Basic researches on treatment and disposal of radioactive waste

Characterization and safe storage of spent zeolite produced by treatment of the contaminated water

Isao YAMAGISHI
Japan Atomic Energy Agency
Secondary wastes produced by decontamination

Circulating Water Cooling at Fukushima-1 NPS

- Damaged reactors

Removal of radioactive materials

- 2nd Cs adsorption (SARRY)
- Cs adsorption (KURION)
- Decontamination by precipitation (AREVA)

Desalination

- Reverse Osmosis
- Evaporative Concentration

Spent adsorbents (inorganic ion-exchangers)

- KURION: zeolite (herschelite for Cs, AGH for I)
- SARRY: zeolite (IE-96), Silicotitanate (IE-911)
  ※Cs removal >99%, high activity

AREVA sludge
  ※low activity

JAEA’s research on secondary waste by decontamination:
characterization, safe storage, conditioning for disposal
Key factors for safe storage of spent zeolite vessels

- **Factors**
  - Radioactive materials
  - Zeolite
  - Water
  - Salt (seawater)

- **Subject**
  - Hydrogen (radiolysis of water)
  - Corrosion of vessel
  - Heat
  - Radiation

- **Safety measures**
  - Ventilation
  - $H_2-H_2O$ catalyst
  - Washing
  - Drying
  - Cooling
  - Shielding

- **Decay with time**

Safe storage of specific vessels of highest activity, water & salt contents are to be evaluated as well as effectiveness of present safety measures.
Estimation of Cs activity in KURION vessel

Cs-134, 137 activities in KURION vessel: $<2.0 \times 10^{15}$ Bq

- Average decay heat ($<300$ W) + thermal conductivity
- Calculation of temperature in vessel

※Estimation using TEPCO press release

Cs activity

Cl− ion

High

Total activity of Cs-134, 137, Bq/vessel

Cl− conc. of contaminated water, ppm
R&D program for safe storage of spent zeolite

Properties of zeolite
- Water content
- Thermal conductivity & stability

Inventory & chemical properties of spent zeolite
- Adsorption (ion-exchange) data
- Simulant of spent zeolite
- Estimation of activity in vessel

Hydrogen generation and measures
- G values for H₂ production
- H₂ concentration in vessel
- H₂ (→H₂O) recombination catalyst

Durability of zeolite vessel against corrosion with salt
- Fundamental data & simulation
- Effectiveness of washing, drying, etc.
- Estimation of lifetime of vessel

Heat generation
- Absorbed dose & generated heat
- Temperature distribution in vessel and behavior of water

Final output: March 2014
Properties of zeolite

- Water content
- Thermal conductivity & stability
Experimental conditions

- Stainless steel cell was used for the measurement of dry KURON herschelite.
- A central heater was fixed in a silica-alumina protection tube for making temperature difference in the packed particles.
- Temperature control:
  - water bath at 20 to 60 °C
  - electric furnace at 80 to 300 °C.
- Thermal Conductivity $\kappa$ [Wm$^{-1}$K$^{-1}$] was determined by the equation,

$$\kappa = \frac{Q}{2\pi(T_1 - T_2)} \ln \left( \frac{R_2}{R_1} \right)$$

- Decay heat ($\rightarrow$ drying water of zeolite)
- Water content of zeolite ($\rightarrow$ H$_2$ production)

Thermal conductivity is fundamental data essential to evaluation of above factors.

$Q$: Linear power density of central heater [W/m]
$R_1$: 10 mm (inner radial position)
$R_2$: 25 mm (outer radial position)
$T_1$: Temperature at $R_1$ [K]
$T_2$: Temperature at $R_2$ [K]

Cell for the measurement
KURION herschelite was dried at 100 °C for 1 week.

- Thermal conductivity: 0.09 - 0.16 Wm\(^{-1}\)K\(^{-1}\) (20 to 320 °C)

- The fitting curve was obtained and is described by,

\[
\frac{\kappa}{(Wm^{-1}K^{-1})} = 2.42 \times 10^{-4}(T/K) + 0.022
\]

※ Thermal conductivity of damp zeolite used in the TMI was 0.16 Wm\(^{-1}\)K\(^{-1}\)\(^{[1]}\)


- Low thermal conductivity: \(\kappa_{air} \times (4\sim6)\)
- Influence of gas (steam) in zeolite bed is important because it conveys heat to the cold wall of the cell better.
Hydrogen generation and measures

- Measurement of fundamental data
  - G values for H₂ production
- How to manage H₂ gas
  - H₂ concentration in vessel (H₂ diffusion)
  - H₂ (→H₂O) recombination catalyst
Measurement of $G$-value for $H_2$ production

- Irradiation tests with KURION media (herschelite...) were carried out to measure $H_2$ production.
  $\Rightarrow$ $G$-values of $H_2$ from mixtures of zeolite and seawater were determined by using Co-60 $\gamma$-ray.
  $\Rightarrow$ The dependences of $G$-values on dilution, water content and temperature were also obtained.
- $H_2$ production in KURION vessel was estimated from distribution of T (activity) and water content.

