Actinide behaviour during severe nuclear accident

Chernobyl

study of Chernobyl “lava”, corium and hot particles:

experience of V.G. Khlopin Radium Institute (KRI)

Boris Burakov

DSc, Head of Laboratory

V.G. Khlopin Radium Institute (KRI)
St. Petersburg, Russia

e-mail: burakov@peterlink.ru

160 employees of V.G. Khlopin Radium Institute have been working in Chernobyl since 1986 till 1992
V.G. Khlopin Radium Institute (KRI)

study of radioactive materials since 1922

at present time KRI is a research institute of Russian State Corporation for Atomic Energy (ROSATOM)

- First European cyclotron built in 1937
- First sample of Soviet Pu, obtained in 1945
- Industrial Soviet technology of Pu extraction 1945-1949
- Chernobyl investigation 1986-1992 (and present time)
- *Unique collection of Chernobyl “lava”, corium and hot particles available for international research and training*
- Hot-cell facility for research using any kind of spent nuclear fuel and liquid HLW
- Study of actinide-doped ceramics and HLW glasses
- Production of isotopes
- Radio-ecological monitoring
- *Applied training of international young scientists in the field of nuclear waste management*
V.G. Khlopin Radium Institute (KRI)

First European cyclotron (1937)

Crystals of NpO$_2$

Hot-cell facility

Solution of PuCl$_3$

Radiation damage effects in zircon crystal doped with Pu-238

Borosilicate glass doped with Pu-238
Background

**basic papers**

After explosion – first days [11]
Background

general information

• About 3.5 wt.% spent fuel was ejected from the core [1,2]
• About 50 kg Pu was spread in European part of USSR [4]
  (it means 6 wt.% of total Pu of Chernobyl NPP’s 4th Unit)
• More than 90 wt.% fuel is inside “Shelter” or “Sarcophagus” [2], but this information is controversial
• At least 11-15 wt.% fuel (inside “Shelter”) is related to Chernobyl “lava” [5], but this information is controversial
Background

basic glossary

• **Chernobyl “lava”** – it is a result of high-temperature interaction between destroyed fuel (including corium), Zr-cladding and silicate materials (concrete, sand, serpentinite) – can be called *silicate-rich corium*

• **Chernobyl corium** – melted fuel-containing material, which does not have silicate matrix

• **Chernobyl “hot” particles** – are highly radioactive solid particles from less than 1 µm to hundreds µm in size

*Note: Chernobyl hot particles usually contain U but not always!*
Natural volcanic lava

Gamma-dose on the surface of “Elephant foot” in 1990 exceeded 10 Sv/h, and gamma-radiation field in the room was 6-7 Sv/h
Chernobyl “lava” in steam discharge corridor, 1990 [2]
Initial mechanical durability of Chernobyl “lava” was very high. **Shooting by machine-gun AK-47** was applied to break “Elephant foot” matrix and collect first samples in 1987 [2].

Essential decrease of mechanical durability and even self-destruction of “lava” matrices was observed in 1990 [2].

Chemical alteration of “lava” matrices was observed in 1990 – formation of “yellow stains” consisted of secondary uranium minerals (**uranyl-phases**) [9].
New-formed yellow minerals at the surface of Chernobyl “lava”, 1991
Samples of Chernobyl “lava”
collection of V.G. Khlopin Radium Institute

• Most samples of “lava” were collected at different locations in 1990 using hands and hammer only. All people involved into sampling were over irradiated

• Some pieces of “lava” (dozens cubic cm each) were partially dissolved in HF in order to extract inclusions of different uranium-bearing phases
Before going inside “Shelter”, 1990

Boris Burakov 1990
Inside “Shelter”:
packing “lava” sample for shipment to Leningrad, 1990

photo by Boris Burakov, 1990
Map of KRI sampling inside “Shelter” (revised from [8])
Formation and stratification of general source of Chernobyl “lava”
(between 5th and 10th day after explosion at 4th Unit)

hypothesis

Black lava (main volume)

