Purification of Construction Materials of Spent Fuel Assemblies by Cold Crucible Induction Melting

M.Yu. Kalenova, A.V. Dmitrieva, I.V.Kuznetsov@, A.M. Koscheev,
O.E. Budin, A.S. Schepin*

JSC «Leading Research Institute of Chemical Technology», Moscow, 115409, Russia
@Corresponding author e-mail: ivan7501966@mail.ru)

«New atomic energy technologies» federal program is being realized in Russia. This program includes experimental energy complex development and building which contains:
- Natural safety lead coolant fast reactor «BREST-300»;
- Spent fuel recycle facility including fuel fabrication and re-fabrication, radioactive waste immobilization and discarding in accordance to radioactively-equivalent state.
Current recycle facility preliminary design involves dry operation of spent fuel elements disassembly using steel shell liquid zinc dissolution. Fuel element shells are made of special radiation-proof steel «EP-823» containing elements at following amounts (%): C - 0,2; Mn – 0,8; Si – 1; S - 0,01; P - 0,015; Cr – 12; Ni - 0,5; Mo - 0,9; V - 0,2; N – 0,05; Fe – 84,3. After dissolution zinc liquid containing steel elements was distilled. Still zinc is sent back to shells dissolution. The bottom product is original steel destructurized particulate composition. Actinides steel shell and bottom product contamination was predicted using computer modeling. In accordance with project technical specification disposable materials actinide content must be under 0,0001%, the bottoms product should be purified. Oxidizing slag cold crucible induction melting purification was chosen and tested in laboratory scale. Following slag types efficiency was investigated: Al_2O_3–SiO_2, B_2O_3–SiO_2, Al_2O_3 – CaO. It was found that the most appropriate slag is B_2O_3–SiO_2, and the optimal process temperature is about 1600°C.

Keywords: *cold crucible induction melting, actinides, purification, oxidizing, EP-823, BREST-300, slag.*

Introduction

In order to provide the possibility of significant increase in the role of nuclear power in the solution of problems of sustainable development of Russia within the Federal Target Program "Nuclear power technologies of new generation for 2010–2015 and long-term period till 2020", project "Proryv" was allocated in 2011. As of today, the project is being implemented. It combines the technologies of fast reactors and closed nuclear fuel cycle that meet the requirements of natural safety (in the nuclear, ecological and political spheres) and resource availability. Project "Proryv" was designed to solve problems that certainly arose and will arise upon operating nuclear power plants, if the concept of obtaining nuclear energy is not changed. The most burning issues are:

- the competitive ability of nuclear power plants as compared to the existing stations using organic fuel and with alternative energy sources; ensuring non-proliferation of nuclear arms;

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- the exhaustibility of the main sources of energy, i.e., fuel providing;
- ecological aspects associated with the possibility of emergencies;
- the safety of plants operation;
- radioactive waste treatment.

One of the strategic directions of project "Proryv" is the construction of an experimental power complex for demonstrating the operability of functional materials and technologies including:

– BREST-OD-300 reactor using a lead heat carrier and mixed nitride uranium-plutonium fuel;

– fuel fabrication/refabrication intended for the production of fuel elements from fresh raw materials and regenerated from nuclear waste (NW);

– plant module: processing SNF with the use of a combined scheme including pyro-, pyroelectrochemical and hydrometallurgical conversions; preparation of radioactive waste for final removal from the production cycle, including temporary storages.

Waste of constructional materials of the exhausted fuel assemblies in the plant nuclear fuel cycle may contain significant amounts of fissionable materials: U, Pu and minor actinides − Np, Am, Cm. According to the requirements of the above-mentioned project their content in disposed constructional materials should not exceed 0.001% by weight. It was decided to decrease the amount of fissionable materials in the metal to the indicated values using the method of oxidizing slagging by cold crucible induction melting. The process flow diagram is shown in Figure 1.

According to the obtained experimental results, the extent of steel EP-823 purification from simulators (neodymium, depleted uranium) is more than 99%. This is insufficient for industrial application in the plant nuclear fuel cycle. In order to increase the process efficiency it is necessary to reduce the number of residual slag inclusions containing fissionable materials.

The purpose of this work was to choose an oxidizer for high-efficiency extraction of fissionable materials (FM) from the fuel-element jacket using a calculation method and to check experimentally the efficiency of the chosen oxidizing additives for induction-slag remelting.

