Evaluating Potential Alternate Getter Materials
and Related Cleaning Methodologies

David W. James
Gregg A. Morgan

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PNNL
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Overview

- Impurity Removal
  - Getters
  - Theory
  - Alternate materials explored

- Minimizing Impurity Introduction – The Best Defense
  - A look at solvent cleaning
  - Hydrogen exchange
Impurity Removal
Getters for Methane and Ammonia Cracking
General Tritium Processing Facility Gases

- **Glovebox atmosphere gases**
  - Ar
  - N$_2$
  - He
  - Minimal O$_2$ from ingress
- **Product gases**
  - Q$_2$ where Q is H, D, T
  - He-3
- **Impurity Gases**
  - Q$_2$
  - He-3
  - Ar, N$_2$, O$_2$, CQ$_4$, NQ$_3$, CO, CO$_2$, Q$_2$O, and Others

- **Material Interactions**
  
  CH$_4$ cracking and potential reformation is material and temperature dependent
ST909® Getter Characteristics

- \( \text{Zr(Mn}_{0.5}\text{Fe}_{0.5})_2 \) or Zr-Mn-Fe (40.5% Zr, 24.5% Mn, 25.0% Fe, 10% Al)

- Manganese and iron – catalytic active sites for decomposition
  - \( \text{CH}_4 \)
  - \( \text{NH}_3 \)
  - \( \text{CO} \)
  - \( \text{CO}_2 \)
  - \( \text{O}_2 \)

- Zirconium - active sites for the gettering of elements
  - O, N, C
  - Getter performance of Zr for methane cracking in an \( \text{N}_2 \) rich atmosphere is lower than in hydrogen isotope and/or helium rich carrier gas streams

  CO, \( \text{CO}_2 \) and \( \text{NH}_3 \) may inhibit \( \text{CH}_4 \) cracking

  Testing showed ~ 0.07 - 0.08 gram \( \text{N}_2 \) captured per gram ST909

- Expensive (~$4.2K to $5.3K/kg depending on quantity ordered)
Objective of Impurity Removal Testing

- Identify a more effective less expensive combination of materials (or a material) that can perform same overall functions of gettering oxygen from water, and carboxides, then nitrogen from ammonia, and carbon from methane gas; with comparable performance capabilities to ST909 for use with nitrogen, and argon carrier gases.

- Tests focused on methane and ammonia removal
All three elements (Zr, Mn, Fe) work together to getter impurities.
Materials Selected for Study

Original patent relating to ST909 covered compounds with the formula $\text{ZrM}_1\text{M}_2$, where $\text{M}$ is any transition metal selected from the group consisting of Cr, Mn, Fe, Co, Ni and mixtures thereof.

Group IV metals – good for gettering
Transition metals – good for cracking

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST909</td>
<td>40.5% Zr, 24.5% Mn, 25.0% Fe, 10% Al</td>
</tr>
<tr>
<td>AME ZrMnFeAl</td>
<td>40.5% Zr, 24.5% Mn, 25.0% Fe, 10% Al</td>
</tr>
<tr>
<td>ST707</td>
<td>70% Zr, 24.6% V, 5.4% Fe</td>
</tr>
<tr>
<td>Ni/k</td>
<td>Nickel on kieslesghur</td>
</tr>
<tr>
<td>AME TiMoZr</td>
<td>83.4% Ti, 11.5% Mo, 4.5% Zr</td>
</tr>
<tr>
<td>AME AlNiFe</td>
<td>50% $\text{Al}_2\text{O}_3$, 25% Ni, 25% Fe</td>
</tr>
<tr>
<td>AME ZrNi</td>
<td>76.5% Zr, 23.5% Ni</td>
</tr>
<tr>
<td>Fe/Ni</td>
<td>Fe, Ni</td>
</tr>
</tbody>
</table>

Like for like compositions
Alternate chemical compositions
Comparing Vendors of Chemically Equivalent Material

