



Fuel Cycle Research and Development

Advances in Off-Gas Treatment for Used Nuclear Fuel Processing

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Outline

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Overview of Off-Gas Sigma Team

- Off-gas Capture Requirements
- Iodine Pathways and Implications
- Selected Technical Accomplishments
 - Iodine / Tritium Co-adsorption
 - Iodine loading mechanistic and performance studies
 - Alternate Iodine Sorbents
 - Iodine Waste Forms
- Summary



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Multidisciplinary team from across the DOE complex working collaboratively to solve a broad technical challenge

- Understand and demonstrate technologies to meet regulatory requirements for recovery and disposal of volatile radionuclides from the processing of used nuclear fuels
- Develop viable methods to control radioiodine, krypton-85, tritium and, if needed, carbon-14 releases from used nuclear fuel recycle
 - Applicable to aqueous, E-chem and advanced separation processes
 - Includes both capture and immobilization
- Understand the scientific basis for the capture and immobilization technologies





Metal organic frameworks (MOFs) for I and Kr immobilization



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Relevant Regulatory Drivers for U.S. Off-gas Treatment

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Volatile off-gas components have wide range of half-lives and disposal requirements:

- ${}^{3}H$ 12.31 y- ${}^{85}Kr$ 10.76 y- ${}^{14}C$ 5715 y- ${}^{129}I$ 1.57 x 107 y
- Xe Stable and very short half-life < 30 days

EPA Regulations

- Standards for normal operation (40 CFR 190) (Applies to Fuel Cycle Facilities)
 - 25 mrem/y whole body
 - 75 mrem/y thyroid
 - 50 000 Ci/GWy ⁸⁵Kr (1.85 x 10¹⁵ Bq / GWy)
 - 5 mCi/GWy ¹²⁹I (1.85 x 10⁸ Bq / GWy)
 - 0.5 mCi/GWy ²³⁹Pu and other alpha-emitters
- 40 CFR 61 (Applies to facilities operated by DOE)
 - Limits equivalent dose to the public to 10 mrem/y

NRC

- Standards for protection from ionizing radiation (10 CFR 20) (Applies to NRC Licensed Facilities)
 - Applies to facilities licensed by NRC
 - Total equivalent dose not to exceed 0.1 rem/y
 - Provides a table of air concentration limits for each radionuclide

40 CFR 190 is the most restrictive of the regulations for non-DOE facilities



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Required decontamination factors (DF)

- What DF is needed to meet the regulations irrespective of what fuel is being processed and how long it has been out of reactor?
- How long must the UNF be stored before the short half-life isotopes (³H and ⁸⁵Kr) no longer need to be removed?



Assumptions for Analysis

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R. Jubin (ORNL), D Strachan (PNNL), N Soelberg (INL)

- Allowable contribution to total dose to maximally exposed individual (MEI) is between 10% and 100% of allowable dose.
 - Same factor will apply to thyroid dose.
- No engineering margins are applied initially.
- Site boundary is at max plume concentrations
- Fuel ages: 2, 5, 10, 20, 30, 50, 70, 100 and 200 y.
- Fuel type: LWR (UOX)
- Burn-up: 60 GWd/tIHM.
- Size of plant: 1000 t/y.



Use of CAP-88 Dispersion Model

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Illustration:

- MEI: 600 m downwind of the hypothetical stack.
- The plume "hits the ground" at this point.
- Ground-level dose is maximum at this point.
- This point is used as location of MEI = conservatively high estimate.







Controlling ⁸⁵Kr and ¹²⁹I to Meet 40CFR190 Fuel Cycle Limits Is Not Sufficient to Meet Dose Limits in U.S.

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Illustrative case:

- 60 GWd/t PWR used fuel; 1000 t/y; 100-m stack;
- 18 m/s stack gas velocity; conservative rural agriculture
- Iodine DF of 190; Krypton DF of 7 decreasing to 1
 Off-Gas Sigma Team
 Advances in Off-Gas Treatment

- Total dose exceeds limit of 25 mrem/y until fuel cooled ~10 y so additional control is needed for ³H (DF of 2)
- If dose contribution for volatile radionuclides is limited to 10% of allowable controls needed for ¹²⁹I, ³H, ⁸⁵Kr