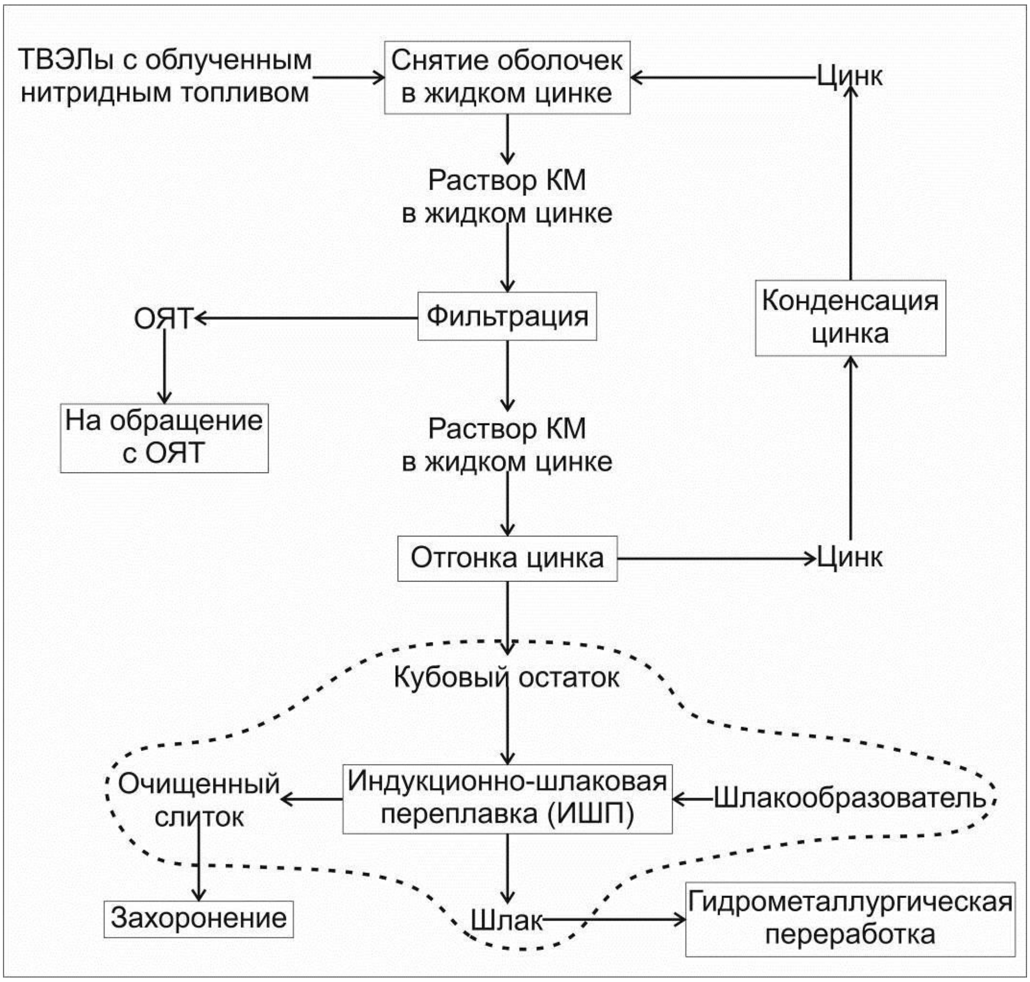

Figure 1. Flow diagram of the site for the removal of the fuel-element jacket with liquid zinc. The dashed line designates the area of this study.

[ТВЭЛЫ с облученным нитридным топливом means Fuel cells with irradiated fuel; снятие оболочек в жидком цинке means Jackets removal in liquid zinc; Раствор в жидком цинке means Solution in liquid zinc; Фильтрация means Filtration; ОЯТ means SNF; На обращение с ОЯТ means Spent nuclear fuel management; раствор КМ в жидком цинке means Solution of construction materials in liquid zinc; отгонка цинка means Zinc distillation; цинк means zinc; конденсация цинка means Zinc condensation; индукционно-шлаковая переплавка means Induction-slag remelting; очищенный слиток means Purified ingot; шлакообразователь means Slag-forming constituent; захоронение means Disposal; шлак means Slag; гидрометаллургическая переработка means Hydrometallurgical processing]

Experimental

The object of the study – the vat residue of zinc distillation – is a metallic composition, the chemical composition of which is identical to that of fuel-element jackets, EP-823 steel, with an addition of neodymium and depleted uranium imitating actinides (fissionable substances). A scheme of obtaining initial samples of the vat residue simulator is shown in Figure 2, and the composition of initial EP-823 steel is presented in Table 1.

Table 1. EP-823 steel composition

Content of elements, %										
C	**Mn**	**Si**	**S**	**P**	**Cr**	**Ni**	**Mo**	**V**	**N**	**Fe**
0.2	0.8	1	0.01	0.015	12	0.5	0.9	0.2	0.05	84.325

The induction-slag remelting experiments were carried out in an induction furnace with a cold crucible. Its technical data are presented in Table 2.