- Irradiation tests for $H_2$ production
  Basic data important for radiation effects in zeolite wastes are obtained.
  - $H_2$ production with many kinds of zeolites
  - Redox of products and dissolved ions together with $H_2$ production
  - $H_2$ production after high-temp heating and high-dose irradiation

- Estimation of $H_2$ produced in vessels
  Based on the experimental and computational data, $H_2$ production at every step of process and disposal is estimated.

  ✓ $G$-values for $H_2$ production in zeolite-seawater system (AESJ, rapid communication in Jpn.)

$\gamma$-ray source specification

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>av.1.25 MeV</td>
</tr>
<tr>
<td>Distance</td>
<td>0–200 cm</td>
</tr>
<tr>
<td>Dose rate</td>
<td>15–0.5 kGy/h</td>
</tr>
</tbody>
</table>

Irradiation procedure

Gas analysis

Co-60 $\gamma$-irradiation room

zeolites
H₂ production in mixtures of zeolite and seawater

Herschelite (KURION-H) - water system
Air-sat., room temp., 1-4 kGy/h

Observed yield (G-value), G(H₂)

<table>
<thead>
<tr>
<th>sample</th>
<th>yield (10⁻⁸ mol/J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>seawater only</td>
<td>4.8 ± 0.3</td>
</tr>
<tr>
<td>50 wt% added</td>
<td></td>
</tr>
<tr>
<td>herschelite</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td>mordenite</td>
<td>3.0 ± 0.1</td>
</tr>
</tbody>
</table>

Primary yield, g(H₂)=4.7 × 10⁻⁸ mol/J

- In seawater: comparable to primary yield.
  ⇒ Oxidation of H₂ by products was repressed by dissolved ions in seawater.

- In mixture of ca.50% zeolite and ca.50% seawater: more than that in 50% seawater.
  ⇒ Water radiolysis was optionally originated from energy dissipation to zeolites.

P [mol/g] = G [mol/J] × D [J/g]

※ unit conversion: 1 μmol/J = 9.649 molecules/100eV
Dependence of $G$-value on weight fraction of water

$G$-values for $\text{H}_2$ production, $G(\text{H}_2)$ obtained in mixtures of zeolite and seawater were compared with those in mixtures of zeolite and pure water.

RESULT 1: Observed $G(\text{H}_2)$ in seawater was larger than that in pure water.

- pure water: $\text{H}_2$ is oxidized by radicals to form $\text{H}_2\text{O}$. 
  $\cdot\text{OH} + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}$

- seawater: the oxidation of $\text{H}_2$ is repressed by dissolved ions such as $\text{Cl}^-$ and $\text{Br}^-$

RESULT 2: At higher fraction of $\text{H}_2\text{O}$, $\text{H}_2$ production is effectively repressed by desalination.

RESULT 3: At lower fraction of $\text{H}_2\text{O}$, dehydration is more effective than desalination in repressing $\text{H}_2$ production.

In order to repress $\text{H}_2$ production in zeolite wastes,
- At high water content just after decontamination, desalination will be important.
- In the long-term storage of vessel, dehydration will be important.
How to manage troublesome hydrogen?

**Passive approach using heat-generation**
- Hydrogen diffusion analysis
  - Hydrogen concentration and temperature distributions in a spent KURION vessel
- Hydrogen diffusion test
  - Visualization of hydrogen mixing gas flow in miniature vessel

**Active approach using catalyst**
- Hydrogen recombination catalyst
  - Performance test of catalyst for automobile
Hydrogen diffusion analysis (1/2)

**Objective**
To comprehend hydrogen concentration increase in long-term storage of KURION adsorption vessel.

**Approach**
- Analytical model: 3-dimensional full structure
- Thermal-hydraulic analysis code: FLUENT

Schematic of KURION adsorption vessel
Results

Opening end lines of water inlet/outlet and vent tubes, a kind of siphon effect occurred by buoyancy and difference of mixed gas density. So that,

