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

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

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160 employees of V.G. Khlopin Radium Institute have been working in Chernobyl since 1986 till 1992
study of radioactive materials since 1922

V.G. Khlopin Radium Institute (KRI)

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 NpO₂

Hot-cell facility

Radiation damage effects in zircon crystal doped with Pu-238

Solution of PuCl₃

Borosilicate glass doped with Pu-238
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, 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]
Background

general information

- 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 overirradiated.

• 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” [8]
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

\textit{collection of V.G. Khlopin Radium Institute}

sample was collected in 1990 and stored at KRI under laboratory conditions.

picture was taken in 2011 \textit{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
Methods of analyses

at V.G. Khlopin Radium Institute

• Optical microscopy
• SEM (BSE imaging)
• Quantitative and qualitative EMPA
• Bulk powder XRD (secondary uranium minerals, mineral inclusions separated from “lava” matrices)
• Precise XRD of single hot particles and mineral inclusions separated from “lava” matrices
• Gamma-spectrometry of bulk samples and single hot particles
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 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>$2 \cdot 10^7$</td>
</tr>
<tr>
<td>Brown</td>
<td>$4.1 \cdot 10^7$</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

1,2 – glass matrix; 3,4 – Zr-U-O, (Zr,U)SiO₄, Fe-Cr-Ni
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, (Zr,U)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, \((\text{Zr},\text{U})\text{SiO}_4\), 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 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 [6])

- $\text{Na}_3\text{H}($$\text{CO}_3$$)_2\times2\text{H}_2\text{O}$
- $\text{UO}_3\times2\text{H}_2\text{O}$
- $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$
- $\text{Na}_2\text{CO}_3\times2\text{H}_2\text{O}$
- $\text{UO}_4\times4\text{H}_2\text{O}$
- $\text{UO}_2\text{CO}_3$
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-bearina hot particles with phases: Zr-U-O and UO$_x$ with Zr etc.

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

polished cross-sections, SEM-BSE
Multi-phase hot particle [10]

SEM-BSE image

Zr-U-O

UO\textsubscript{x} with Zr

UO\textsubscript{x}
No interaction between fuel ($\text{UO}_x$) 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!
Formation of Zr-U-O melt

1) In corium of Chernobyl reactor (before explosion) – *it is matrix of real hot particle*

2) Laboratory experiment (melting at 2600°C in vacuum) of Zr + UO₂ – *it is synthetic sample*

*photo by Boris Burakov, 1990*
Crystalline U-bearing phases identified in Chernobyl “lava” and hot particles

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

- **Cubic $\text{UO}_x$ with Zr** (0.5 to 20 wt.% Zr) ($a$ decreases from **5.468 to 5.318** 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: $a = 6.617$; $c = 5.990$ 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.

- 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.**
KRI collaboration on study of Chernobyl “lava” and “hot” particles
KRI collaboration with French colleagues on study of Chernobyl “lava”, 1991-1993
KRI collaboration with German colleagues on study of Chernobyl “lava” and hot particles since 2004 till now


- Two fragments of black and brown Chernobyl “lava” are under investigation at ITU now in the framework of ITU-KRI Agreement.
KRI collaboration with Russian colleagues (from Moscow) on study of Chernobyl “lava” and hot particles since 2012 till now


- Some polished micro-samples of Chernobyl “lava” and hot particles are under joint analysis at Radiochemical Department of Moscow State University now in the framework of collaboration between KRI, MSU and A.N. Frumkin Institute of Physical Chemistry and Electrochemistry.
Testing of neutron detector (developed by “PDC UGR” JSC) using samples of Chernobyl “lava”, February 2017

Collaboration between KRI and Russian Pilot and Demonstration Center for Decommissioning of Uranium-Graphite Nuclear Reactors” JSC (“PDC UGR” JSC)
KRI proposals on cooperation with Japanese colleagues

- Consulting on fuel-debris and corium investigation, removal, treatment and final disposal
- KRI participation in material study of Fukushima’s corium in Japan
- Training of Japanese colleagues at KRI using real highly radioactive Chernobyl samples (“lava”, corium, hot particles)
- *Joint search, extraction and study of Fukushima’s hot particles*
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