Chemistry Study on the Nuclear Fuel Debris for Decommissioning of Fukushima NPP

Akira Kirishima
IMRAM, TOHOKU university, JAPAN
Tohoku University in Sendai city, Japan

Location
- North-east of Japan, in the Tohoku region
- Sendai-Tokyo: 352 km, 1h34min by bullet train

Size of Sendai
- Area: 783,54 km² = New York City
- Population: 1,073,681
- Population density: 1,301 inh/km² = 1/5 of Tokyo
- Latitude: 38°16' = same as Athens, Palermo, Sacramento, San Francisco, Washington DC, Tianjin
Sendai city and its surrounding at a glance

- Hot springs in Naruko
- "Maru no miyako" - The city of trees
- The Okama Crater lake in Mount Zao
- The bay of Matsushima - one of the three most scenic views of Japan
- Masamune Date - founder of Sendai city
Tohoku University
Five campuses

Main Campus of Tohoku University is located in Sendai. Sendai is the largest city and the center of Tohoku district. It is about 350 kilometers north of Tokyo, a less than two-hour bullet train ride from the metropolis.

BUS

Buses leave the bus terminal at the JR Sendai Station (bus stop No. 9) every 30 minutes for the 20-minutes trip to the "Kogakubu-chuo" bus stop in front of the School of Engineering. The fare from the station to the "Kogakubu-chuo" bus stop is 230 yen (as of 2014), paid when leaving the bus.

Taxi

You may take a taxi to the School of Engineering from Sendai Airport or Sendai Station. Fares are about 6,000 yen from Sendai Airport and 1,600 yen from Sendai Station. Taxi can be found at the taxi stands in front of Sendai Airport or Sendai Station.
First University in Japan to accept female students (1913)

First woman to obtain a bachelor of Science in Japan, went to study at Oxford University afterwards
Chinese novelist Lu Xun

Medical school of Tohoku University, 1902-1904
Prof. Koichi Tanaka, Nobel Prize in Chemistry 2002

Graduated from the School of Engineering, Tohoku University in 1983
Greatest inventions

High Power Magnetron (1927)
- Prof. Okabe
- Used in microwave oven

Yagi-Uda Antenna (1929)
- Prof. Yagi and Uda
- Used for Telecommunications radio.

Static Induction Transistors, Pin Diode (1975, 1950)
- By Prof. Nishizawa
  - "Father of Japanese Microelectronics"
  - Used for audio amplifier, radar, switches...

Flash Memory (1980)
- Prof. Masuoka

Light Emitting Diode
Optical Fiber
Research and Education Organization.
The Number of Students (As of May, 2014)

- Undergraduate: 11,060
- Doctor: 2,651
- Master: 4,106
- Research Institutes: 7
- Graduate Schools: 17
- Other: 35

Total: 17,852 Students (Including 1,532 international Students)
3,000 Faculty Members (As of May, 2012)

- Assistant: 163
- Assistant Professors: 1,202
- Senior Assistant Professors: 186
- Professors: 886
- Associate Professors: 737

Total: 3,174

Outstanding LAUREATE AWARDS:
- Nobel Prize: 1
- Recipient of the Japan's Order of Culture / The Persons of Cultural Merit Award: 52
- Japan Academy Prize: 104
- Japan Academy Members: 108
Table of Contents

1. Background and Motivation
2. Outline of Experiment
3. Discussion
1. Background
Scale of the Earthquake and Tsunamis

This was a massive M9.0 earthquake (fourth largest ever recorded in the world) that was caused by a coupling movement of several regions off-shore of Miyagi prefecture, the southern trench off-shore of Sanriku to the east, off-shore of Fukushima prefecture, and off-shore of Ibaraki prefecture.

| Time: | 2:46 pm on Fri, March 11, 2011 |
| Place: | Offshore Sanriku coast (northern latitude of 38 degrees, east longitude of 142.9 degrees), 24km in depth, Magnitude 9.0 |
| Intensity: | Level 7 at Kunihara in Miyagi prefecture |
|          | Upper 6 at Naraha, Tomioka, Okuma, and Futaba in Fukushima pref. |
|          | Lower 6 at Ishinomaki and Onagawa in Miyagi pref., Tokai in Ibaraki pref. |

![Intensity Distribution of the earthquake](image1)

![The source area of the earthquake](image2)

![Slip amount (m)](image3)

(Evaluated by Tokyo University)

(Evaluated by TEPCO)
Tsunami struck Fukushima Daiichi NPS

2011/03/11, 13-m height tsunami followed by M9.0 earthquake

Cross section view of NPP

Figure 4: Path of inundation of major buildings.
Earth quake collapsed land line cable supply of Electricity.