- The maximum temperature of zeolite bed (less than 200°C) became **lower than the self-ignition temperature of hydrogen** (about 560°C), and
- Hydrogen concentration in the vessel was kept much less than 4% of the lower explosive limit.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Hydrogen molar fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 200</td>
<td>Less than 4% (the lower explosive limit)</td>
</tr>
<tr>
<td>(mol/mol)</td>
<td></td>
</tr>
<tr>
<td>1.29e-02</td>
<td>4.44e+02</td>
</tr>
<tr>
<td>1.18e-02</td>
<td>4.37e+02</td>
</tr>
<tr>
<td>1.10e-02</td>
<td>4.00e+02</td>
</tr>
<tr>
<td>1.03e-02</td>
<td>4.25e+02</td>
</tr>
<tr>
<td>9.87e-03</td>
<td>4.16e+02</td>
</tr>
<tr>
<td>9.02e-03</td>
<td>4.08e+02</td>
</tr>
<tr>
<td>8.39e-03</td>
<td>4.01e+02</td>
</tr>
<tr>
<td>7.73e-03</td>
<td>5.44e+02</td>
</tr>
<tr>
<td>7.09e-03</td>
<td>5.80e+02</td>
</tr>
<tr>
<td>6.44e-03</td>
<td>6.18e+02</td>
</tr>
<tr>
<td>5.89e-03</td>
<td>6.87e+02</td>
</tr>
<tr>
<td>5.04e-03</td>
<td>3.22e+03</td>
</tr>
<tr>
<td>3.28e-03</td>
<td>3.22e+03</td>
</tr>
<tr>
<td>2.58e-03</td>
<td>3.65e+02</td>
</tr>
<tr>
<td>1.93e-03</td>
<td>3.65e+02</td>
</tr>
<tr>
<td>1.29e-03</td>
<td>3.58e+02</td>
</tr>
<tr>
<td>6.44e-04</td>
<td>3.51e+02</td>
</tr>
<tr>
<td>0.00e+00</td>
<td>3.43e+02</td>
</tr>
</tbody>
</table>

Temperature

Less than 200°C

In zeolite bed

Hydrogen concentration:
Less than 4% (the lower explosive limit)
Hydrogen diffusion test (1/2)

Objective
To validate the hydrogen diffusion analysis in a spent vessel.

Approach

- Hydrogen mixing gas flow patterns in an acrylic vessel, which simulated an adsorption upper plenum, was visualized by PIV (Particle Image Velocimetry).

![Appearance of test apparatus](image-url)

- Pressure gauge
- Gas outlet
- Gas diffusion layer
- $\phi 300\text{mm}$
- $750\text{mm}$
- $150\text{mm}$
- H$_2$ recombination catalyst
- Gas inlet
Hydrogen diffusion test (2/2)

Results

• Analytical results using FLUENT agreed well with visualized flow patterns except for the existence of weak circulating flows.
• Analytical code will be developed so as to appear the weak circulating flows.

Visualized image
Velocity vector diagram
Result of PIV measurement

Hydrogen concentration measurement

- With catalyst
- Without catalyst

Results of hydrogen concentration measurement

- H2 Concentration [ppm] vs. Time [min]
- Time 0 to 120 minutes
- H2 Concentration 0 to 14,000 ppm

Circulating flow
0.05 m/s
Hydrogen recombination catalyst (1/2)

**Objective**
To show effectiveness of hydrogen recombination by using catalysts developed for automobile exhaust gas.

**Approach**
Catalyst performance was examined under high dew point and wet conditions using a gas chromatography.

**Appearance of hydrogen recombination catalyst**

**Catalyst test apparatus**
- Gas inlet
- Gas outlet (to dehumidifier)
- Humidifier
- Catalyst test section
Hydrogen recombination catalyst (2/2)

Results

• 100% of fed humidified hydrogen gas was recombined up to 80°C, and
• under the condensation condition, hydrogen was recombined at a rate of more than 50%.

We plan to examine its durability under irradiation condition.
Durability of zeolite vessel against corrosion with salt

- Fundamental data & simulation
- Effectiveness of washing, drying, etc.
- Estimation of lifetime of vessel
Objective

To estimate corrosion conditions of KURION and SARRY adsorption vessel including contaminated water with seawater

- Estimation of corrosion condition with corrosion simulator based thermodynamics (OLI systems)
- Corrosion test of vessel material (Type 316L) with simulant of contaminated water including chloride from seawater under γ irradiation.