Foreign Supplier
- Cost: 10 kg > $4210/kg
  < 10 kg $5200/kg
- SAES ST909
- Preparation: Powdered Metallurgy
  greater surface area

Domestic Supplier
- Cost: 10 kg > $784/kg
  < 10 kg variable
- AME ZrMnFeAl
- Preparation: Melted Ingots
  lower surface area

Composition
- Zr Mn Fe Al

SAES
SAVANNAH RIVER NATIONAL LABORATORY
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS
### SRNL Perkin Elmer ICP-MS Results

<table>
<thead>
<tr>
<th>Element</th>
<th>Anticipated ST909 (wt%)</th>
<th>SAES ST909 (wt%)</th>
<th>AME ZrMnFe (wt%)</th>
<th>AME Reported (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>10</td>
<td>10.5 (10.1 %RSD)</td>
<td>10.5 (10 %RSD)</td>
<td>10</td>
</tr>
<tr>
<td>Ba</td>
<td>0.00599 (18.4 %RSD)</td>
<td>&lt; 0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.0499 (11.8 %RSD)</td>
<td>&lt; 0.065</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.0424 (10.7 %RSD)</td>
<td>&lt; 0.038</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.0549 (15.4 %RSD)</td>
<td>&lt; 0.122</td>
<td>0.0045</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>25</td>
<td>24.1 (10.1 %RSD)</td>
<td>23.2 (10 %RSD)</td>
<td>25</td>
</tr>
<tr>
<td>Mn</td>
<td>24.5</td>
<td>25.4 (10 %RSD)</td>
<td>19.8 (10 %RSD)</td>
<td>24.5</td>
</tr>
<tr>
<td>Si</td>
<td>0.915 (19.8 %RSD)</td>
<td>1.55 (22.5 %RSD)</td>
<td>0.0028</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.634 (10.8 %RSD)</td>
<td>&lt; 0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.0596 (12.5 %RSD)</td>
<td>&lt; 0.085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>40.5</td>
<td>39.5 (10 %RSD)</td>
<td>34.6 (10 %RSD)</td>
<td>40.5</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td>0.0032</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td>0.0008</td>
<td></td>
</tr>
</tbody>
</table>
Comparing Composition Through XRD and XRF

**XRD**

The XRD patterns show similarities between ST909 and AME ZrMnFeAl samples.

**EDXRF**

The EDXRF K-ratios (Ka, Kb, La) from the two samples are similar. For Zr, Fe, Mn:

Differences in minor elements:

- The ST909 sample has V, Cr, Ni, Cu and Sn (all at < 0.5%) missing from AME.
- The AME sample has Hf (at < 0.5%) missing from ST909.
Comparing Products Visually

Virgin SAES ST909 Pellets
- Dull silver color

Used SAES ST909 Pellets
- Lustrous silver coloration
- Golden discoloration
- Decrepitation

Virgin AME ZrMnFeAl Pieces

Used AME ZrMnFeAl Pieces
- Some small particles showed magnetic properties
## Test Matrix

