Fluidized Bed Steam Reforming

Technology Overview

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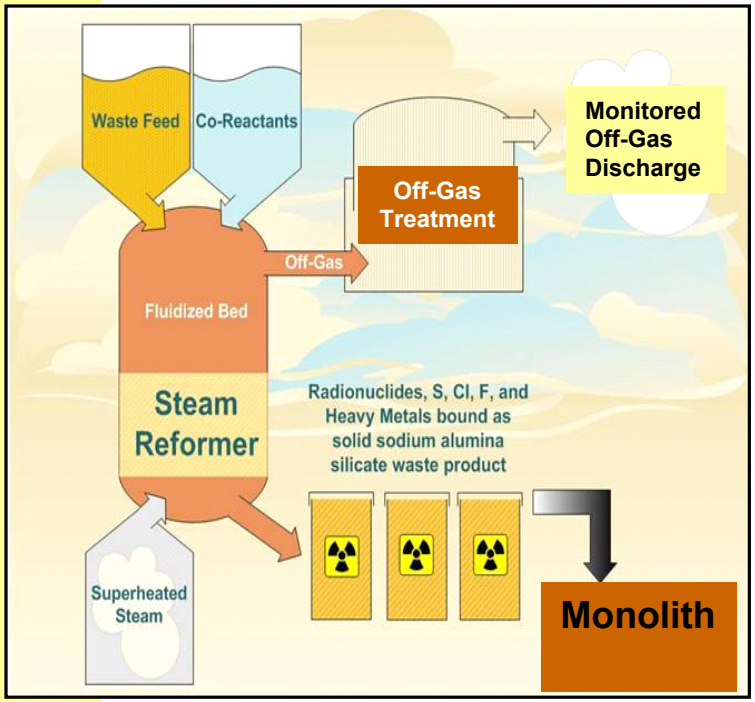
Technology Overview -Outline

- *What is steam reforming?*
- *How does it work?*
- *Background and development history*
- *Process applications*
- *Product characteristics*

What is Fluidized Bed Steam Reforming?

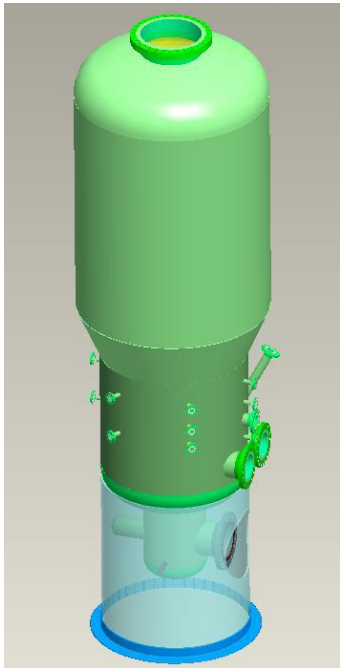
- ***Thermal process***
  - ***Fluidized bed of granular solids***
  - ***Fluidized with low pressure steam***
  - ***Operates at 620-750°C***
  - ***Operates at near-ambient pressure***
- ***Waste preparation and inputs***
  - ***Tank waste mixed with clay for mineralized product; no clay for carbonate product***
  - ***Waste feed air atomized into fluidized bed***
  - ***Coal added as reductant and for energy***
- ***What happens inside the reformer?***
  - ***Water evaporates***
  - ***Nitrates reduced to nitrogen gas***
  - ***Waste constituents react to form water insoluble minerals (with clay); soluble carbonate product (without clay)***



- ***Fluidized bed agitated by low pressure steam***
- ***Energy produced by carbon reductant and oxygen (autothermal steam reforming)***

Why Use Fluidized Bed Steam Reforming?

- ***Accommodates widely varying wastes***
  - ***High or low pH (no adjustment required)***
  - ***Treats high organic content wastes***
  - ***Radionuclides (Cs, Tc, most I) captured in solid product; converted to water insoluble minerals with clay additive***
  - ***Cl, F, P, and SO_4 and heavy metals (except mercury) captured in solid product; converted to water insoluble minerals with clay additive***
  - ***Nitrates converted to nitrogen; no off-gas NOx abatement required***
- ***Moderate temperature (620-750°C)***
  - ***Does not volatize radionuclides (e.g., Cs, Tc, and I)***
  - ***Simple off-gas treatment system; no off-gas scrubber required***
  - ***No liquid effluents***
- ***Non-Incineration***
  - ***Operates below flammability limits, no flame***



Idaho National Laboratory

Integrated Waste Treatment Unit FBSR - CRR

How Does Steam Reforming Work?