Approach

Assumed material corrosions in vessel

Estimation of corrosion condition by using corrosion simulator
Three simulants for contaminated water with typical chloride ion concentrations for corrosion tests.

- **High Cl⁻**: 18000ppm (Artificial sea water)
- **Middle Cl⁻**: 6000ppm (Diluted artificial sea water)
- **Low Cl⁻**: 2000ppm (Diluted artificial sea water)

- In the point of the material corrosion, only chloride ions should be considered.
- It is considered that eluted ions (Cs⁺, Ba²⁺, Pr³⁺, I⁻ etc.) from fuel constituent elements don’t accelerate corrosion and the ion concentration is small using by corrosion simulator.
Small mock-up vessel for estimating residual chloride concentration in zeolite and dripped water

- Estimating corrosion conditions such as residual chloride concentration in zeolite and dripped water using by small mock-up vessel.
- Corrosion test for adsorption vessel by using estimated corrosion conditions in zeolite and dripped water.
On going
- Characterization
- Safe storage of existing spent zeolites
- Conditioning
- Waste package
- Long-term storage
- Disposal
**Options for long-term storage and conditioning (1/2)**

## Conditioning for waste packaging and disposal

<table>
<thead>
<tr>
<th>Conditioning of zeolite</th>
<th>Procedure, merits &amp; demerits</th>
</tr>
</thead>
<tbody>
<tr>
<td>No conditioning (Storage only)</td>
<td>Drawing the spent zeolite from the vessel, and putting in a new cask for disposal.</td>
</tr>
<tr>
<td>Pressing zeolite</td>
<td>Pressing spent zeolite before putting in the cask. Merit: better packaging than zeolite grain. Demerit: fragile, rotten</td>
</tr>
<tr>
<td>Hot-pressing zeolite (Pressing &amp; heating)</td>
<td>Merit: volume reduction, strength better than pressing.</td>
</tr>
<tr>
<td>Zeolite with cement</td>
<td>Merit: 30wt% of zeolite in cement package. Demerit: Low temperature (= Low Cs content)</td>
</tr>
<tr>
<td>Vitrification of Cs recovered from zeolite</td>
<td>Eluting Cs from zeolite, concentrating and vitrifying Cs. Demerit: low-level zeolite waste, handling of Cs solution</td>
</tr>
</tbody>
</table>
## Options for long-term storage and conditioning (2/2)

Table: Estimation of waste packages of 400 spent vessels of KURION.

<table>
<thead>
<tr>
<th>Method</th>
<th>Waste volume</th>
<th>Density</th>
<th>Waste weight</th>
<th>Zeolite content</th>
<th>Zeolite content</th>
<th>Number of packages</th>
<th>Heat (Sept-11, 2011)</th>
<th>Heat (50 years later, 2061)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No conditioning</td>
<td>150</td>
<td>0.593</td>
<td>89</td>
<td>100%</td>
<td>89</td>
<td>3500</td>
<td>27</td>
<td>2.8</td>
</tr>
<tr>
<td>Pressing</td>
<td>150</td>
<td>1.2</td>
<td>180</td>
<td>100%</td>
<td>180</td>
<td>1700</td>
<td>56</td>
<td>5.8</td>
</tr>
<tr>
<td>Hot-pressing</td>
<td>150</td>
<td>2.5</td>
<td>375</td>
<td>100%</td>
<td>375</td>
<td>800</td>
<td>119</td>
<td>12.4</td>
</tr>
<tr>
<td>Cement</td>
<td>150</td>
<td>2.0*1</td>
<td>297</td>
<td>30%</td>
<td>89</td>
<td>3500</td>
<td>27</td>
<td>2.8</td>
</tr>
<tr>
<td>Vitrification of zeolite*2</td>
<td>150</td>
<td>2.67</td>
<td>400</td>
<td>60%</td>
<td>240</td>
<td>1300</td>
<td>73</td>
<td>7.6</td>
</tr>
<tr>
<td>Vitrification of Cs only</td>
<td>150</td>
<td>2.67</td>
<td>400</td>
<td>1%*3</td>
<td>4.0 *3</td>
<td>48</td>
<td>1982</td>
<td>207</td>
</tr>
</tbody>
</table>

*1 Void volume between zeolite grains are 60wt% and filled with cement.  
*3 Content of Cs element. Zeolite after removal of Cs is low level waste and not included in above table.
Vitrification test of KURION zeolites (1/2)

1. Purpose
- JAEA is collecting fundamental information for stabilization and solidification of zeolites. Vitrification is one of the options.
- KURION herschelite (H) for Cs and AGH for iodine were vitrified as a preliminary evaluation.