<table>
<thead>
<tr>
<th>Test</th>
<th>Material</th>
<th>Gas Impurity Constituents (percent by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ST909</td>
<td>99.5% N₂, 0.5% CH₄</td>
</tr>
<tr>
<td>2</td>
<td>ST909</td>
<td>99.5% N₂, 0.5% NH₃</td>
</tr>
<tr>
<td>3</td>
<td>ST909</td>
<td>93% N₂, 1.5% Ar, 0.5% He, 5% CH₄</td>
</tr>
<tr>
<td>4</td>
<td>ST909</td>
<td>32% N₂, 67% Ar, 0.5% He, 0.5% CH₄</td>
</tr>
<tr>
<td>5</td>
<td>ST909</td>
<td>32% N₂, 66% Ar, 1% He, 0.5% NH₃, 0.5% CH₄</td>
</tr>
<tr>
<td>6</td>
<td>AME ZrMnFeAl</td>
<td>99.5% N₂, 0.5% NH₃</td>
</tr>
<tr>
<td>7</td>
<td>AME ZrMnFeAl</td>
<td>93% N₂, 1.5% Ar, 0.5% He, 5% CH₄</td>
</tr>
<tr>
<td>8</td>
<td>AME ZrMnFeAl</td>
<td>32% N₂, 67% Ar, 1% He, 0.5% CH₄</td>
</tr>
<tr>
<td>9</td>
<td>AME ZrMnFeAl</td>
<td>32% N₂, 66% Ar, 1% He, 0.5% NH₃, 0.5% CH₄</td>
</tr>
<tr>
<td>10</td>
<td>ST707</td>
<td>99% N₂, 0.5% He, 0.5% NH₃</td>
</tr>
<tr>
<td>11</td>
<td>ST707</td>
<td>32% N₂, 67% Ar, 0.5% He, 0.5% CH₄</td>
</tr>
<tr>
<td>12</td>
<td>Ni/k</td>
<td>93% N₂, 1.5% Ar, 0.5% He, 5% CH₄</td>
</tr>
<tr>
<td>13</td>
<td>Ni/k</td>
<td>99% N₂, 0.5% He, 0.5% NH₃</td>
</tr>
<tr>
<td>14</td>
<td>AME TiMoZr</td>
<td>93% N₂, 1.5% Ar, 0.5% He, 5% CH₄</td>
</tr>
<tr>
<td>15</td>
<td>AME TiMoZr</td>
<td>99% N₂, 0.5% He, 0.5% NH₃</td>
</tr>
<tr>
<td>16</td>
<td>AME TiMoZr</td>
<td>32% N₂, 67% Ar, 0.5% He, 0.5% CH₄</td>
</tr>
<tr>
<td>17</td>
<td>AME AlNiFe</td>
<td>32% N₂, 66% Ar, 1% He, 0.5% NH₃, 0.5% CH₄</td>
</tr>
<tr>
<td>18</td>
<td>AME ZrMnFeAl + AME AlNiFe</td>
<td>32% N₂, 66% Ar, 1% He, 0.5% NH₃, 0.5% CH₄</td>
</tr>
<tr>
<td>19</td>
<td>AME ZrNi</td>
<td>32% N₂, 66% Ar, 1% He, 0.5% NH₃, 0.5% CH₄</td>
</tr>
<tr>
<td>20</td>
<td>Fe/Ni</td>
<td>86.32% H₂, 2.27% N₂, 10.93% He, 0.48% NH₃</td>
</tr>
</tbody>
</table>
Experimental Test System

- Flow through testing
- Pressure transducers
- MKS Flow Controllers
- Gas supplies of Ar, N₂, He, H₂, and others
- Residual Gas Analyzers

~6 grams of materials per test unless otherwise noted
ST909 Methane Cracking in N₂ Rich Stream

RGA Methane Cracking Efficiencies
~2100 Torr, 670°C, 30 sccm

\[
\text{RGA Methane Cracking Efficiency} = 1 - \frac{\text{(Signal}_{\text{CH}_4})_{\text{rest}}}{\text{(Signal}_{\text{CH}_4})_{\text{feed}}}
\]

- **Sample 1**: SAES ST909 99.5 N₂ 0.5 CH₄
- **Sample 2**: SAES ST909 99.5 N₂ 0.5 CH₄

*Fairly reproducible results are observed*

As Received
SAES ST909

Post Testing
SAES ST909
Ni/k tests had trouble with clogging, carbon strands observed

As Received
AME TiMoZr
Post Testing
AME TiMoZr

As Received
AME ZrMnFeAl
Post Testing
AME ZrMnFeAl
Methane Cracking in Ar Rich Stream