↓ Tsunami water destroyed emergency E-generators installed in the basement

↓ Complete lost of electricity

↓ Lost of Cooling

↑ Temporary batteries used as power source for instruments (photographed on March 22, 2011)

← Water injection to unit 4 spent fuel pool using a concrete pumper
Melt down and H$_2$ gas explosion (unit 1)

Severest melting down occurred at unit 1

Bird view of Unit 1

Dropped fuel
Melt down (unit 2 and 3)

Bird view of unit 3
(no H$_2$ explosion at unit 2)
Here we are! Sasaki ↓ Kirishima ↑

On the NPS site, 2012/10/19
Summary of the accident

*the earthquake struck at 14:46 on March 11, 2011, *(lost of electricity by land cables)*

*At 15:27, the first tsunami struck, followed by the second tsunami at 15:35 *(lost of electricity supplied by emergency Diesel generators →black out)*

---

### Table 1: Operational status of Fukushima Daiichi NPS units during the Tohoku - Pacific Ocean Earthquake

<table>
<thead>
<tr>
<th>Unit</th>
<th>Output</th>
<th>Status when the earthquake occurred</th>
<th>Aftermath Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit 1</td>
<td>460MW</td>
<td>Operating at rated output</td>
<td>Automatic shutdown</td>
</tr>
<tr>
<td>Unit 2</td>
<td>460MW</td>
<td>Operating at rated output</td>
<td>Automatic shutdown</td>
</tr>
<tr>
<td>Unit 3</td>
<td>784MW</td>
<td>Under regular inspection</td>
<td>Automatic shutdown</td>
</tr>
<tr>
<td>Unit 4</td>
<td>784MW</td>
<td>Under regular inspection</td>
<td>Not under operation at that time</td>
</tr>
<tr>
<td>Unit 5</td>
<td>784MW</td>
<td>Under regular inspection</td>
<td>Not under operation at that time</td>
</tr>
<tr>
<td>Unit 6</td>
<td>1,100MW</td>
<td>Under regular inspection</td>
<td>Not under operation at that time</td>
</tr>
</tbody>
</table>

Melt down

H₂ gas explosion

No explosion, but the greater part of radio activities were released to the environment from this reactor.
Map of spread Cs contamination

Data on 2011/04/29

90 km
大学連携土壌探取テーマ
2011.6
Evacuation Area (at present)

20 mSv/y >

> 50 mSv/y

Evacuation area

1,150 km² (2013/08)

↓

370 km² (2017/04/01)

Number of evacuees in Fukushima

164,865 persons (2012/05/01)

↓

44,366 persons (2018/08/06)
Past: Temporary cabins (house rent free)

Now: Public Apartments supplied by government, ($300 - 500 / month)
Data on 2017/11/16
Over 4000 tons of Seawater was injected for urgent cooling of Fukushima Daiich NPS → Seawater (salty water) contacts with damaged fuel at high Temp.

Seawater was not used for cooling at Chernobyl and TMI accidents. → earned knowledge from the past sever accidents is insufficient for Fukushima
### 4–3. Current Status of Each Unit

<table>
<thead>
<tr>
<th>Core Region</th>
<th>Unit 1</th>
<th>Unit 2</th>
<th>Unit 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Little fuel remains.</td>
<td>Little fuel remains.</td>
<td>Little fuel remains.</td>
<td>Little fuel remains.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RPV Lower Head</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A small amount of fuel debris is present.</td>
<td>A large amount of fuel debris is present.</td>
<td>Fuel debris remains on the RPV lower head partly.</td>
<td>A small amount of fuel debris is present in the inside and on the outer surface of the CRD housing.</td>
</tr>
<tr>
<td>A small amount of fuel debris is present in the inside and on the outer surface of the CRD housing.</td>
<td>A small amount of fuel debris is present in the inside and on the outer surface of the CRD housing.</td>
<td>A small amount of fuel debris is present in the inside and on the outer surface of the CRD housing.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pedestal Inside</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Most of fuel debris is present.</td>
<td>A small amount of fuel debris is present.</td>
<td>Amount of fuel debris in Unit 3 is more than that in Unit 2.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pedestal Outside</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel debris may have spread on the pedestal outside through the personal entrance.</td>
<td>The possibility of fuel debris spreading on the pedestal outside through the personal entrance is low.</td>
<td>Fuel debris may have spread on the pedestal outside through the personal entrance.</td>
<td></td>
</tr>
</tbody>
</table>

* Based on the document provided by IRID and internal survey performed in 2017.
Unit 2, Internal status of PCV (TEPCO, 2018)
Figure 4.3-3: Result of Unit 3 Internal PCV Survey

Source: TEPCO "Unit 3 Internal PCV Survey Status – Flash Report on 21st & 22nd Survey"
### Table 1. Milestones (main target processes) in the Mid-and-Long-Term Roadmap