- **Gas phase reactions, partial list:**
  - $C + O_2 \leftrightarrow CO_2$ — Oxidation of carbon (energy)
  - $C_xH_yO_z \leftrightarrow C + CH_4 + CO + H_2$, etc. — Decomposition of organics
  - $H_2O + C \leftrightarrow H_2 + CO$ — Water gas reaction
  - $CO + H_2O \leftrightarrow CO_2 + H_2$ — Water gas shift reaction
  - $2NO_3 + 3C \leftrightarrow N_2 + 3CO_2$ — Conversion of nitrates to nitrogen gas
  - $2NO_3 + 6H_2 \leftrightarrow N_2 + 6H_2O$

- **Waste constituent reactions:**

Waste Constituent or Characteristic	No Clay Additive (Carbon Dioxide)	Clay Additive (Alumino-silicate)
Organics	Destroyed	Destroyed
Alkali Metals	Carbonate	Alkali alumino-silicate mineral (NAS)
Inorganic Metals	Oxides, Spinels	Spinels and Oxides bound in NAS matrix
Cl, S, F, P, I, B	Alkali Salt	Bound in NAS matrix
Radionuclides	Oxides or Carbonates	Spinels and Oxides bound in NAS matrix
Resulting Waste Form	Mostly water soluble carbonate	Leach resistant NAS mineral Maximum immobilization and leach resistance

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FBSR Development and Deployment History

• 1997	• Performed pilot plant simulant testing of Hanford LAW and commercial ion exchange resins
• 1997 - 1999	• Constructed first THOR® process facility and started commercial radioactive operations (Studsvik Processing Facility in Erwin, TN)
• 2000 - 2009	• Performed 15 pilot plant simulant test programs for treating INL Sodium Bearing Waste (SBW), SRS Tank 48 Waste, Hanford LAW and WTP Secondary Waste (WTP SW), and commercial nitrate wastes
• 2005	• INL SBW treatment project commenced
• 2009	• SRS Tank 48 treatment project commenced
• 2010	• Commenced bench-scale testing of radioactive Hanford LAW and WTP SW at SRNL
• 2011	• Start-up INL IWTU facility for SBW treatment
• 2011 -	• Continue support for Hanford LAW waste form qualification

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Steam Reforming – Pilot Plant Experience

- ***Performed pilot plant testing with multiple surrogate wastes to qualify process and waste form***
- ***15 pilot plants test programs performed*** *(6", 15" and 24" diameter FBSRs)*
- ***Scale up from pilot plant to radioactive waste treatment plants:***
  - ***Studsvik Processing Facility: Ion exchange resins*** *(45" diameter FBSR)*
  - ***DOE Idaho Integrated Waste Treatment Unit: SBW treatment*** *(48" diameter FBSR)*
  - ***DOE Savannah River: Tank 48 waste treatment*** *(23" diameter FBSR)*

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THOR® Process – Studsvik Processing Facility

- *Granular alumina bed fluidized with low pressure steam*
- *Coal additive reacts with steam and oxygen to provide process heat*
- *Mineralizing additive converts salts to aluminates*
- *Operates at 600 to 750ºC and near ambient pressure*
- *Treats wide range of radioactive wastes (>380,000 cu ft to date):*
  - *Ion exchange resins (up to 600R/hr)*
  - *Organic or inorganic sludges*
  - *Filters*
  - *Oils*
  - *Aqueous wastes*
  - *Dry active wastes (paper, plastics, rubber, wood)*
- *No liquid waste effluents*
- *Over 11 years successful LLRW operations*
- *High Cs and Tc Retention (>99.999%)*