Table 2. Technical data of the induction furnace with a cold crucible

Cold crucible internal diameter, mm		95
Cold crucible height, mm		150
Maximum charge weight by EP-823 steel		3
Temperature in the cold crucible, °C		1600
Operating mode		periodic
Atmosphere		argon
Power supply source	Power, kW	320
	Frequency, kHz	4
Method of temperature measurement		Pyrometric

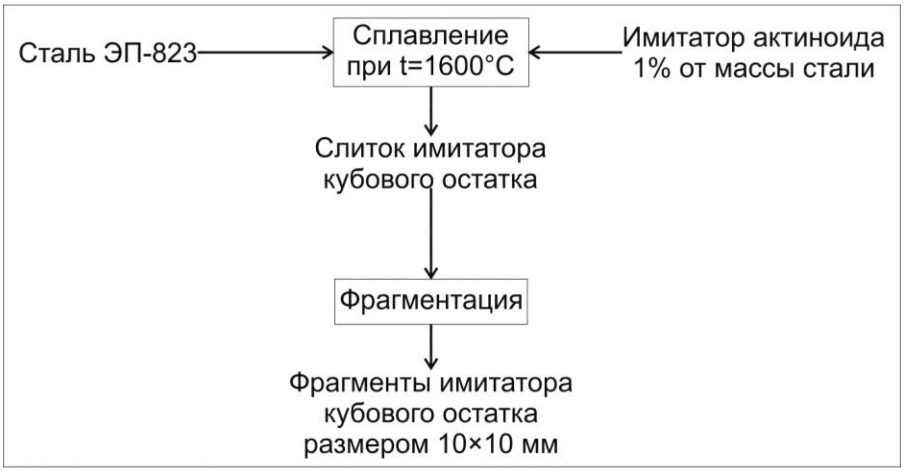

Figure 2. Scheme of simulative vat residue preparation. Simulators of actinides were neodymium or natural uranium.

[Сталь ЭП-823 means EP-823 steel; Сплавление при t=1600°C means Remelting at t = 1600°C; Слиток имитатора кубового остатка means Ingot of vat residue imitator; Фрагментация means Fragmentation; Фрагменты имитатора кубового остатка размером 10×10 мм means Fragments of vat residue imitator (10 × 10 mm); Имитатор актиноида 1% от массы стали means Actinoid imitator (1% of steel mass)]

The slag mixture with the oxidizer (150% surplus with respect to the simulator) was loaded onto a tantalic/steel substrate of the crucible located at the level of the lower coil of the inductor. The fragmented imitative vat rest was placed above. The furnace camera was hermetically sealed and vacuumized to 0.1 Pa, and then filled with high purity argon to attain an excessive pressure of 0.1 kPa. High frequency current was applied to the inductor. In the course of EP-823 steel melting the slag, after passing through the melt volume, was concentrated in the top part of the crucible absorbing the oxidized fissionable substance simulators. The melting process is presented visually in Figure 3. Remelting time was 160–200 min. Then the high frequency current was turned off. The obtained ingot was cooled. The camera was depressurized. The ingot was unloaded from the crucible. The solid layer of the slag saturated with the fissionable substance simulator was separated from the steel ingot.

The vat residue samples obtained after the remelting, the slag-forming constituent and the slag were transformed into a liquid water-soluble state in a microwave system for tests decomposition "Milestone Ethos" (Italy) and analyzed in order to obtain mass balance on simulators of actinides and to estimate their redistribution in the course of the oxidative slagging. The solutions were analyzed with the use of a certified Varian Vista-PRO inductively coupled plasma optical emission spectrometer (Australia) and a certified Varian AA 240 FS atomic adsorptive spectrometer (Australia).