<table>
<thead>
<tr>
<th>Area</th>
<th>Description</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>1. Contaminated water management</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduction of contaminated water generation to about 150 m³ / day</td>
<td>Within 2020</td>
</tr>
<tr>
<td></td>
<td>All purified water by purification equipment etc. is stored in welding type tank</td>
<td>FY2018</td>
</tr>
<tr>
<td></td>
<td><strong>Completion of stagnant water treatment</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>① Separation of the penetrations between Units 1 and 2 and between Units 3 and 4</td>
<td>Within 2018</td>
</tr>
<tr>
<td></td>
<td>② Reduction of radioactive materials in stagnant water in buildings up to about one tenth of the end of FY 2014</td>
<td>FY2018</td>
</tr>
<tr>
<td></td>
<td>③ Completion of treatment of stagnant water in buildings</td>
<td>Within 2020</td>
</tr>
<tr>
<td></td>
<td><strong>2. Fuel removal from spent fuel pools</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>① Start of fuel retrieval from Unit 1</td>
<td>Estimate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FY2023</td>
</tr>
<tr>
<td></td>
<td>② Start of fuel retrieval from Unit 2</td>
<td>Estimate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FY2023</td>
</tr>
<tr>
<td></td>
<td>③ Start of fuel retrieval from Unit 3</td>
<td>Mid FY2018</td>
</tr>
<tr>
<td></td>
<td><strong>3. Fuel debris retrieval</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>① Determination of fuel debris retrieval methods for the first implementing unit</td>
<td>FY2019</td>
</tr>
<tr>
<td></td>
<td>② Start of fuel debris retrieval at the first implementing unit</td>
<td>Within 2021</td>
</tr>
<tr>
<td></td>
<td><strong>4. Waste management</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Technical prospects concerning processing/disposal policies and their safety</td>
<td>Around</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FY2021</td>
</tr>
</tbody>
</table>
Fuel Debris research (outline) being conducted by JAEA-TEPCO

- Synthesis of Mock up Debris
- Characterization of Mock up Debris
  - Melting point measurement
  - Thermal conductivity measurement

The main stream Fuel Debris research (conducted by JAEA-TEPCO) tends to focus on the physical characterization of the debris.

However, the debris in the reactors is continuously being cooled by water flow, which dissolves some amount of FPs, MA, U and Pu to the accumulated waste water in the bottom of the plants.

The chemistry research is also important and demanded for the debris.
Goal of the research

Our research

*Goal is*
To know *How much and by What chemistry, U, Pu, are dissolved from Fuel Debris into the cooling water* (ASAP-subject)

*The outputs are utilized to...*

✓ Estimating U, Pu inventory in the spent absorbents (zeolite, sludge) → *for waste management* (near future subject)

✓ Information for the Debris treatment
Pu, $^{241}$Am, $^{244}$Cm were detected in water samples of unit-2. In addition these actinides, $^{242}$Cm was detected at unit-3. 

Actinides are in contaminated water. They will be in wastes. Ac amount governs future of waste management!
Purpose of research

[Question]
Chemistry of debris (structure, properties). What happens to actinide when seawater contacts with fuel debris? (Seawater was not used for cooling at Chernobyl and TMI accidents)

[key to solution]
- Understanding of Solubilities, leaching rate and Chemical Speciation of MA, U and Pu in this reaction system.

research plan

Seawater

Soluble Species of U, Pu etc

Fuel Debris (Partial solid solution of U, Pu, Zr etc)

T = 25/90 °C

Precipitation → Liquid phase analysis → Dissolution

Solid phase analysis
2. Outline of experiment
2. Sample preparation and leaching test

1. FP and MA tracer UO₂ was synthesized.

<table>
<thead>
<tr>
<th>Element</th>
<th>²³⁸U</th>
<th>²³⁷Np</th>
<th>²³⁶Pu</th>
<th>²⁴¹Am</th>
<th>¹³⁷Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abundance to ²³⁸U</td>
<td>1</td>
<td>0.0024</td>
<td>8.2×10⁻¹¹</td>
<td>3.6×10⁻⁸</td>
<td>8.2×10⁻¹⁰</td>
</tr>
</tbody>
</table>

2. (Heat treatment)
1:1(atm.) of UO₂ (tracer doped) and (ZrO₂, CaCO₃, SiO₂) were mixed, and heated at 1200 °C or 1600 °C in controlled atmosphere. (= simulated debris)

3. (Leaching test)
The simulated debris were immersed and shaken in a real Fukushima seawater for leaching.