Brown lava

Concrete

molten steel enriched with Ru-106

Concrete
Questions and expectations related to F-1

• Can we expect formation of “lava” (silicate-rich corium) at Fukushima Daiichi F-1? Yes, of course! The probability of fuel and corium high-temperature interaction with concrete at F-1 is very high (in particular at Unit-3)
• Will composition of Fukushima’s “lava” be similar to Chernobyl “lava”? In general yes. However, there was no time for “lava” stratification at F-1. Volume of “lava” at F-1 should be less.
• What is main difference between Chernobyl “lava” and expected “lava” at F-1? As assumed, there should be three main differences:
  1) Chernobyl “lava” are much more homogeneous;
  2) Chemical alteration of Fukushima’s “lava” (as a result of interaction with water) should be extremely high;
  3) “Lava” at Unit-3 of F-1 may contain inclusions of Pu-phases
Current study of highly radioactive Chernobyl samples – what for?

- Transfer of experience to young scientists
- Tutorials on material science of highly radioactive solids
- Modeling of severe nuclear accidents and corium behavior
- Modeling of properties of Fukushima’s corium
- Chernobyl “lava” as analogue of HLW glass
- New-formed artificial unstable radioactive phases as a result of corium and “lava” chemical alteration
- New-formed very stable crystalline radioactive phases (inclusions in the “lava” matrices) as perspective durable host-phases of radionuclides
Samples of black “lava” – “Elephant foot” collection of V.G. Khlopin Radium Institute samples were collected in 1990 and stored at KRI under laboratory conditions partial self-destruction was observed for some pieces in 2011 (picture 4).

photo by V. Zirlin and B. Burakov
Samples of brown “lava” – from steam discharge corridor

*collection of V.G. Khlopin Radium Institute*

samples were collected in 1990 and stored at KRI under laboratory conditions
pictures were taken in 2011 by V. Zirlin and B. Burakov
Samples of brown “lava” – from room #305
collection of V.G. Khlopin Radium Institute
sample was collected in 1990 and stored at KRI under laboratory conditions
pictures were taken in 2011 by V. Zirlin and B. Burakov
formation of secondary uranium minerals under laboratory conditions?
Some Chernobyl samples from KRI collection have not been studied yet
Sample of corium (fuel-steel melt) – from room #305

collection of V.G. Khlopin Radium Institute

sample was collected in 1990 and stored at KRI under laboratory conditions
picture was taken in 2011 by V. Zirlin and B. Burakov
Sample of corium (fuel melt on the surface of steel pipe)  
room #305  
collection of V.G. Khlopin Radium Institute  
sample was collected in 1990 and stored at KRI under laboratory conditions  
picture was taken in 2011 by V. Zirlin and B. Burakov
Sample of corium (fuel-steel melt) – near “Elephant foot”

collection of V.G. Khlopin Radium Institute

sample was collected in 1990 and stored at KRI under laboratory conditions
picture was taken in 2011 by V. Zirlin and B. Burakov
Samples of Chernobyl “hot” particles

collection of V.G. Khlopin Radium Institute

• Some particles were separated from soil samples collected near 4th Unit in 1986
• Most particles were separated from soil samples collected at Western Plume (0.5-12 km from 4th Unit) in 1990-1991
• Some fuel fragments and particles were collected inside “Sarcophagus” in 1990
“Red forest” – pine-tree forest died as a result of Chernobyl fallout, June 1986

photo – courtesy of Dr. R.V. Arutyunyan (IBRAE, Russia)
Collecting hot particles, 1990

Boris Burakov, 1990
Separation of hot particles from soil sample [10]
at V.G. Khlopin Radium Institute – using collimated beta-gamma-detector
Chernobyl “lava”

brief summary or the results obtained at V.G. Khlopin Radium Institute
Images of polished “lava” samples

1,2 – in reflected light in optical microscope; 3,4 – SEM-BSE

1,3 – brown “lava” from steam discharge corridor; 2 – black “lava” from “Elephant foot; 4 – black “lava” from steam discharge corridor
Chernobyl “lava” consist of silicate glass-like matrix + inclusions
Radionuclide composition of Chernobyl “lava” on June 2013 [12]


<table>
<thead>
<tr>
<th>Type of “lava”</th>
<th>Radionuclides, Bq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{137}$Cs</td>
</tr>
<tr>
<td>Black</td>
<td>2·10$^7$</td>
</tr>
<tr>
<td></td>
<td>(2.3·10$^7$)</td>
</tr>
<tr>
<td>Brown</td>
<td>4.1·10$^7$</td>
</tr>
</tbody>
</table>
Simplified bulk chemical composition (*matrix + inclusions*) of Chernobyl “lava” [6,7]

