The cesium precipitation from the spent electrolyte LiCl-KCl composition simulator

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Abstract. Spent nuclear fuel reprocessing generates a significant amount of radioactive waste. Main contribution to the specific activity of such wastes, especially in the time interval from 5 to 300 years after irradiation, is made by the long-lived β-emitting radionuclide $^{137}$Cs together with the daughter, short-lived nuclear isomer $^{137m}$Ba that is in balance with it. To reduce waste volumes, pyrochemical methods for the reprocessing of SNF are possible. On this way, fission products accumulate in the electrolyte especially during recycle and can reach up to 10-15%. A pair of $^{137}$Cs/$^{137m}$Ba provides high heat generation, which is fraught with loss of electrolyte control: calculations show that a situation of electrolyte self-heating is possible above the melting point and its existence in the liquid state even if the heating of the apparatus furnace is turned off. An experimental verification of the possibility of removing caesium from 3LiCl-2KCl spent electrolyte imitators with the presence of up to 10% Cs was main goal of this paper. The insoluble in water and strong mineral acids caesium compound was obtained, so we can talk about the possibility of creating a new matrix for immobilizing caesium, as well as a new working medium of ionizing radiation sources. The share of caesium in the resulting compound reaches 50%. Sufficiently complete precipitation is shown (up to 80%), because within the framework of the pyrochemical SNF reprocessing technology, the electrolyte is supposed to be recycled and caesium that is not removed at the current step will be removed at the next step.

1. Introduction
During spent nuclear fuel reprocessing, a significant amount of radioactive wastes are formed. It can contaminate the hydrosphere objects with fissile materials, fission products, transuranic elements, if not properly managed. A significant contribution to the specific activity of such wastes, especially in the time interval from 5 to 300 years after irradiation, is made by the long-lived β-emitting radionuclide $^{137}$Cs together with the daughter, short-lived nuclear isomer $^{137m}$Ba that are in balance together.
To reduce waste volumes, pyrochemical methods for the SNF reprocessing are under development. Electrochemical separation of nuclear materials from salt based on alkali chlorides systems is realized. At the same time, after the selection of the valuable products: uranium, plutonium and minor actinides - fission products accumulate in the electrolyte, and, after multiply recycle, their concentration can reach up to 10-15%.

Disposing electrolyte without cleaning it has an extremely negative effect on the fuel cycle economy. Lithium contained in electrolyte is a valuable component, and, against the background of the boom in the production of batteries, its price is constantly increasing. Technologies for incorporating alkali chlorides into insoluble, leach-protected, matrices are complex and are currently poorly developed. The conversion of chlorides to oxides is accompanied by the discharge of a large amount of chlorine-containing gases — the problem of gas cleaning which is also under development.

At the same time, a pair of $^{137}$Cs/$^{137m}$Ba provides high heat generation, which is fraught with loss of electrolyte control: calculations show that a situation of electrolyte self-heating above the melting point and its existence in the liquid state is possible even if the heating of the apparatus is turned off. All this forces us to search for technological approaches to the removal of caesium from spent electrolyte. The matter is complicated by the proximity of the properties of alkali metals and the almost complete absence of insoluble caesium compounds.

Various approaches are currently being studied to remove caesium and other fission products from alkali metal chloride melts. Such methods are zone melting [1], directional crystallization [2], sorption purification using zeolites [3], precipitation with various reagents, distillation. Unfortunately, none of these methods has high cleaning coefficients (less than 10) and is not selective to caesium; as a result, up to a one-third of the electrolyte is discarded.

Our approach to the removal of caesium is its precipitation from the melt using transition metal salts and cyanic acid. Sorbents based on alkali metal hexacyanoferrates have shown their effectiveness in binding caesium in aqueous solutions, which gives hope for their effectiveness in alkali metal chloride melts.

The aim of the work was to experimentally verify the possibility of removing caesium from spent 3LiCl-2KCl composition electrolyte simulators with the presence of up to 10% CsCl by adding dedicated precipitator.

It should be noted that the authors did not set the goal of completely clean up the spent electrolyte simulator from caesium: since the electrolyte is recycled, then inevitably caesium will again come into it and deep cleaning turns out to be meaningless. It is important to develop a simple and rapid method for the discharge of macro quantity of caesium to maintain control over heat generation in the apparatus.

2. Experimental part
The following materials were used in the work: anhydrous lithium chloride, “P.A.”, STP TU COMP KOM 2-477-11, JSC “Komponent-Reactiv”; potassium chloride, “P.A.”, GOST 4234-69, JSC "REACHIM"; caesium chloride, grade “R”, GOST 4162-79, JSC "REAHIM.