RGA Methane Cracking Efficiencies
~2100 Torr, 670°C, 30 sccm

\[
\text{RGA Methane Cracking Efficiency} = 1 - \frac{\text{Signal}_{\text{CH4}}}{\text{Signal}_{\text{inert}}/\text{feed}}
\]

- SAES ST909 32 N2 67 Ar 0.5 He 0.5 CH4
- SAES ST707 32 N2 67 Ar 0.5 He 0.5 CH4 after previous 23 hours with NH3 mixture
- AME TiMoZr 32 N2 67 Ar 0.5 He 0.5 CH4
- AME ZrMnFeAl 32 N2 67 Ar 0.5 He 0.5 CH4

Steep decrease in methane cracking efficiency

Consistent methane cracking efficiencies

Post Testing
AME ZrMnFeAl
Ammonia Decomposition in N₂ Rich Stream – Comparing ST909 to AME

RGA Ammonia Decomposition Efficiencies

\[ \text{RGA Ammonia Decomposition Efficiency} = 1 - \frac{(\text{Signal}_{\text{NH}_3})_{\text{test}}}{(\text{Signal}_{\text{NH}_3})_{\text{feed}}} \]

~2100 Torr, 670°C, 30 sccm

AME ZrMnFeAl had ~ 1% better ammonia decomposition efficiency than ST909
Ammonia Decomposition with Inert Present

RGA Ammonia Decomposition Efficiencies
~2100 Torr, 670°C, 30 sccm

\[
\text{RGA Ammonia Decomposition Efficiency} = 1 - \frac{\text{Signal}_{\text{inert}}}{\text{Signal}_{\text{NH}_3}}
\]

- **Ni/k (15 pellets longer residence time)**
  - ~40% drop in ammonia decomposition efficiency

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Post Testing AME TiMoZr

As Received
SAES ST707

Post Testing
SAES ST707

As Received
Ni/k

Post Testing
Ni/k

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Savannah River National Laboratory

We put science to work.™
Combination Testing with Both NH₃ and CH₄ Present

Mass 15 signal

RGA Methane Cracking Efficiencies
~2100 Torr, 670°C, 30 sccm
32% N₂, 66% Ar, 1% He, 0.5% NH₃, and 0.5% CH₄

RGA Mass 15 Reduction = 1 - \frac{\text{Signal}_{\text{Total}} - \text{Signal}_{\text{pure Ar}}}{\text{Signal}_{\text{pure Ar}}}

- 3 gm AME ZrMnFeAl and 3 gm AME AlNiFe
- 6 gm AME ZrMnFeAl and 6 gm AME AlNiFe
- 6 gm AME AlNiFe
- 6 gm AME ZrNi

Elapsed Time (hr: min: sec)

Mass 17 signal

RGA Ammonia Decomposition Efficiencies
~2100 Torr, 670°C, 30 sccm
32% N₂, 66% Ar, 1% He, 0.5% NH₃, and 0.5% CH₄

RGA Ammonia Decomposition Efficiency = 1 - \frac{\text{Signal}_{\text{NH₃}}}{\text{Signal}_{\text{NH₃ pure Ar}}}

- 3 gm AME ZrMnFeAl and 3 gm AME AlNiFe
- 6 gm AME ZrMnFeAl and 6 gm AlNiFe
- 6 gm AME AlNiFe
- 6 gm AME ZrNi

Elapsed Time (hr: min: sec)

Mass 16 signal

RGA Methane Cracking Efficiencies
~2100 Torr, 670°C, 30 sccm
32% N₂, 66% Ar, 1% He, 0.5% NH₃, and 0.5% CH₄

RGA Mass 16 Reduction = 1 - \frac{\text{Signal}_{\text{Total}} - \text{Signal}_{\text{pure Ar}}}{\text{Signal}_{\text{pure Ar}}}

- 3 gm AME ZrMnFeAl and 3 gm AME AlNiFe
- 6 gm AME ZrMnFeAl and 6 gm AME AlNiFe
- 6 gm AME AlNiFe
- 6 gm AME ZrNi