2. Experimental
- Kurion-H or AGH sample was mixed with reagents (see table below) and melted to prepare borosilicate glass. Volume reduction ratio was checked but volatilization of cesium is under investigation.

Table Composition of zeolite, cesium and glass reagents

<table>
<thead>
<tr>
<th>Target glass composition</th>
<th>Mixing of zeolite and reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>wt%</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>10</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>10</td>
</tr>
<tr>
<td>Cs$_2$O</td>
<td>5*</td>
</tr>
<tr>
<td>Kurion-H or AGH</td>
<td>80</td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>

*Total weight percentage including Cs$_2$O is 105 w%.
Vitrification test of KURION zeolites(2/2)

3. Results

(1) Bulk density before melting
- Kurion-H: 0.60 ± 0.01 g/cm³ (n=3)
- Kurion-AGH: 0.75 ± 0.02 g/cm³ (n=3)

(2) Vitrified products
- Quality of product: Good (see photos)
- Density of products:
  - Kurion-H: 2.52 g/cm³
  - Kurion-AGH: 2.61 g/cm³

**Volume reduction** (Volume of glass product/Volume of zeolite)
- Kurion-H: 0.31
- Kurion-AGH: 0.38

◆ High volume reduction (0.3 ~ 0.4) was achieved by melting 80wt% of Kurion zeolite and 20wt% of glass reagents.
Cs activity and disposal category of vessels

◆ Estimation of Cs activity concentration

<table>
<thead>
<tr>
<th>Spent zeolite</th>
<th>Present Cs activity※1</th>
<th>Present category※2</th>
</tr>
</thead>
<tbody>
<tr>
<td>KURION</td>
<td>7.91E+14 Bq/t</td>
<td>Sub-surface disposal ?</td>
</tr>
<tr>
<td>SARRY</td>
<td>2.37E+15 Bq/t</td>
<td>Sub-surface disposal ?</td>
</tr>
</tbody>
</table>

◆ Decay of Cs activity

- ※1 Estimation by TEPCO press release (29 June to 9 Nov.)
- ※2 Limit of Cs-137 for surface disposal (1.00E+14 Bq/t): government ordinance

- Cs activity of spent zeolite of both KURION and SARRY will be lower than the upper limit for surface disposal, respectively, after 91 and 138 years.

- More information is needed to discuss category of disposal such as analyses and evaluation of inventories of minor nuclides.
Summary

- **Thermal conductivity of zeolite**
  KURION-H (dry) 0.09 - 0.16 Wm\(^{-1}\)K\(^{-1}\). Gas in zeolite bed is to be evaluated. SARRY adsorbents are ready for the measurement.

- **G values for H\(_2\) production**
  G - seawater > G - pure water. Because H\(_2\) is recombined to H\(_2\)O in pure water but not in seawater. More H\(_2\) was produced by adding zeolite to seawater. Desalination & Dehydration are keys.

- **Estimation of H\(_2\) concentration in vessel**
  FLUENT code is a good tool to describe visualized flow patterns. Estimated temperature and H\(_2\) concentration are less than the self-ignition temperature and explosive limit of H\(_2\), respectively. Catalyst for automobile exhaust gas recombines H\(_2\) to H\(_2\)O well.

- **Corrosion of vessel with seawater**
  Corrosion condition was estimated by using corrosion simulator.
Thank you for your attention
1. How to valuate distribution of activities in vessel

[Which radionuclide? how much? Where in the vessel?]

Estimation shown in this presentation was based on average Cs-134,137 concentration in vessel. Our approach will be evaluation of:
1) detailed analyses of contaminated water before and after treatment
2) measurement of surface dose of vessel
3) estimation by adsorption code & miniature column test.

2. How to confirm safe storage

[No hydrogen explosion, No corrosion]

Our approach is mainly simulation by using fundamental data and results of small scale test. Boundary conditions used for simulation might be different from the real vessel. For example, dried zeolite and no water in vessel (simulation), wet zeolite and drip salty water (real?). Direct measurement of concentration of H₂ and chloride inside vessel is necessary?

Please advise, if you have knowledge about other approaches.