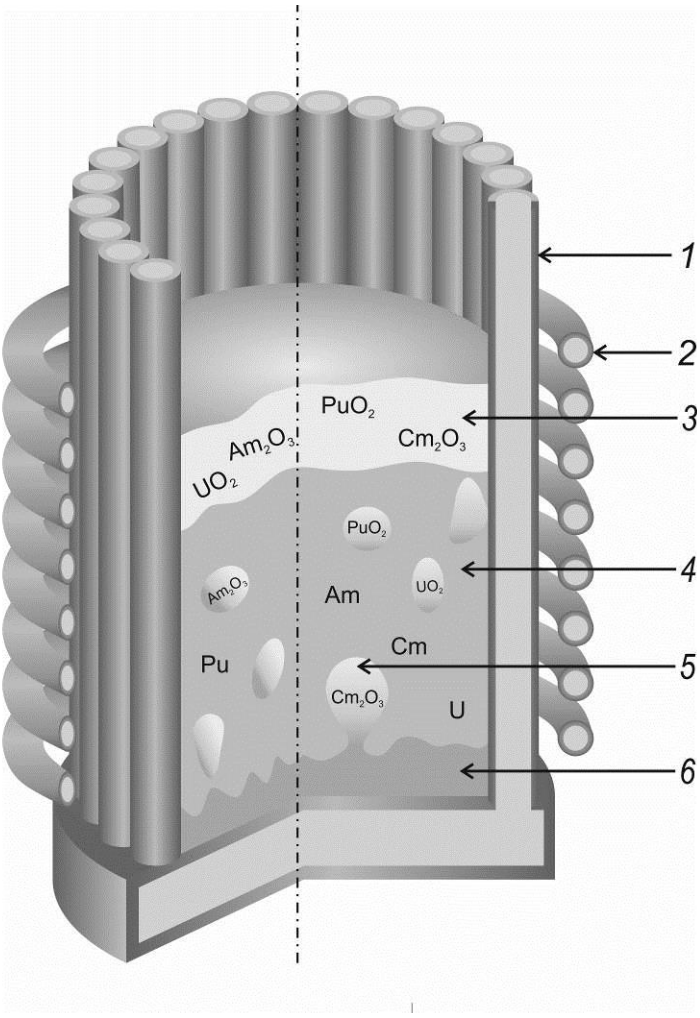

Figure 3. Induction slag remelting:
1 –water-cooled sections of the cold crucible; 2 –water-cooled inductor;
3 – slag saturated with actinides; 4 – melted vat residue;
5 – emerging slag drops; 6 – slag-forming constituent.

Results and Discussion

We studied previously Al_2O_3–SiO_2, B_2O_3–SiO_2 and Al_2O_3–CaO systems in order to extract the fissionable materials into the slag phase. Calculation showed that using aluminum metasilicate can provide a high extent of steel purification from actinides. Using the borosilicate system is also characterized by high performance in the purification of EP-823 structural steel from uranium. Using CaO–Al_2O_3 flux was unrealizable, because this requires an essential overheat of the reaction mass.

According to literature data [1], using slag-forming mixtures characterized by a high content of SiO_2 and containing CaF_2 calcium fluoride promotes uranium oxide concentration in the slag phase. However, using slag-forming mixtures containing silicon and fluorine compounds causes in practice a number of difficulties. First of all, it is planned to subject *the slag* phase containing actinides to hydrometallurgical processing after the induction-slag remelting. Therefore, there will be a problem of slags opening. Leaching the slag phase that contains silicon compounds can result in the formation of pulp difficult to filter due to the large evolution of silicon gel. The presence of fluorides, reagents highly aggressive with respect to the equipment, imposes restrictions for the choice of constructional materials of the devices.

Most countries use borosilicate or phosphate systems for immobilizing radioactive waste by vitrification. The used borosilicate system has a good capacity with respect to actinides. However, it has a high content of SiO_2 (up to 68 % by weight) [2].

Previously developed systems for radioactive waste immobilization should be considered as slags for fissionable materials extraction. These systems are characterized by low values of melting temperature and viscosity, as well as by high saturation capacity with respect to actinides. Besides, it is expedient to study also slag-forming mixtures of various compositions used in metallurgy.

Taking into account the values of physical parameters of the systems for transforming the fissionable substances by cold crucible induction melting indicated in [2] the following intervals of parameters for the optimization of slag composition were chosen: viscosity $0.6 \div 6$ Pa×s, conductivity $20 \div 80$ S. The slag melting temperature should be ≈1400 °C. This value was chosen in order to decrease the slag viscosity when carrying out induction-slag remelting taking into account that steel melting temperature is ≈1600 °C. The vapor pressure of the oxide phase will increase at melting temperatures below 1400 °C.

We tested the following substances as fluxes:

- aluminum metasilicate,

- borosilicate glass with a homogeneously included oxidizer: Fe_2O_3 + MnO_2;
- borosilicate glass.

Gaseous oxygen and oxygen-containing compounds can be used for oxidative slagging of fissionable materials and uranium. The most widely used and cheap oxidizers in metallurgical practice are iron and manganese oxides.

The flux compositions are presented in Table 3.

Table 3. Compositions of used fluxes

Slag-forming constituent	**Components, % by weight**								**Oxidizer**	
	SiO_2	Na_2O	B_2O_3	Li_2O	MgO	Al_2O_3	MnO_2	Fe_2O_3	% with respect to stoich.	Formula
Borosilicate glass	55.4	17.2	14.1	5.8	2.2	5.3	-	-	150	Fe_2O_3
Iron-containing borosilicate glass	34.9	11.9	8.5	3.5	1.4	5.5	7.8	26.5	150	Fe_2O_3 + MnO_2
Aluminum metasilicate	36.17	62.83	–	–	–	–	–	–	150	Fe_2O_3

FactSage 6.4 program based on the method for phase diagrams calculation CALPHAD (abbreviation from CALculation of PHAse Diagrams) was used to calculate equilibrium states of this system under the preset conditions.