Observations on Capture Requirements

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Isotope	Required DF - 100% allocation of dose limit to volatiles - No Margin	Required DF - 10% allocation of dose limit to volatiles - No Margin	Required DF - 100% allocation of dose limit to volatiles - 5X Margin	Required DF - 10% allocation of dose limit to volatiles - 5X Margin
³ Н	1.9 – 1	38 – 1	10 – 1	190 – 1
¹⁴ C	1	1	1	1
⁸⁵ Kr	7 – 1	7 – 1	35 – 1	35 – 1
129	190	570	950	2850



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Observations on Iodine Pathways

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R. Jubin (ORNL), D Strachan (PNNL), N Soelberg (INL)

Completed a study in FY13 on the iodine speciation and pathways

- Laboratory experiments report > 99% iodine evolved to off-gas streams
- However, reports from actual reprocessing plants indicate significant amounts of iodine remained in spent – fuel solutions
 - Up to 5%
 - Extensive treatment of dissolver solution may reduce this to ~1%
 - Limiting DF in DOG to a value of only 20 to 100.
- Forms of iodine reported in the dissolver solution include dissolved I₂ and IO₃⁻, organic iodide, and undissolved colloidal iodine



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Prepared for U.S. Department of Energy Campaign or Program R.T. Jubin, D.M. Strachan, and N.R. Soelberg Oak Ridge National Laboratory, Pacific Northwest National Laboratory and Idaho National Laboratory September 15, 2013 FCRD-SWF-2013-000308 ORNULTR-2013083 INUEXT-13-30119



Anticipated Iodine Pathways

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"Fuel Age" study examined total release requirements





Achieving the Desired Overall Plant lodine DF can be a Challenge

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	Case 1	Case 2	Case 3	Case 4
Assumed Iodine Partition – Percent of iodine split to specified process / operation (%)				
Percent of iodine released to Head-end cell (%)	0.01	0.01	0.01	0.01
Percent of iodine fed to dissolver released from dissolver solution to dissolver off-gas (DOG) (%)	96	96	96	99
Percent of DOG released to Dissolver Cell (%)	2	2	2	2
Percent of iodine reaching processes released from tanks / processes to vessel off-gas (VOG) (%)	50	50	50	50
Percent of iodine in waste released from waste solidification to off-gas (%)	80	80	80	80
lodine DF by off-gas stream				
Head end cell off-gas	10	10	10	10
DOG	1000	1000	1000	1000
Dissolver cell off-gas	10	10	100	100
VOG	1000	100	100	100
Waste solidification off-gas	100	100	100	100
Overall Plant DF	330	310	670	790



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Assessment of water (tritium) and iodine co-adsorption on MS3A

B. Spencer, S. Bruffey, K. Anderson, J. Walker, R. Jubin (ORNL)

- Objective: Evaluate iodine adsorption on type 3A molecular sieve; evaluate the impact of iodine co-adsorption on water (tritium) adsorption
- Significance: Tritium effluent control
 - Adsorption from very dilute streams
 - Establish practical performance criteria
 - Impacts of co-adsorption on process design and process sequencing
 - Develop techniques to avoid co-adsorption of long half-life radionuclides



- Thin-bed tests show > 2 wt% iodine retention
- About 0.2 wt% not easily desorbed
- Little change in water capacity
- Column tests underway

Areas of further research:

- > Desorption of iodine/water—preferential or not
- Techniques to separate iodine/water (prevent ¹²⁹I contamination of ³H which is otherwise low-level waste)

Results:



Assessment of water (tritium) / iodine coadsorption on AgZ

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B. Spencer, S. Bruffey, K. Anderson, J. Walker, R. Jubin (ORNL)

- Objective: Evaluate water (tritium) adsorption on silver-exchanged mordenite, and evaluate the impact of the co-adsorption of water on subsequent iodine adsorption on Ag^oZ
- Significance: lodine effluent control
 - Capture/immobilize iodine from dilute streams
 - Effect of co-adsorption and release of sorbed species in downstream processes



Results:

- Both thin-bed and column tests performed
- Water sorption front precedes iodine front
- AgºZ absorbs 2%–3% water by weight
- Short term water exposure does not significantly impact iodine capacity

Areas of further research:

- Desorption of water in subsequent processing
- Degree of water and iodine separation



CH₃I Adsorption on Ag⁰Z

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S. H. Bruffey, R. Jubin, B. B. Spencer (ORNL) N. Soelberg (INL), T Nenoff (SNL)

Objective:

- Evaluate the adsorption rates and capacities of selected sorption media.
- Identify the gaseous by-products of CH_3I loading on capture materials
- Significance: Organic iodides present in the off-gas streams have been shown to be more difficult to capture. Preliminary tests at INL have shown elemental iodine in the effluent from deep beds treating only gas streams containing only organic iodides.