Studsvik's THOR® facility Meets All Air Permit and Emissions Limits

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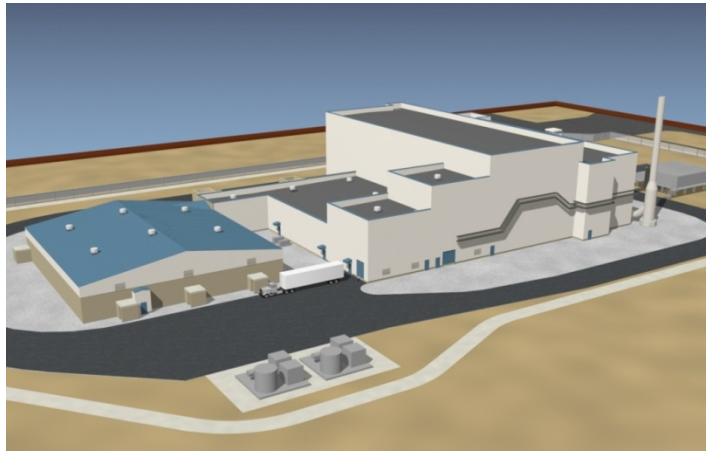
DOE Idaho Cleanup Project
THOR® Integrated Waste Treatment Unit

- *THOR® treatment of ~3.8 million liters of Sodium Bearing Waste (SBW): sodium nitrate with nitric acid, ~100 R/hr)*
- *SBW generated from spent nuclear fuel process systems decontamination and deactivation*
- *Carbonate product to be packaged into RH-72B canisters and stored; alternative for future mineral product flowsheet*
- *THOR® plant construction underway*
- *Treatment to start 2011-2012*



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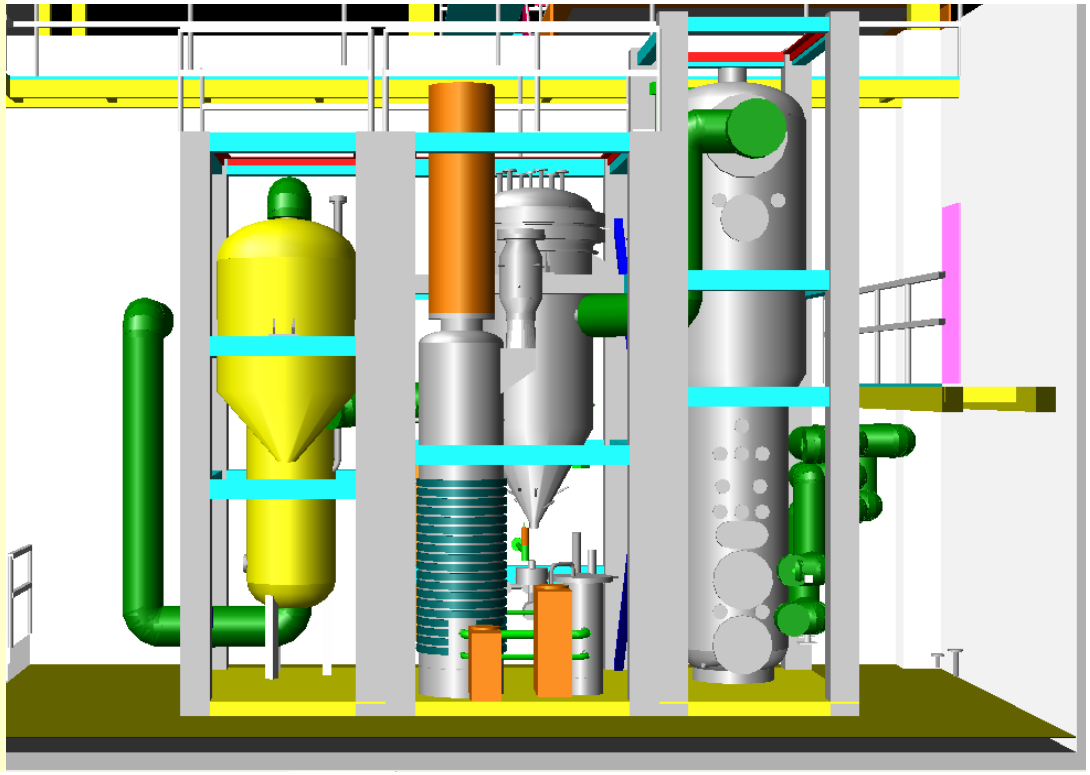
DOE Savannah River Remediation
Tank 48H – THOR® Process

- *THOR® treatment of ~1 million liters of radioactive high-level liquid waste in Tank 48H (sodium nitrate, >100 R/hr)*
- *Complex nitrate mixture with ~ 21,800 kg tetraphenylborate*
- *Two separate independent technical review teams selected THOR®*
- *Integrated pilot plant tests complete*
- *Detailed design for full-scale plant underway*