Basic data for the calculation were the mole fractions of all the components of the system. Besides, for the cases of using gaseous oxygen and iron(III) oxide a variable parameter <A> was introduced. It meant the mole fraction of the oxidizer included in the system (for solid oxides) or not included (oxidizer: gaseous oxygen). The following boundary conditions were set for parameter <A>: boundaries χ = 0.0001 – 0.015 with a step of 0.0001. The calculated equilibrium concentrations of the components **o**f the Fe–Cr–U–Pu–Np–Am system depending on the excess of oxygen introduced as O_2 (gas), MnO_2 (solid), Fe_2O_3 (solid) are presented graphically in Figures 4–15 in the form of dependences of mole fractions of the components $\chi(i)$ on χ (oxidizer).

According to the state diagram of U−Fe [4], uranium is present in the initial system in the form of intermetallic compound UFe_2. The addition of an oxidizer in one of three forms to the reaction system decreases the molecular ratio of UFe_2, while the amount of the oxidized uranium, UO_2, increases and reaches a maximum. Quantitative comparison leads to the conclusion that the best oxidizer for uranium is MnO_2. According to the results of calculation, using this oxidizer provides the minimum concentration $\chi(UFe_2)$ 4.3×10^{-7} and its maximum transformation into UO_2.

It follows from Figures 7–9 that the best reagent for neptunium oxidation into NpO_2 is

MnO_2, because it provides the minimum fraction of neptunium in EP-823 melt $\chi(Np) = 7.07 \cdot 10^{-7}$ and its maximum transformation into the oxide.

The results presented in Figures 10–12 show that the most effective oxidizer for plutonium is gaseous O_2. However, because it is difficult to use gaseous oxygen for the process in a hot camera, we shall consider Fe_2O_3 providing the minimum concentration of plutonium in melt $\chi(Pu) = 7.02 \cdot 10^{-5}$ to be most effective.

Americium is most active with respect to oxidation among the considered actinides. This is evidenced by its compete absence in the metal state upon using gaseous oxygen even before $\chi(O) = 0.001$ is reached (Figures 13–15), which is the lower limit of the explored area.

As the calculation showed, MnO_2 and Fe_2O_3 are rather effective oxidizers. Using them allows reaching the residual content of fissionable substances and minor actinides in the steel. As noted above, using gaseous oxygen is hardly acceptable in the conditions of an inert camera. Despite the high effectiveness of pyrolusite in the reaction with neptunium, it was decided to refuse using it, because it decomposes at 535°C releasing gaseous oxygen. This can break the inertness of the atmosphere in the processing camera (1):

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2\uparrow$$

So, the experiment was made further with the use of iron(III) oxide as an oxidizer.

The conditions and results of the experiments on induction-slag remelting with aluminum metasilicate are presented in Table 4. It can be seen that melting with aluminum metasilicate showed insufficient efficiency not providing the target purification degree. It was found that the necessary and sufficient time of remelting in case of aluminum metasilicate is 160 min. Borosilicate glass containing Fe_2O_3 oxidizer proved to be most effective.

Table 4. Results of induction-slag melting experiments

Slag-forming constituent (flux)	Holding time, min	Purification degree, %	Average residual content of the imitator in the ingot, %
Aluminum metasilicate	120	93.2	0.002 – 0.004
	160	94.9	–
	200	95.3	–
Borosilicate glass containing Fe_2O_3	160	~ 100	0.0002
Borosilicate glass containing charge-adjusting Fe_2O_3	160	~ 100	0.00012

Conclusion

The efficiency of cold crucible induction melting for the removal of residual actinides from EP−823 steel was proved experimentally. It was found that slags based on low-melt-point borosilicate glass are most suitable for induction-slag remelting. The preferable oxidizer is charge-adjusting Fe_2O_3 added to borosilicate frit.

Although calculation showed that using aluminum metasilicate was expected to give an acceptable result, its efficiency in practice was insufficient.

The optimal time and temperature of induction-slag remelting are 1600°C and 160 min, respectively.