Results:

- Multilab test plan has been developed and is being executed.
 - Thin bed tests at ORNL Preliminary result shown on a later slide
 - Deep bed tests underway at INL
 - Loaded media provided to SNL



CH₃I Adsorption on Ag⁰Z: Results

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S. H. Bruffey, R. Jubin, B. B. Spencer (ORNL)





Methyl iodide deep-bed adsorption testing Nick Soelberg (INL)

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- Update prior CH₃I absorption data on silver zeolite (What happens to the iodine?)
- Determine by-products (What happens to the CH₃ moiety?)
- Can high iodine capture (DF ≥ 1,000) be achieved for organic iodide?
- Other sorbents (How will silver-functionalized aerogel perform?)
- What are CH₃I adsorption phenomena:
 - Adsorption capacity (How much iodine can the sorbent adsorb?)
 - Adsorption efficiency (decontamination factor [DF]?)
 - Silver utilization efficiency (how much of the silver forms AgI?)
 - Mass transfer zone (What is the depth of adsorption in sorbent; how does it progress through the sorbent bed?)
 - Impacts of other gas species (NO, NO₂, H_2O)

Results to date:

- CH₃I molecule splits; iodine can react with Ag to form AgI
- CH₃ moiety can follow a separate path
- After sorbent saturation, then iodine can be released as other compounds (I₂ or HI)
- More detail in: Nenoff, et al, "Silver-Mordenite for Radiologic Gas Capture from Complex Streams: Dual Catalytic CH₃I Decomposition and I Confinement", submitted to Microporous and Mesoporous Materials





Silver-Functionalized Silica Aerogel for Capture and Immobilization of ¹²⁹I

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J Matyáš (PNNL)

- **Objective:** Develop a Ag⁰-functionalized silica aerogel for highly selective and efficient capture of ¹²⁹I. Consolidated into a durable high-iodineloaded silica-based waste form.
- Significance: Potential sorbent material suitable for direct conversion to waste form.
- Production of Ag⁰-functionalized silica aerogel for testing at ORNL and INL
 - Bulk density ~500 kg/m³
 - High silver content ~35 mass%
 - Sorption capacity ~45.4 ± 0.7 mass%

Demonstration of consolidation

- Hot uniaxial pressing in air
- 1200 °C for 30 min under 29 MPa
- Iodine retention 92.1%



Assembly used to determine I_2 loading capacity (iodine vapors at 150 °C for 24 h)





Low-Temperature Sintering Glass Composite (GCM) Waste Forms – Minimum Ag Addition T. Nenoff, T. J. Garino, M. A. Rodriguez (SNL)

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Objective

 Develop a compact, monolithic waste form for iodine that is mechanically, thermally and chemically stable, and requires minimum to no additional Ag

Significance

- Development of a low temperature sintering WF
 with equal or surpassing durability to nuclear glass WFs
- Optimize composition and/or synthesis conditions to minimize added silver.

Accomplishments

- Determined minimum Ag flake addition AgI-Z utilizing standard composition of GCM: 20wt% AgI-Z, 80wt% Glass; FOR SINTERING IN AIR
 - Maximum iodine loaded AgZ (samples provided by ORNL) = 7.8 wt%
 - Determined 1.1wt% Ag flake necessary to eliminate any iodine loss during sintering
 - Determined no Ag flake necessary for lower loading levels iodine in AgZ (including 0.5 wt % and 3.3 wt%)
- Determined minimum Ag flake addition AgI-Z utilizing standard composition of GCM: 20wt% AgI-Z, 80wt% Glass; FOR SINTERING IN INERT ATMOSPHERE
 - No Ag flake needed to mixture
 - Lack of oxygen in sintering atmosphere appears to limit or eliminate reoxidation of Ag° in mordenite and prevent the loss of iodine from AgI





HIPping of AgZ

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S. H. Bruffey, K. Patton, R. Jubin (ORNL)