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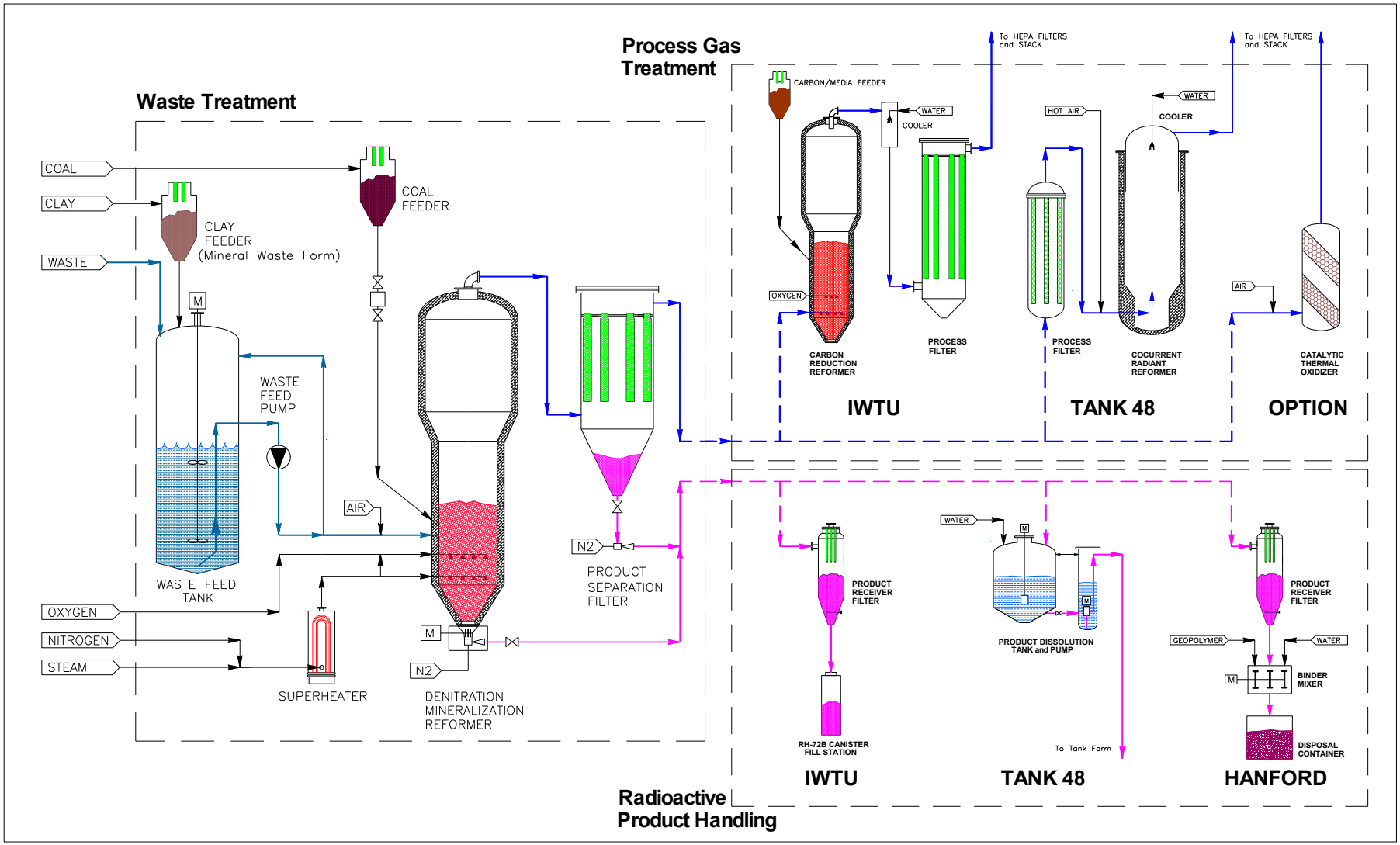
Steam Reforming Process – Flow Diagram



FBSR Mineralized Product – Simple Formulation

Simple formulation to determine waste-clay mixture:

1. **Determine Na, Al and Si content of waste**
2. **Select type and quantity of clay**