Before the experiment, the initial components of the chloride melts were dehydrated in a drying oven at a temperature of 150°C. The dehydrated reagents were stored in a desiccator filled with calcined anhydrous magnesium perchlorate (anhydrite).

Before the experiment, the calculated amounts of the required reagents were weighed on an analytical balance of the Sartorius brand with an accuracy of 0.001 g, homogenization of the mixture of reagents was achieved by joint melting, additional preliminary operations were not used. The resulting mixture was introduced into a glassy carbon crucible and melted in a furnace in an air atmosphere at a temperature 500°C at 2-hour exposure. A typical appearance of the ingot before the start of the experiment is shown in figure 1.
We used a model electrolyte of composition 3LiCl-2KCl with the addition of CsCl of 3, 5 and 10% by weight for study the complete deposition of caesium from model electrolyte melts by adding dedicated precipitator. The weight of the melt sample was 28.45, 29.00 and 30.39, respectively.

The charge was placed in a glass carbon crucible located in a quartz cell in an ohmic heating furnace. The temperature was controlled using the ThermoMatic TM100P thermo controller; the control thermocouple (type K) was located between the quartz cell and the furnace pit body. To maintain the equipment used, as well as to protect the melt, a quartz glass cap was used.

The temperature of the process was 500°C. The heating rate was 300°C/h. After complete melting and at reaching a predetermined temperature, a previously prepared and weighing (1.62, 2.70, 5.40 gram respectively) sample of dedicated precipitator was added. Exposure in the melt was 2 hours. Every 15 minutes melt samples were taken, followed by dissolving in 50 ml of distilled water to determine the caesium content in the melt. For this, a quartz tube was placed in the melt; a column of melt was drawn down with a medical syringe. The tube was removed from the melt and cooled. This method of sampling allowed us to guarantee the compliance of its composition with the composition of the electrolyte. Saline growths that had fallen on the outer surface of the tube were not included in the sample and were transferred to waste.

During the addition of the precipitator, the presence of foaming, gas evolution, facts of its spontaneous combustion, etc. were recorded. After the end of the exposure, the melt cooled to room temperature in a natural way.

The resulting ingot was crushed, checked for the presence of different phases. The obtained ingot was removed, a sample was taken for XRD analysis of the obtained compounds, with visual detection of two or more phases, samples for XRF and determination of caesium content were taken from each type of phase.

The solid phase was separated from the chloride salts by washing in distilled water. Washing was carried out at a temperature of 50°C. The precipitates were separated from the solution using a “Blue tape” deashed filter, dehydrated and weighed. The solution was transferred to a 250 ml volumetric flask and fill with distilled water to its volume.

Liquid and solid phases samples were subjected to XRD and XRF. A typical view of an ingot obtained by fusing a model electrolyte with precipitator is shown in figure 2.

**Figure 1.** Typical ingot appearance for composition 3LiCl-2KCl + CsCl.

**Figure 2.** A typical ingot obtained by fusing a model electrolyte with precipitator appearance.
The samples phase composition was identified by XRD using a photo method. Samples were prepared on glass rods. To do this, the test sample was ground in an agate mortar and applied onto a thin glass rod (diameter 10 μm) lubricated with epoxy resin. The glass rod was placed into the Debye-Scherrer camera holder to adjust the sample in the centre position. X-ray diffraction of the samples was performed on an X-ray film, with copper radiation with a Ni filter using an URS-2.0 X-ray source. At the end of the shooting, the film was developed. Reflexes were displayed on the film. According to the reflexes, the phase composition was identified using the JCPDS X-ray diffraction data files [4] and the RENTGEN software package using the PICAR automatic X-ray image processing system [5, 6] taking into account the main systematic errors for the absorption and film shrinkage. Some samples were X-rayed on a diffractometer DRON-3M. For this purpose, the sample under study was added with diamond powder as an internal standard.

Chemical composition investigation of the samples were performed by the method of arc atomic emission spectrometry on an installation that includes STE-1 spectrometers with the MAES photodiode line No.M10052 and PGS-2 with the MAES photodiode line No.M08077 with the Atom-3.3 software and the Vesuvius-3 generator.

For express analysis of samples, we also used an X-ray fluorescence energy dispersive analyser “REAN” designed for non-destructive X-ray fluorescence elemental analysis. The analyser is a stationary, single-function, automated device. The principle of operation is based on the energy dispersive X-ray fluorescence method.

To improve the conditions for separating the precipitate from the purified melt, a deposition was checked in the applied magnetic field. In connection with the alleged presence of alkali metals in the precipitated sediment, in which Fe$^{3+}$ has ferromagnetic properties, it was suggested that the application of an external magnetic field can have a beneficial effect on the sedimentation of the resulting precipitate.