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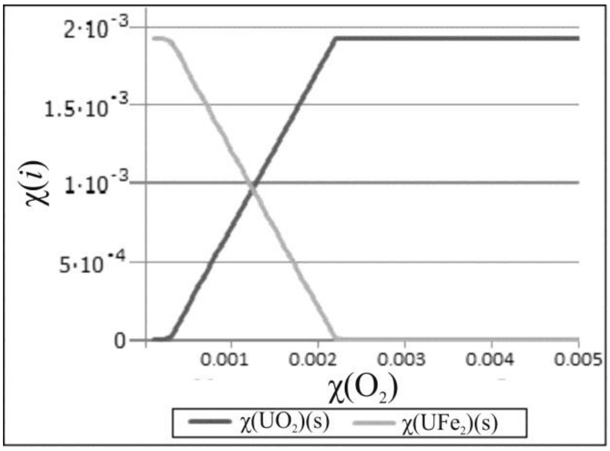

Figure 4 . Calculated dependences of $\chi(UO_2)$ and $\chi(U)$ on $\chi(O_2)$.

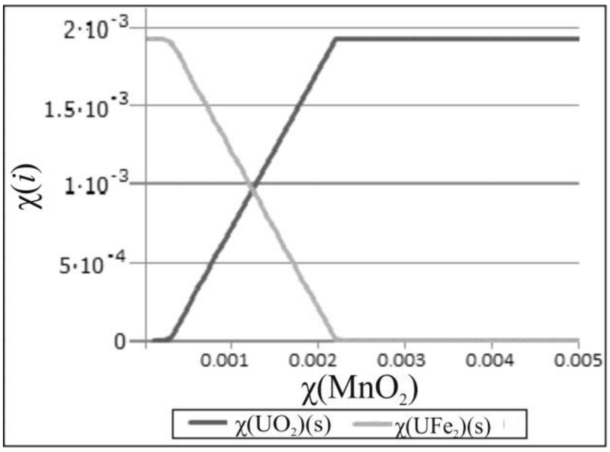

Figure 5. Calculated dependences of $\chi(UO_2)$ and $\chi(U)$ on $\chi(MnO_2)$.

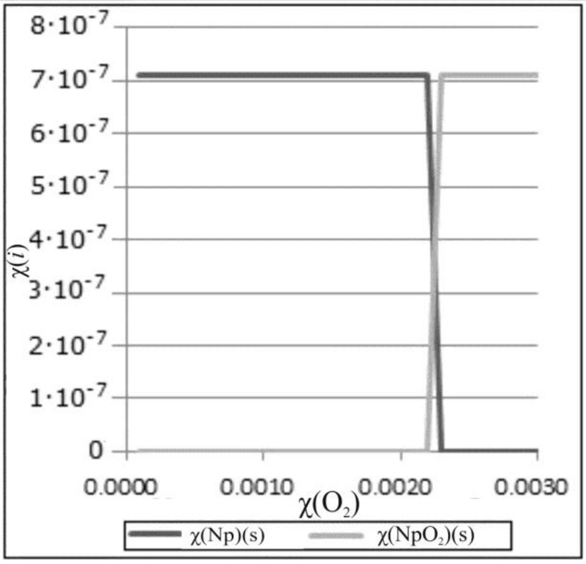

Figure 7. Calculated dependences of $\chi(NpO_2)$ and $\chi(Np)$ on $\chi(O_2)$.

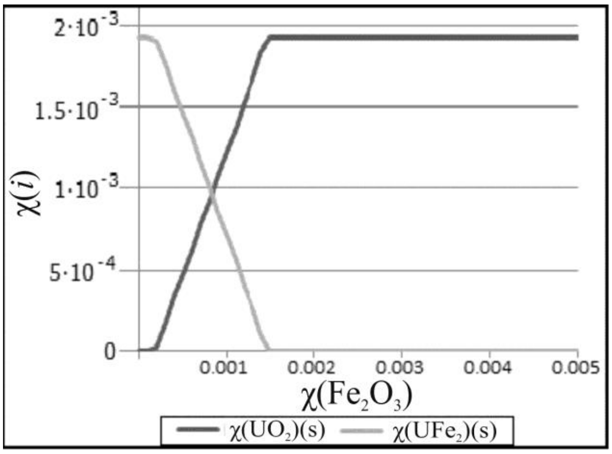

Figure 6. Calculated dependences of $\chi(UO_2)$ and $\chi(U)$ on $\chi(Fe_2O_3)$.