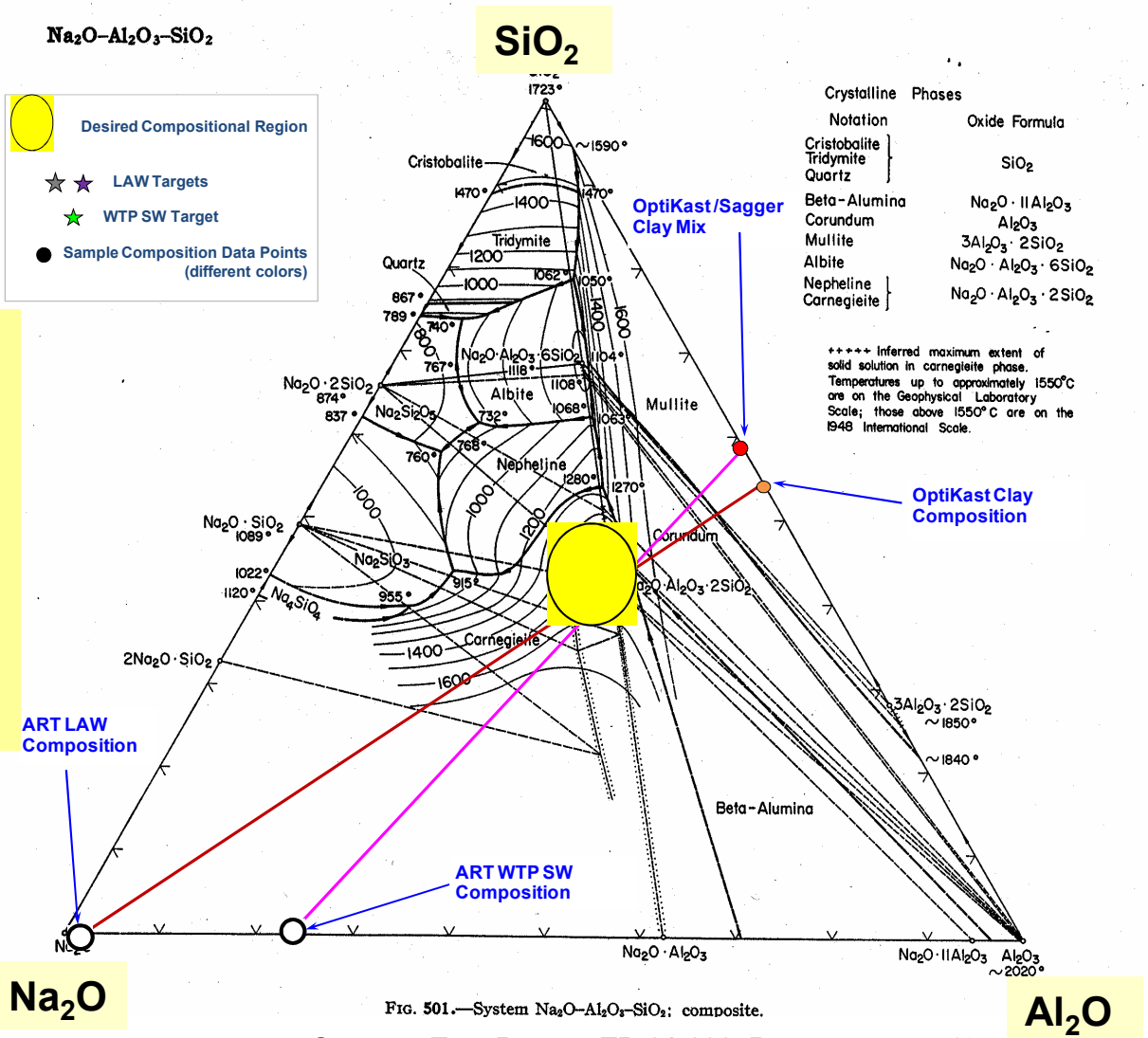


FIG. 501.—System Na_2O–Al_2O_3–SiO_2: composite.