<table>
<thead>
<tr>
<th>Type of “lava”</th>
<th>Element content, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
</tr>
<tr>
<td>Black</td>
<td>4 - 5</td>
</tr>
<tr>
<td>Brown</td>
<td>8 - 7</td>
</tr>
</tbody>
</table>

Results of electron-probe microanalyses of glass-like silicate matrix of Chernobyl “lava” avoiding inclusions of crystalline phases [6,8]

<table>
<thead>
<tr>
<th>Type of “lava”</th>
<th>Element content, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
</tr>
<tr>
<td>Black</td>
<td>2.7-4.0</td>
</tr>
<tr>
<td>Brown</td>
<td>2.0-2.4</td>
</tr>
<tr>
<td>Porous</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Inclusions in matrices of Chernobyl “lava” are of very different phase and chemical compositions!
Inclusions in brown “lava” matrix
(from steam discharge corridor)
1,2 – in reflected light in optical microscope; 3,4 – SEM-BSE
photo by Boris Burakov, 1990-1991
Inclusions in black and brown “lava” matrices

**SEM-BSE**

1, 2 – black “lava” from steam discharge corridor; 3 – brown “lava” from steam discharge corridor;
4 – black “lava” from “Elephant foot

*photo by Boris Burakov, 1990*
Inclusions in black and brown “lava” matrices
(from steam discharge corridor)

SEM-BSE

1,2 – brown “lava”; 3,4 – black “lava”

photo by Boris Burakov, 1990
Crystals of high-uranium zircon, \((\text{Zr,U})\text{SiO}_4\), are typical for all types of Chernobyl “lava”

Up to 10 wt. % uranium was incorporated into the crystalline structure of zircon in the form of solid solution!
High-uranium zircon, \((\text{Zr,U})\text{SiO}_4\), from Chernobyl “lava” crystals were extracted after partial dissolution of “lava” matrix in HF

*photo by Boris Burakov, 1990*
New-formed yellow minerals at the surface of Chernobyl “lava”, 1991
SEM-BSE image of new-formed minerals (uranyl-phases) at the surface of Chernobyl “lava” [9]

photo by Boris Burakov, 1990
Phase composition of new-formed minerals at the surface of Chernobyl “lava” (from powder XRD analysis [9])

- $\text{Na}_3\text{H}(\text{CO}_3)_2 \times 2\text{H}_2\text{O}$
- $\text{UO}_3 \times 2\text{H}_2\text{O}$
- $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$
- $\text{Na}_2\text{CO}_3 \times 2\text{H}_2\text{O}$
- $\text{UO}_4 \times 4\text{H}_2\text{O}$
- $\text{UO}_2\text{CO}_3$
Questions and expectations related to F-1

• Can we expect formation of uranyl-phases at Fukushima Daiichi F-1? Yes, of course! In much larger volume than in Chernobyl.
Chernobyl “hot” particles

brief summary or the results obtained at V.G. Khlopin Radium Institute
SEM-BSE images of fuel fragment (A) and hot particles (B, C, D) of fuel composition ($\text{UO}_x$) [10]

*possible mechanical self-destruction along grain boundaries*
Multi-grain fuel ($\text{UO}_x$) hot particles (collected in 1990)

photo by Boris Burakov, 1990

non-altered

altered ???
dissolution along grain boundaries ?
Fuel hot particles ($\text{UO}_x$) with molten morphology (?)

*photo by Boris Burakov, 1990*
We also found Zr-bearing hot particles with phases: \( \text{Zr-U-O} \) and \( \text{UO}_x \) with Zr etc.

*Therefore, these particles are solidified drops of corium melt*

up to 40 % of all particles in some places of Western Plume !
Multi-phase hot particles [10]

polished cross-sections, SEM-BSE

Zr-U-O

UO$_x$ with Zr

A

10 µm

Zr-U-O

UO$_x$ with Zr

B

10 µm
Multi-phase hot particle [10]

SEM-BSE image

Zr-U-O

UO\textsubscript{x} with Zr

UO\textsubscript{x}
No interaction between fuel (UO$_x$) and zircaloy (almost pure **metallic Zr**) is possible in air. Fast oxidation of metallic Zr blocks this process.