Elapsed Time (hr: min: sec)

Single Material Summary

RGA Methane Cracking Efficiencies
~2100 Torr, 670°C, 30 sccm
SAES T909 32 N₂ 67 Ar 0.5 He 0.5 CH₄
SAES T707 32 N₂ 67 Ar 0.5 He 0.5 CH₄ after previous 23 hours with NH₃ mixture
AME TiMo₂Zr 32 N₂ 67 Ar 0.5 He 0.5 CH₄
AME ZrMnFeAl 32 N₂ 67 Ar 0.5 He 0.5 CH₄

- Steep decrease in methane cracking efficiencies
- Consistent methane cracking efficiencies

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We put science to work.
Continued Combination Testing Testing for Ammonia Decomposition

Bench Scale Test System

Parr vessel filled with Fe and Ni pellets
Ammonia Decomposition Efficiency Iron and Nickel-Based Materials

RGA Ammonia Decomposition Efficiencies
~2000 Torr, 750°C, 5 sccm
86.32% H₂, 10.93% He, 2.27% N₂, and 0.48% NH₃ gas mixture

Equilibrium conversion expected: 96.4%

Identified Potential Causes
- Optimization needed
- Channeling
- Impurities in material (aka bad chemistry)
Iron and Nickel – the Poor Man’s Ruthenium

As Received

Eggshell Coating
Summary of Observations for Impurity Removal Testing

• Similar composition does not guarantee similar CH₄ and NH₃ decomposition efficiencies

• Ni/k – excellent CH₄ cracking capabilities – not carbon gettering

• ZrNi performed quite well for both CH₄ and NH₃ decomposition – potential hydride material needs further evaluation

• Combination testing of AME ZrMnFeAl with AME AlFeNi showed better decomposition efficiencies than ST909 and further evaluation recommended
Minimizing Impurities
Looking at Solvent Cleaning and Hydrogen Exchange
Minimizing Impurity Introduction (The Best Defense)

• Minimize chemical incompatibilities that cause impurities to form in a process

• Reduction by minimizing impurity occurrence (Vendor Technical Specifications)
  – Minimal carbon
  – Minimal sulfur
  – Low chlorine content
  – Requires verification prior to installation

• Clean Materials
  – Solvent for non-porous materials or polymers
    • CFC’s Ozone Depletion Potential – Banned by EPA
    • Must follow EPA Significant New Alternatives Policy (SNAP) substitutes in metal cleaning
  – Steam/Detergent cleaning
  – High Pressure Water Blast Cleaning
  – Vendor Cleaning
  – Drying with oil free inert gas
  – High temperature bake-out for equipment that could be at elevated temperatures in process

Example
Iron powder vendor reported composition
• Carbon 60 ppm
• Sulfur 180 ppm
Requires lubricating oil during iron sintering which can change the impurity concentrations

Many cleaning methods are good for piping and tubing but not generally ideal for catalyst and getters
Objective of Minimizing Impurity Introduction Testing

- Evaluate potential of solvent cleaning and hydrogen reduction treatments to help minimize impurities of potential materials

- Tests focused on analytical characteristics of materials following treatments
Hydrofluorocarbon-Based Solvent

- **Vertrel® MCA**
  - Azeotrope
    - Vertrel XF hydrofluorocarbon (2,3-dihydrodecafluoropentane)
    - Trans-1,2-dichloroethylene
  - Cleaning:
    - Vapor degreasing
    - Manually wiping
    - Spraying
    - Flushing

- **Benefit:** hydrocarbon content of solvent can be measured
### Californium Neutron Activation Analysis for Chlorine Content

- **Material**
  - **Chlorine mg/g**
  - Sintered Iron Virgin: 63.0
  - Sintered Iron Post Testing: 48.4
  - Sintered Iron Solvent Cleaned: 48.0