Source: Test Report, TR-21-002, Rev 1

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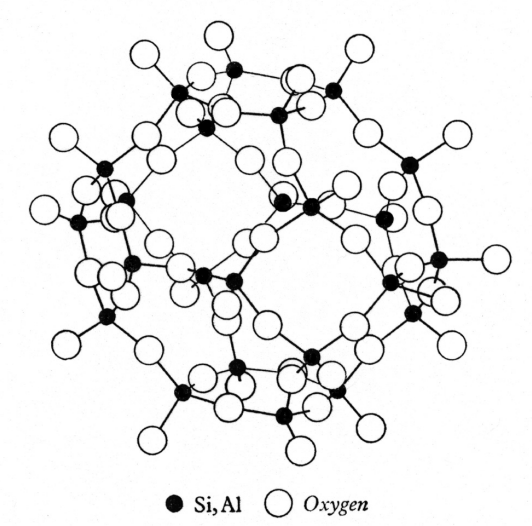
Steam Reforming – Mineral Product Form

Ceramic mineral waste form:

- ***Clay additive is mixed with waste***
- ***Waste/clay slurry is injected into FBSR***
- ***Alumino-silicate minerals form that incorporate:***
  - ***Radioactive materials (Tc, Cs, most I)***
  - ***Sodium and potassium (alkali metals)***
  - ***Sulfur***
  - ***Chlorides***
  - ***Fluorides***
- ***Spinel minerals form that incorporate***
  - ***Metals (Cr, Ni, Fe, etc.)***



Na_2O-Al_2O_3-$2SiO_2$
(Nepheline)

Na_2SO_4 or NaCl
Plus 6 Nephelines
(Nosean or Sodalite)

Source: SRNL Reports

LAW and WTP SW Mineral Waste Form Properties

- *Granular mineral products are mixed with geopolymer binder to make monolithic final waste form*
- *Geopolymer binder has chemical properties similar to mineral product*
- *Monolithic final waste form properties:*
  - *Compressive strength of >1,500 psi*
  - *PCT test: passes with ≤0.12 g/m^2 Na compared with LAW glass standard of <2 g/m^2 Na*
  - *TCLP test: passes for all heavy metals*
  - *PNNL currently testing WTP SW monoliths using EPA and ANSI methods*

Monolithic waste form needed to pass Hanford IDF requirements for:

- *Compressibility (>500 psi)*
- *Intruder scenarios*

Binder

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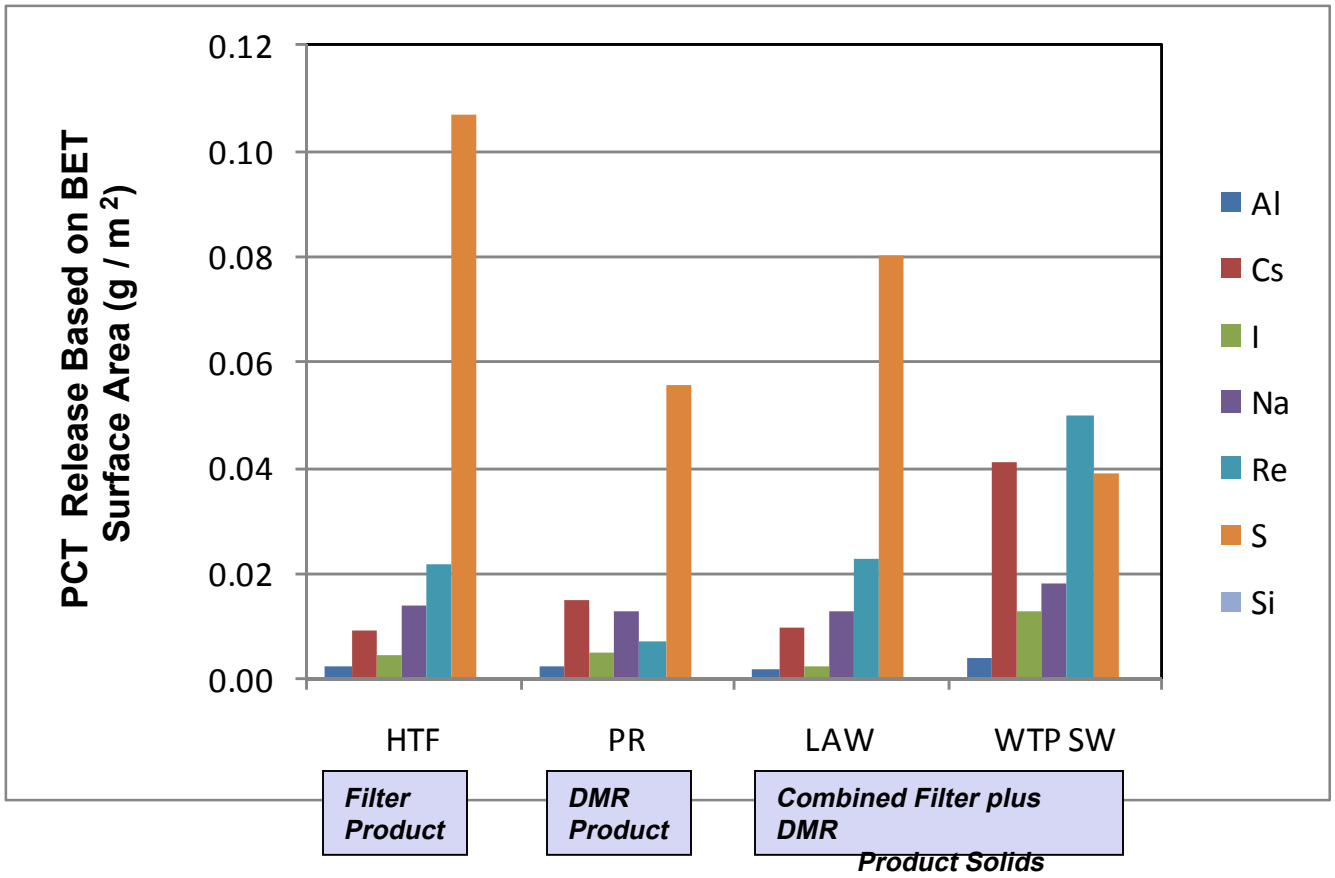
Granular Mineral Product Durability