*No conditions for Zr-U-O melt formation after explosion of reactor core!*

*Therefore, study of hot particles with corium matrices can tell us many interesting things about high-temperature process happened inside reactor core before explosion. Such process accompanied severe nuclear accident should be similar at different types of nuclear reactors.*
Detailed study of unusual hot particle from Chernobyl allowed us to confirm supercriticality nature of Chernobyl explosion

Study of a “hot” particle with a matrix of U-bearing metallic Zr: Clue to supercriticality during the Chernobyl nuclear accident

P. Pöml a, *, B. Burakov b

a European Commission, Joint Research Centre, Directorate G - Nuclear Safety and Security, P.O. Box 2340, 76125 Karlsruhe, Germany
b V.G. Khlopin Radium Institute, 28, 2-nd Murinskiy ave., St. Petersburg, 194021, Russia
Questions and expectations related to F-1

- Can we expect formation of hot particles with corium matrices at Fukushima Daiichi F-1? *Yes, of course! But not so many as in Chernobyl*
- Will composition of Fukushima’s hot particles with corium matrices be similar to Chernobyl corium particles? *In general yes. However, it is possible to expect hot particles with high content of plutonium at Unit-3. This is a results of MOX-Zr interaction accompanied with formation of Zr-U-Pu-O melt*
- Should we study relatively small amount of corium hot particles at F-1? *Yes, no doubt! It can tell us at least some important information about composition of corium inside Units 1, 2 and 3.*
Crystalline U-bearing phases identified in Chernobyl “lava” and hot particles

- Cubic $\text{UO}_x$ – similar to stoichiometric $\text{UO}_2$ ($a = 5.462$-$5.473 \, \text{Å}$)

- Cubic $\text{UO}_x$ with Zr (0.5 to 20 wt.% Zr) ($a$ decreases from $5.468$ to $5.318 \, \text{Å}$). Chemical composition – $(\text{U}_{0.985}\text{Zr}_{0.015})\text{O}_2$-$(\text{U}_{0.895}\text{Zr}_{0.105})\text{O}_2$. In some hot particles Zr content is higher – up to $(\text{U}_{0.56}\text{Zr}_{0.44})\text{O}_2$

- Tetragonal phase Zr-U-O with varied chemical composition from $(\text{Zr}_{0.86}\text{U}_{0.14})\text{O}_2$ to $(\text{Zr}_{0.89}\text{U}_{0.11})\text{O}_2$

- Monoclinic zirconia with U (up to 6 wt.% U) with varied chemical composition from $(\text{Zr}_{0.995}\text{U}_{0.005})\text{O}_2$ to $(\text{Zr}_{0.967}\text{U}_{0.033})\text{O}_2$

- Solid solutions with non-identified structures: $(\text{Zr}_{0.56}\text{U}_{0.44})\text{O}_2$; $(\text{Zr}_{0.68-0.71}\text{U}_{0.32-0.29})\text{O}_2$; $(\text{Zr}_{0.75-0.77}\text{U}_{0.25-0.23})\text{O}_2$ – only in hot particles

- High-uranium zircon, $(\text{Zr}_{0.95}\text{U}_{0.05})\text{SiO}_4$-$(\text{Zr}_{0.90}\text{U}_{0.10})\text{SiO}_4$
  (for bulk concentrate: $a = 6.617$; $c = 5.990 \, \text{Å}$).
Conclusions

• High-temperature (at least 2600°C) interaction between nuclear fuel and zircaloy cladding took place in local part of Chernobyl reactor core before the explosion. Nature of Chernobyl explosion is related to supercriticality process.

• Solid highly radioactive materials were formed and partially dispersed as a result of Chernobyl accident. They have different phase and chemical composition. It means their different behavior in environment.

• Active chemical alteration of Chernobyl corium is going on.

• Results of Chernobyl material study can be used for modeling severe nuclear accident at different types of nuclear reactors (not only RBMK).

• Results of Chernobyl material study can be used for development of ceramic waste forms and other durable advanced materials.