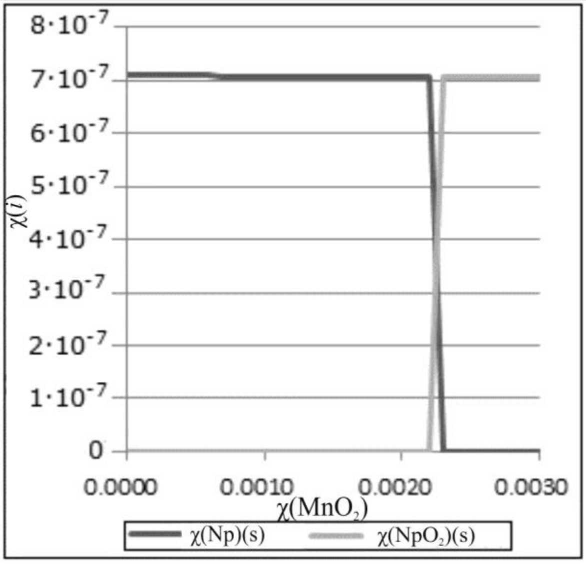

Figure 8. Calculated dependences of $\chi(NpO_2)$ and $\chi(Np)$ on $\chi(MnO_2)$.

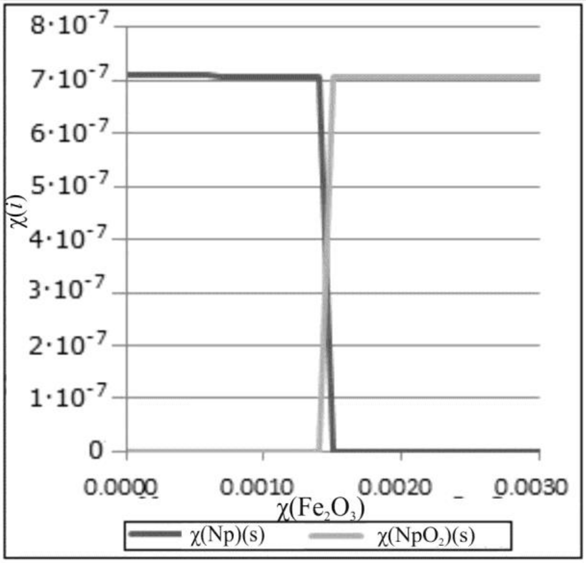

Figure 9. Calculated dependences of $\chi(NpO_2)$ and $\chi(Np)$ on χ (Fe_2O_3).

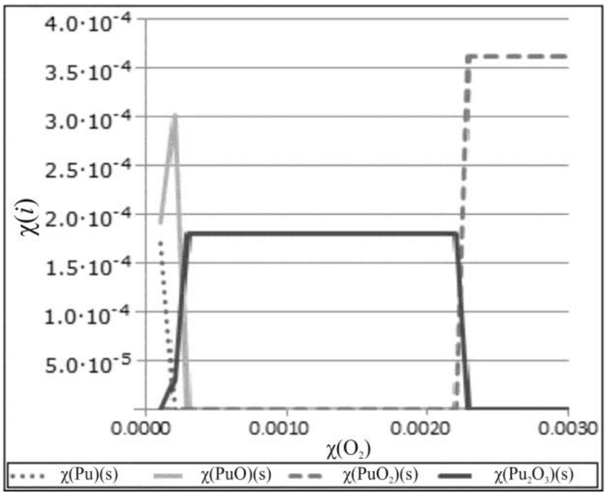

Figure 10. Calculated dependences of $\chi(PuO_2)$, $\chi(Pu_2O_3)$, $\chi(PuO_2)$ and $\chi(Pu)$ on $\chi(O_2)$.

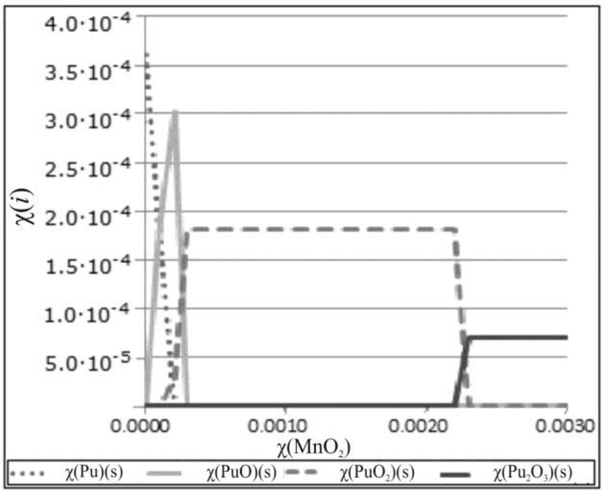

Figure 11. Calculated dependences of $\chi(PuO_2)$, $\chi(Pu_2O_3)$, $\chi(PuO_2)$ and $\chi(Pu)$ on $\chi(O_2)$.