To do this, magnet based on ferrite was used during adding a precipitator powder. To increase the completeness of sedimentation, a magnet was located in the lower part of the furnace shaft, a quartz cell was located above it. The subsequent part of the experiment is identical to the above. To assess the completeness of sedimentation, melt samples were taken and the distribution of the solid phase was visually assessed depending on the exposure time.

To study the effect of the method of adding precipitator, weighed amounts of powder and tablets of our own production were used. Tablets were made by pressing on a TDP-0.5 tablet press. The pressing pressure was 0.5 MPa.

3. Results and discussion

In accordance with the experiments matrix, shown in table 1, the caesium deposition process from the spent electrolyte simulator of the pyrochemical technology of spent fuel processing was experimentally verified.

| Molar ratio Cs: Precipitator | Caesium content in the melt |
|-----------------------------|-----------------------------|
|                             | 3 %wt. | 5% wt. | 10 % wt. |
| 1:1                         | Run #1 | Run #2 | Run #3   |
| 1:1,5                       | -      | -      | Run #4   |
| 1:2                         | Run #5 | Run #6 | Run #7   |

An XRD of the precipitates were carried out. All analysed samples have identical phase composition. A typical XRD result of the samples is shown in figure 3. The presence of potassium chloride can be explained by its incomplete washing due to capture by closed pores.
According to the results of dissolution of the obtained ingots, the caesium contained in the solution will be considered as not removed by caesium. The results of the completeness of the removal are presented in table 2.

Table 2. Completeness of caesium removal in various experiments.

| Run # | Start caesium content,%wt. | Caesium distribution |  |
|-------|--------------------------|----------------------|---|
|       |                          | Solution             | Precipitate |
| 1     | 3                        | 99%                  | 1%          |
| 2     | 5                        | 60%                  | 40%         |
| 3     | 10                       | 20%                  | 80%         |
| 4     | 10                       | 34%                  | 66%         |
| 5     | 3                        | 48%                  | 52%         |
| 6     | 5                        | 47%                  | 53%         |
| 7     | 10                       | 24%                  | 76%         |

From table 2, it can be concluded that caesium is removed from the melt to a level of ~ 2% by weight, which allows the electrolyte to be sent for reuse after such removal step. An increase in the excess of the precipitant contributes to a more complete removal of caesium, however, it can lead to accumulation of iron in the recycled electrolyte, which will require additional operations for its removal.

During the study effect of the adding a precipitant method, the addition of a tableted precipitator was compared to the addition of its powder. Moreover, in the case of the addition of tablets, significant foaming in the melt is observed; foam rises above the heating zone of the furnace and its partial freezing. Due to the smaller contact area, the interaction time during the precipitation with a preformed precipitator must be increased. Completeness of removal remains at the same level. Data on the completeness of the deposition are presented in table 3.
Table 3. Experimental verification of precipitator introduction method influence.

| Precipitator form | Start caesium content,%wt. | Caesium distribution |
|-------------------|-----------------------------|---------------------|
| Powder            | 5                           | 49%                 |
| Tablet            | 5                           | 48%                 |

Experimental verification of the external magnetic field application does not affect the insoluble precipitate in the electrolyte distribution. The magnetic field influence on the completeness of sedimentation is absent. The precipitate is unevenly distributed in the volume of the melt, and full precipitation was not achieved. This indirectly indicates the difference in the degree of oxidation of iron in the sediment from that assumed at the beginning of work.

As part of testing the analytical methods for studying this compound, its insolubility is shown for water and mineral acids (nitric, hydrochloric) of various concentrations for a long time at room temperature and heated. This suggests the potential suitability of the obtained precipitate for use as a matrix for removed caesium immobilization, as well as the use as an ionizing radiation sources working medium.

4. Conclusion
During this work, the caesium removing possibility from the spent electrolyte simulator of the pyrochemical technology of processing SNF to a technologically acceptable level is shown. As the electrolyte is supposed to be recycled within the framework of the SNF processing technology and caesium not removed at the current stage will be removed at the next stage.

The insoluble at room temperature and heated in water and strong mineral acids caesium compound was obtained. It opens up the possibility of creating a new matrix for caesium immobilizing, as well as a new of ionizing radiation sources working medium. The share of caesium in the resulting compound reaches 50%

The influence of the method of introducing the precipitant in the form of tablets and powder were studied. Significant foaming is shown with a single volley injection of the precipitator, which complicates the process and requires smooth dosing of the precipitator into the melt.

The absence of the influence of the magnetic field on the deposition of caesium from the chloride melt by precipitator was shown.

A fairly complete precipitation is shown (up to 80%), while the results show that there is some constant residual level of caesium in the melt, which does not reduce the value of this work.

It is planned to continue the study of the process of extraction of caesium, including experiments with real spent electrolyte from the nitride SNF processing.

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