STUDY OF ELECTROCHEMICAL PROCESSES FOR SEPARATION OF THE ACTINIDES AND LANTHANIDES IN MOLTEN FLUORIDE MEDIA

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Abstract

The technology of the Molten Salt Reactors (MSR) is developed for two possible applications: For one thing as the Molten Salt Transmutation Reactor (MSTR) incinerating plutonium and minor actinides within reprocessing of spent fuel from PWR or FBR and for another thing as electricity generating MSR working under thorium – uranium fuel cycle. Electrochemical separation processes are one of promising pyrochemical techniques that should enable the "on-line" reprocessing of circulating fuel salt in MSR (fuel cycle back-end). The former application represents the Czech P&T concept, in which framework the electrolytic separation can be applied both in the front-end and back-end of the MSTR fuel cycle. Within the front-end electroseparation should follow the Fluoride Volatility Method (FVM), which should separate 95 % of uranium from the spent fuel in the form of volatile uranium hexafluoride. The residual uranium and fission products (FP) are supposed to be separated among others also by electrochemical methods.

The presented work comprises the results reached within development of electrochemical separation of the actinides and fission products from each other by electrolytic deposition method on solid cathode in molten fluoride media, that represent he carrier salts of MSR technology. The knowledge of electrochemical properties – red-ox potentials, mainly of deposition potentials – is necessary for determination of separation possibilities of individual components by electrolysis.

The electrochemical properties of uranium, thorium, neodymium, gadolinium and other lanthanides were measured by the Linear Sweep Potential Cyclic Voltemmetry Method in the molten eutectic mixture of LiF-NaF-KF (46.5 – 11.5 – 42 molar %, melting point 454°C, acronym FLINAK) at the temperature 530°C under inert atmosphere of highly pure argon (99.995 %).

Experimental measurements were realized in three electrode system of solid working electrode, glassy carbon crucible used as auxiliary electrode and originally developed reference electrode. The reference electrode was designed to provide reproducible electrochemical measurements in molten fluorides and it is based on Ni^{2+}/Ni red-ox couple. The whole electrochemical cell was gas tightly closed inside of nickel tube and placed in vertical resistance oven. The experimental set-up consisted of electrolyser and high power potenciostat coupled by analogue scan generator. These apparatuses were connected with computer for control and data acquisition.

The measured voltammograms has shown that it is thermodynamically feasible to separate uranium and thorium from FP. Concerning the representatives of FP – neodymium and gadolinium,

their deposition potentials lie out of the exploitable potential range of FLINAK melt. For this reason, electrochemical characteristics of the selected actinides and lanthanides are studied also in other fluoride melts, at present in eutectic mixture of $LiF\text{-}CaF_2$ with melting point 766°C.