documented in detail in report INEEL/EXT-04-02492.*

Phase 3 (July, Sept. 2004) Demonstration Of The Processing Of SBW Into A Mineralized Alkali Aluminosilicate Product

- *Funded by DOE-HQ.*
- *Carbon and clay additives and addition ratios were specified through collaborative experimental laboratory work at Savannah River National Laboratory (SRNL). Temperature was ~725°C.*
- *Successfully produced a granular alkali aluminosilicate product, predominantly Nepheline and Carnegieite.*
- *NOx destruction averaged >90% in July and >96% for the September run, both without iron catalyst. >99% NOx destruction was demonstrated for specific carbon reductant conditions.*
- *Feed nozzle issues impacted operations during the first runs in July. Improvements allowed a successful longer-term test in September.*
- *Greater than 99% of radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste product and Hg was captured with >99.9% efficiency in a GAC bed in the off-gas system for all the runs.*
- *Results documented in detail in report INEEL/EXT-04-02564.*

Engineering Scale Test & Demonstration (ESTD)

- *Located at Hazen Research Inc. in Golden, CO*
- *One-tenth scale 15-inch diameter DMR pilot scale system*
- *Objectives were:*
  - *Demonstrate long-term, integrated operation of SBW processing system*
  - *Confirm process chemistry and material flows*
  - *Confirm technical parameters for system design and operation*
  - *Gather emissions data for environmental permitting*
  - *Produce granular product for solids handling and packaging equipment demonstration*
  - *Confirm solid product data for requesting WIPP transportation and disposal*

ESTD Installation at Hazen

ESTD SBW Carbonate Tests
(Nov 2005 – June 2006)

- ***CP1 Tests:***
  - *Approximately 334 hours of ESTD operation with simulant feed were logged, processing ~5,450 gallons (~61,000 pounds) of liquid SBW simulant into ~11,500 pounds of solid product. An overall input/output material balance closure of about 98% was achieved*
  - *Demonstrated safe correlation between hydrogen and oxygen in DMR at process temperatures from start-up conditions up to normal maximum operating conditions of 680°C and that there is no potential for concurrent accumulation of H_2 and O_2 in the DMR.*
  - *Produced a sodium carbonate-based granular product demonstrated to be chemically and physically compatible with WIPP disposal*
  - *Off-gas emissions were demonstrated to be within MACT or other expected permit levels for the IWTU.*

ESTD SBW Carbonate Tests (cont.)

- *Corrosion coupons were placed in strategic locations throughout the process system. These coupons were removed and selected coupons submitted to SRNL for metallurgical analysis. The metallurgical analyses are completed and have provided required data to select IWTU process system materials of construction and corrosion rates.*

- ***CP2 Tests:***
  - *Approximately 164 hours of ESTD operation with simulant feed were logged, processing ~2,450 gallons (~28,000 pounds) of liquid SBW simulant into ~4,700 pounds of solid product.*
  - *Demonstrated DMR particle size control without UDS in feed*
  - *Determined DMR product density that facilitated estimate of IWTU product canister count*
  - *Selected material of construction for PGF filter elements*
  - *Optimized CRR operation with respect to CO, THC, and NOx destruction*
  - *Demonstrated GAC bed Hg removal performance*
- *Results for CP1 & CP2 documented in detail in report RT-ESTD-PMR-001.*

ESTD Tank 48H Tests (Sept./Oct. 2006)

- *The safe operation (over 100 hr) of the process and key components was demonstrated, including the destruction of organic TPB in the waste.*
- *Reductants that melt before gasification (e.g., polyethylene beads and granular sugar) or that readily gasify (e.g., propylene glycol and liquid invert sugar) tend to produce elevated levels of total hydrocarbons in the DMR freeboard and were not effective in providing the autothermal energy required in the DMR bed to achieve required waste processing rates.*
- *Coal is the preferred reductant/energy source for the DMR for a Tank 48H production unit.*
- *The relatively low level of nitrates in the Tank 48H waste simulant required the use of increased amounts of oxygen input to the steam fluidizing gas (FG) to the DMR. This, in turn, required installing a fluidizing gas distributor in the bottom of the DMR, below the elevation of the FG distributors, through which carbon dioxide was introduced to the lower regions of the bed.*

ESTD Tank 48H Tests (cont.)

- *The preferred energy source for the Tank 48H production CRR is propylene glycol instead of carbon. A dramatic reduction in the collection of fine carbon solids was achieved in the filter downstream of the CRR when using propylene glycol.*
- *DMR bed particle size control was a challenge throughout the testing but was acceptable. The post-test discovery of a plugged gas outlet on the DMR may have impacted particle size control by impeding the efficiency of the cyclone function. Efforts to-date to determine when the plug occurred have been inconclusive.*
- *Sufficient off-gas emissions data was obtained for environmental permitting.*
- *Results documented in detail in report 28927-RT-001 Rev 0.*

ESTD SBW Mineralizing Tests (Dec. 2006)

- *Approximately 175.4 hours of ESTD operation with simulant feed were logged, processing ~1,436 gallons of liquid SBW simulant into ~6,093 pounds of solid product.*
- *Four different clay addition ratios were demonstrated. All gave good performance in PCT and TCLP tests for control of hazardous and simulated radioactive compounds.*
- *Two different carbon reductants were tested in the DMR during the scoping tests. The charcoal performed better than the coal based on carbon reactivity, hydrogen production, and NOx destruction efficiency.*
- *All of the TCLP results for the product solids samples were less than the reporting limit and the UTS value.*
- *The product solids were demonstrated to be chemically and physically compatible with disposal in a federal repository. Demonstrated durability and leach performance were superior to the EA and LRM glass standards for sodium. Normalized release rates for cesium and rhenium (surrogate for technetium) were less than that of sodium in the LRM glass standard.*

ESTD SBW Mineralizing Tests (cont.)

- *Non-detectable quantities of cesium, cerium, and rhenium were found in stack gas samples, indicating that the THOR® mineralizing process retains these constituents of interest in the solid product as desired.*
- *An overall input/output material balance closure of about 99% was achieved, with detailed material balances for individual elements being completed with generally good to excellent closure.*
- *The organic DRE was 99.989%. The Hg SRE was not met because of previous Hg contamination in the stack. Off-gas emissions were demonstrated to be within MACT or other expected permit levels*
- *The NOx destruction efficiency was greatly enhanced at a lower feed rate, suggesting that NOx destruction is kinetically controlled.*
- *Corrosion coupons were placed in strategic locations throughout the process system. These coupons were removed and selected coupons submitted to SRNL for metallurgical analysis. The metallurgical analysis showed that the corrosion rates were similar to those in the CP1/CP2 tests.*
- *Results documented in detail in report 28266-RT-002, Rev. 0.*

Integrated Steam Reforming Process

- *Several years of activities have demonstrated the long-term, safe, reliable, predictable series operation of the DMR and CRR FBSRs and downstream off-gas system*
- *The material flows, pressures, and temperatures from the DMR through the process system match the theoretical mass and energy balance used to design both the Hazen ESTD and the IWTU*
- *FBSR is a robust treatment technology with broad applicability to DOE complex waste streams*