- **Material**
  - **Chlorine mg/g**
  - Ni-Ceramic Virgin: 170
  - Ni-Ceramic Post Testing: 167
  - Ni-Ceramic Solvent Cleaned: 137

**Ni catalyst is a porous material. Solvent use not advisable on porous catalyst.**
LECO Carbon/Low Sulfur Determination

<table>
<thead>
<tr>
<th>Material</th>
<th>Sulfur, ppm</th>
<th>Carbon, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered Iron Virgin</td>
<td>61.7 ± 9.9</td>
<td>358.4 ± 17.2</td>
</tr>
<tr>
<td>Sintered Iron Post Testing</td>
<td>49.4 ± 14.9</td>
<td>14.0 ± 1.4</td>
</tr>
<tr>
<td>Sintered Iron Solvent Cleaned</td>
<td>45.5 ± 10.3</td>
<td>349.7 ± 28.7</td>
</tr>
<tr>
<td>Ni-Ceramic Virgin</td>
<td>3.1 ± 2.4</td>
<td>18.8 ± 6.6</td>
</tr>
<tr>
<td>Ni-Ceramic Post Testing</td>
<td>9.8 ± 4.39</td>
<td>7.9 ± 5.0</td>
</tr>
<tr>
<td>Ni-Ceramic Solvent Cleaned</td>
<td>1.7 ± 0.19</td>
<td>13.5 ± 2.5</td>
</tr>
</tbody>
</table>

Solvent analysis indicated 43 ppm
Solvent analysis accounts for surface contaminants NOT bulk!

Solvent analysis indicated 19 ppm

Transference of sulfur from Fe to Ni catalyst
A Look at a Thermocouple Place Holder Post – Vertrel Cleaning

Description
The inner and outer portion of the tube “Cleaned” using Vertrel MCA

Reported Results
3/8” SS tubing < 100 ppm carbon

Vendor stamp still observed after solvent cleaning. Removable with acetone
Hydrogen Reduction at Elevated Temperatures Test Setup
A Look at the Quartz Cylinder Throughout the Test – Pre Startup After Bake-out

21°C

775°C
Moisture observed on tube walls and exhaust line.

Condensed moisture leaves black residue after it evaporates.

Yellow residue

Gray black residue
A look at the Exhaust – Day 2

Exhaust gas has residual material that can be captured by DI water trap
A look at the Quartz Cylinder Throughout Protium Cleaning Test – Day 2 Morning

Filament residue formation

Striation observed
Continued darkening of tube wall
A look at the Quartz Cylinder Throughout Protium Cleaning Test – End of Test

Carbon and sulfur contaminates that could be introduced to process if materials used without protium treatment
## LECO Carbon/Low Sulfur Determination

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<td>Sintered Iron Solvent Cleaned</td>
<td>45.5 ± 10.3</td>
<td>349.7 ± 28.7</td>
</tr>
<tr>
<td>Sintered Iron Post Solvent and Elevated-Temperature Protium-Cleaning</td>
<td>23.6 ± 5.3</td>
<td>5.3 ± 4.3</td>
</tr>
</tbody>
</table>

Remember: Solvent analysis indicated that the surface carbon of the virgin sintered iron pellets was unofficially 43 ppm compared to the 358.4 ppm observed by LECO testing.
Summary of Observations For Minimizing Impurity Testing

• Analytical method of determining impurity introduction needs to account for environment a material may be subjected to
  – Vertrel MCA may not work well for hydrocarbon removal
    • Didn’t remove ink from vendor stamp
    • Analytical only measures surface contaminants not bulk

• Pretreatment of materials outside of a tritium process may be advisable when appropriate to reduce impurity introduction
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  – Anita Poore
  – Brittany Hodge
  – Robbie Allgood
  – Melissa Golyski
  – Jared Clark
  – Gary Dobos
  – David Missimer

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Thank you for your attention