- Objective: Convert iodine-loaded sorbent directly into a waste form with minimal processing
- Significance: Provide high-capacity, dense waste form that eliminates the need for additional matrix materials

FY13 Results:

- Pressed 6 samples of Ag⁰Z and 2 samples of I-Ag⁰Z
- Analyzed by SEM and XRD: primarily amorphous with some SiO₂ phases
- Mordenite structure not observed in most samples

FY14 ongoing work:

- Designed 24-sample test matrix, using pure chemical precursors
- Pressing of the first 17 samples is underway







Summary - Progress Towards Closing Knowledge Gaps

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- Shortly after Sigma Team was formed we assessed our knowledge of off-gas treatment and highlighted the following gaps:
- <u>lodine:</u>
 - Effects of aging Demonstrating impacts to iodine capture behavior on both Ag⁰Z and Ag⁰-aerogel – To be covered in subsequent talk
 - Detailed gas stream compositions Several reports issued, most recently an FY13 report on the balance of plant streams
 - Competition for binding sites, etc *Limited studies to date*
 - Co-adsorption of other off-gas constituents Fundamental work performed, integrated testing of methods to control I₂/H₂O co-adsorption to take place FY14
 - Impact of changes in base material Lower iodine loading other impacts TBD



Progress Toward Closing Knowledge Gaps - #2

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<u>lodine, con'd:</u>

- Efficiency of capture media as a function of concentration *Limited to dissolver off-gas concentration for the most part*
- Methods to improve iodine volatilization from the head-end processes
- Importance of process chemistry highlighted in new FY 13 report

<u>Tritium:</u>

- Extent of co-adsorption of other off-gas constituents (e.g. I₂, ¹⁴CO₂)
 - In progress, integrated testing of I_2/H_2O co-adsorption FY14
- Tritium capture decontamination factors (DFs) at very low concentrations –
 In progress



Progress Towards Closing Knowledge Gaps #3

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Krypton-85:

- Selectivity for Kr vs Xe Multiple capture materials under testing: (MOF and zeolite based sorbents)
- Cost effective capture and storage methods Room temperature testing of MOF and zeolite based sorbents in progress

Waste forms:

- Loading and retention
 - Initial work on GCM waste form optimization for AgZ
 - Scoping tests on HIPping of AgZ
 - Direct consolidation of Ag-Aerogel, SiC for lodine and Kr





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Max Plant Size with No Controls

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- Total dose to MEI limited to 25 mrem/y
- Dose to MEI attributed to only volatile radionuclides
- Ignores the power based requirements in 40CFR190



Illustrative case:

- 36-m stack height;
- 18 m/s stack gas velocity; conservative rural agriculture



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Species that might arise in off-gas due to organic iodine (CH₃I)

B. B. Spencer (ORNL)

- Thermodynamic modeling program HSC 6.1 was used to evaluate favorability of certain reactions (gas phase, no heterogeneous catalysis)
- Reactions NOT favored at 0 < T < 200°C in the gas phase</p>

$I_2(g) + H_2O(g) = HIO(g) + HI(g)$ CH ₃ I(g) + H ₂ O(g) = CH ₃ OH(g) + HI(g)	Neither hyperiodus acid or methanol are likely to form in the gas phase.					
Reactions favored at 0 < T < 200°C in the gas phase						
$\begin{array}{l} CH_3I(g) + NO_2(g) = CH_3NO_2(g) + \frac{1}{2} I_2(g) \\ CH_3I(g) + CH_3NO_2(g) = CH_3\text{-}O\text{-}CH_3 + NOI(g) \\ 2NOI(g) = I_2(g) + 2NO(g) \end{array}$	Nitromethane is possible when nitrogen dioxide is available. It enables the formation of dimethyl ethe					

Nitrosyl iodide is unstable, and if formed will rapidly decompose.

■ At T >~ 200°C, methanol becomes a potential product

 $2CH_3NO_2(g) + H_2O(g) + \frac{1}{2}O_2(g) = 2CH_3OH(g) + 2NO_2(g)$

Nitromethane is a possible precursor to methanol.

Hyperiodus acid may form if a condensed phase is present

 $I_2(a) + H_2O = HIO + HI(g)$

Thomas et al., J.Inorg.Nucl.Chem., 42, p183, (1980) describes the equilibria, including iodate, in detail.