4. (Analysis)
The dissolution ratios of U, Cs, Np, Pu and Am were determined by α- and γ-ray spectrometry.
Synthesis of tracer doped UO₂

236Pu, 237Np, 241Am in HNO₃ sol. → NH₃ sol. → ADU co-precipitation → Filtration (0.45µm pore size) → Drop 137Cs sol. to ADU precipitate → Calcination in air at 800°C, 2h → U₃O₈ doped with 236Pu, 237Np, 241Am and 137Cs → H₂ gas Reduction At 1000°C, Ar+10%H₂, 4h → Tracers doped (236Pu, 237Np, 241Am, 137Cs) UO₂ → tracer doped UO₂
Pictures of heat treatment apparatus

Electric furnace

Setting sample inside the tube
Pictures of heat treatment apparatus and sample

Heat treatment in Ar + 2% O₂ at 1600 °C

Before: UO₂+ZrO₂+CaCO₃+SiO₂

After: Sample in Quartz tube

Open Electric furnace

Gas inlet

Gas outlet
Different products were formed depended on Temp., redox, and components.
3. Characterization of Simulated Fuel Debris

Heat treatment of UO₂-ZrO₂ mixture in Ar-atomosphere, at 1100°C for 6h. This treatment was repeated.

The FP and MA doped simulated debris (Zr_yU_{1-y}O_{2+x}) was synthesized.

Leaching test of simulated debris by seawater

Leaching condition
Debris: 40 mg   T: 25 °C
Fukushima seawater: 10ml   Shaking time: 4, 10, 30 d

Shaking

Dissolved by c.HNO₃

γ-ray spectrometry

α-ray spectrometry

Filtration by 0.45 μm filter

Soluble Fraction

Insoluble Fraction

$R_{\text{dissol.}}(\%) = \frac{A(\text{Bq}) \text{ soluble}}{A(\text{Bq}) \text{ total}} \times 100$
Evaluation of dissolution ratio by γ- and α-ray spectrometry

**Ge detector**

**γ-ray spectrum**
- $^{137}$Cs at 662 keV

**α-ray spectrum**
- $^{238}$U at 4.20 MeV
- $^{237}$Np at 4.79 MeV
- $^{236}$Pu at 5.77 MeV
- $^{241}$Am at 5.49 MeV
- $^{147}$Sm at 2.23 MeV

**Si detector for alpha-ray**
3. Discussion
Leaching ratio of Cs

Leaching from Mixed powder > from Debris
Leaching: Cs >> U > Np ≈ Am ≈ Pu

Leaching ratio of Ac from the debris is **0.1% or less (very small!)**. The formation of S.S. makes Ac leaching smaller.

Discussion 3, Effect of seawater components on Ac leaching

$\text{UO}_2\cdot\text{ZrO}_2 = 50:50$ (solid solution) at $1200~\text{oC}$ in Ar

**Leaching to Seawater**

- DO: $8.44\text{mg/l}$
- pH: $7.8 \pm 0.1$
- Eh: $0.49\text{mV}$
- $\text{CO}_3^{2-}: 3\text{mM (calc.)}$

**Leaching to Pure water**

- DO: $7.4\text{mg/l}$
- pH: $6.1 \pm 0.1$
- Eh: $0.53\text{mV}$
- $\text{CO}_3^{2-}: <1 \times 10^{-5}\text{M (calc.)}$

**U (matrix) leaching:** Seawater $>$ Pure water

$\rightarrow$ Carbonate ion in seawater may promote U dissolution by forming U-carbonate complex.

**Tracer Ac (Np, Am, Pu) leaching:** Pure water $>$ Seawater

$\rightarrow$ higher pH of seawater may suppress the leaching?
4. Summary

• The solid solution of U(Zr)O$_2$ was formed after the heat treatment of UO$_2$ and ZrO$_2$ mixtures. This reaction stabilized actinides in the debris, and suppressed their leaching to water.

• The cement components formed silicate glass coating on the surface of the debris, which remarkably suppressed the actinide leaching to detection limit level (0.01 %).

• The leaching of actinides depends on the partial oxygen pressure in the reactor core when the debris is generated; i.e., debris generated under oxidative conditions releases more actinide nuclides to water than that generated under reductive conditions, which is thought to be due to the oxidative dissolution of U from the debris.

• Seawater leaches more actinides from the debris than pure water, which is thought to be caused by the complexation of actinides by carbonate ions in seawater.
Acknowledgment

• This study was supported by JSPS KAKENHI Grant-in-Aid for Scientific Research, Grant Number 24226021 and 16H02447.

• Prof. Nobuaki Sato (Tohoku Univ.)
• Prof. Takayuki Sasaki (Kyoto Univ.)
• Dr. Daisuke Akiyama (Tohoku Univ.)
• Masahiko Hirano (student)
• Akito Nagatomo (student)
• Mayu Saito (student)