LAW glass standard: <2.0 grams/m^2 for Na, Si, and B per DOE/ORP-2000-24

Source: Draft SRNL Test Report, Data

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Summary – THOR® FBSR Process

Benefits and features:

- *Accommodates widely varying wastes*
  - *Treats solids, liquids, or sludges with high or low pH (no pH adjustment required)*
  - *Provides high organic destruction*
  - *Does not volatize radionuclides*
    - *Re (Tc): >99.998% retention in mineral, no Re detected in off-gas system*
    - *Iodine: ~94% retention in Hanford LAW and ~19% retention in WTP SW mineral (detection limited), radioiodine testing on-going*
    - *Cs: >99.999% retention in mineral*
  - *Uses single-component mineralizing additive; low cost clay*
- *Robust final waste form – monolithic*
  - *Qualifications to date validate highly leach resistant granular and monolith waste forms*
  - *Radioactive materials (Cs, Tc, most I) converted into water insoluble mineral waste form that passes PCT and TCLP tests*

Summary – THOR® FBSR Process (cont'd)

Benefits and features:

- ***Safe, robust process operations***
  - ***Moderate temperature (620-750°C)***
  - ***Near-ambient pressure***
  - ***Non-incineration; operates below flammability limits***
  - ***Reviewed by DNFSB for IWTU (RH-TRU) and Tank 48 (HLW) systems***
  - ***Very small mass of in-process material at any given time***
  - ***Process shutdown capable in <15 minutes***
- ***No off-gas scrubber system required***
  - ***Mineralizes Cl, F, P, and SO_4 into leach resistant mineral solid with clay addition***
  - ***Simple off-gas system, as no wet scrubber is required***
  - ***No liquid effluents***
  - ***Meets MACT gaseous emissions limits with Hg absorber***

Summary – THOR® Steam Reforming

Ongoing work:

- **PNNL surrogate WTP SW product and monolith analyses**
  - Performing ASTM and EPA method testing of WTP SW granular and monolithic products
  - Performing performance assessment comparison of WTP SW technology waste forms
- **SRNL radioactive WTP SW testing**
  - Performing bench-scale FBSR testing of radioactive DWPF solution spiked with radioactive Tc, Iodine, and Cs
  - Verify radioactive Cs, Tc, and I retention in mineral form and mass balance closure
- **SRNL radioactive Hanford LAW testing**
  - Performing bench-scale FBSR testing of radioactive DWPF solution spiked with radioactive Tc, Iodine, and Cs
  - Performing bench-scale FBSR testing of four radioactive LAW solutions including radioactive Tc, Iodine, and Cs
  - Verify radioactive Cs, Tc, and I retention in granular mineral form and geopolymer monoliths and mass balance closure

Questions and Answers

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