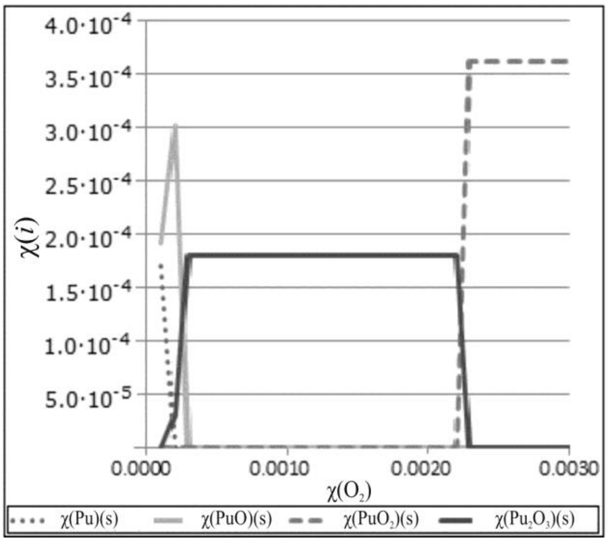

Figure 12. Calculated dependences of $\chi(PuO_2)$, $\chi(Pu_2O_3)$, $\chi(PuO_2)$ and $\chi(Pu)$ on $\chi(O_2)$.

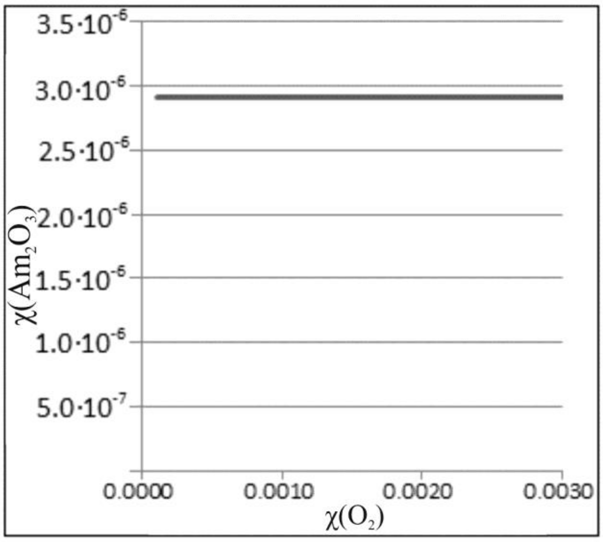

Figure 13. Calculated dependences of $\chi(Am_2O_3)$ and $\chi(Am)$ on $\chi(O_2)$.

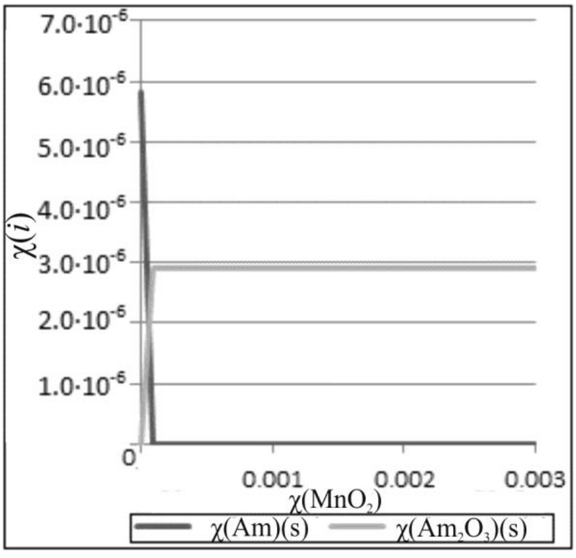

Figure 14. Calculated dependences of $\chi(Am_2O_3)$ and $\chi(Am)$ on $\chi(MnO_2)$.

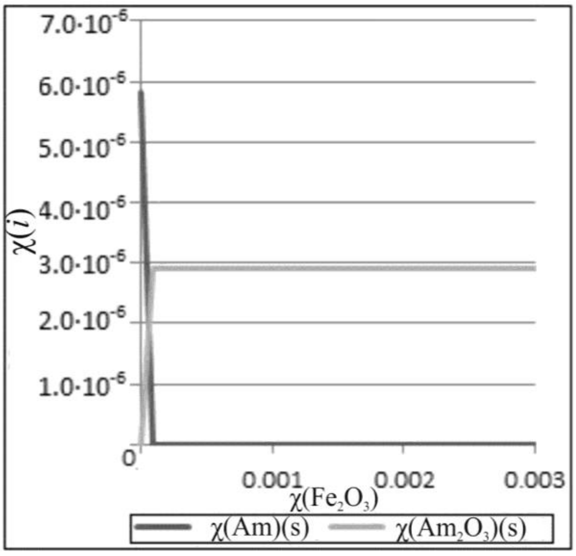

Figure 15. Calculated dependences of $\chi(Am_2O_3)$ and $\chi(Am)$ on χ (Fe_2O_3).

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