

microscopic roughness of the electrode surface led to the necessity of using constant phase elements.

Visual observations were made using optical and scanning electron microscopy with chemical microanalysis of the corrosion products. This showed that iron was preferentially oxidised within the pits, there being debris around the edge of the pit on top of the polished surface which was rich in iron - presumably iron oxide. Pit density was greatest for sulphate-containing solutions followed by chloride.

General analysis of the experimental data shows that there is a marked influence of the anion present on the corrosion rate and corrosion mechanism. In the presence of sulphate, chloride, bromide and perchlorate there is significant pitting corrosion, observed electrochemically and through visual observation. With respect to iodide ion, the corrosion rate is much lower but experimental evidence obtained from current-voltage profiles and impedance plots points to the mechanism being the same. For nitrate anion there are clear inhibition effects and the pitting potential is significantly more positive than for the other anions. The effect of the cation being sodium or potassium is very small, observed differences being attributable to differences in solution conductivity.

We conclude with a general order of anion aggressivity in these type of media towards M2 steel:

sulphate > chloride > bromide > perchlorate > iodide > nitrate

with little influence arising from the presence of sodium or potassium cation.

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CHEMICAL AND ELECTROCHEMICAL BEHAVIOR OF URANYL COMPOUNDS IN OXIDE SALT MELTS

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Influence of the composition of molten mixtures Me_2RO_4 - $\text{Me}_2\text{R}_2\text{O}_7$ - UO_2RO_4 (Me = Li, Na, K, Cs; R = S, Mo, W) and of the main potentiostatic electrolysis parameters on the chemical, phase composition of cathode deposits and on their current efficiencies have been studied. Experiments were carried out at temperatures of up to 900°C in the air. It has been showed that uranyl-containing oxide salt melts with various cationic and anionic composition can be used for electrochemical obtaining of granular uranium oxides with the O / U atomic ratio ranging from 2.014 to 2.667.

Key words: salt melt, electrolysis, cathode deposit, uranium oxides, current efficiency, uranyl salts, sulphates, molybdates, tungstates.

The poured nuclear reactor fuel elements manufactured from UO_2 - PuO_2 or UO_2 electrolytic granules by the vibro-compaction method went through the prolonged reactor tests and demonstrated the high performance characteristics. At the same time it is well known that the gaseous chlorine used at the stage of the irradiated fuel dissolution in

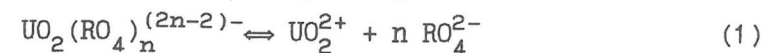
molten mixture of alkali metals chlorides and evolved during the electrolysis of the obtained solutions is very aggressive. Therefore the choice of the structural and electrode materials that are used for the purpose of technological apparatus production is limited by the insecure carbonic materials. Moreover there is a problem of the chlorine-contained gases neutralization at the exit from apparatus. Substitution of chloride salt melts by oxide ones permits to eliminate these problems and to retain main advantages of electrochemical methods for granulation and refabrication of oxide fuels.

We investigated an influence of the composition of molten mixtures $Me_2RO_4 - Me_2R_2O_7 - UO_2RO_4$ (Me = Li, Na, K, Cs; R = S, Mo, W) and of the main potentiostatic electrolysis parameters (cathodic polarization, temperature) on chemical, phase composition of cathode deposits and on their current efficiencies. The salt mixtures $Me_2RO_4 - Me_2R_2O_7$ contained from 0 to 100 mol.% $Me_2R_2O_7$ were considered as a solvent for electrochemically active component UO_2RO_4 which concentration did not exceed 50 mol.% . The experiments were carried out in the open 3-electrode electrochemical cell at the temperatures of up to 900°C in the air. A composition of the cathode deposits was determined by chemical and x-ray analyses.

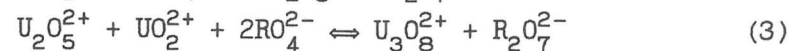
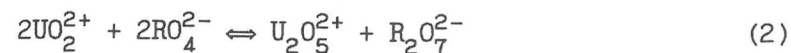
It has been established that if the cathodic potential does not exceed the potential of the solvent decomposition the products of electrolysis will be individual uranium oxides U_3O_8 , U_4O_{9+y} , UO_{2+x} ($x > 0.014$) or their mixtures. As a result of investigations the following

empiric dependences were revealed. A rise of uranium concentration in all electrolytes, other things being equal, leads to increase of the oxygen coefficient (an atomic ratio of oxygen to uranium) of electrolysis products [1]. A similar effect is observed at lowering of $Me_2R_2O_7$ concentration, of cathodic polarization or at increasing of temperature. The current efficiency of UO_{2+x} phase is risen with increase of UO_2RO_4 concentration in all investigated electrolytes. A successive substitution of lithium salts by sodium, potassium, cesium ones at the constant salt mixture composition and parameters of electrolysis leads to decrease of the oxygen coefficient of uranium oxides in the cathode deposits. At the same temperatures and salt mixture $Me_2RO_4 - Me_2R_2O_7 - UO_2RO_4$ compositions the thermal stability of electrolytes is decreased in succession: tungstate-molybdate - sulphate mixtures (the volatility of RO_3 is rose). That is why impossible to obtain the dependence of phase and chemical compositions of electrolytic uranium oxides on the anionic composition of electrolytes at comparable temperatures.

For a qualitative explanation of these dependences it was used the model of ionic composition of uranyl-contained oxide electrolytes that supposes a participation of uranyl ions in processes of complexing

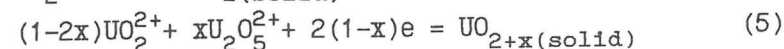


and of the stage solvolysis [1]:



A formation of the cathode deposits of UO_2 , U_3O_8 and non-

stoichiometric uranium oxides within the framework of this model can describe as follows:



A difference of deposition potentials of the most electro-negative and electropositive uranium oxides (accordingly, UO_2 and U_3O_8) in tungstate melts reaches 0.9 V. If to alter the acid-basic properties of melts and parameters of the electrolysis it can use this process for separation of uranium and some radionuclides.

It is known that uranium oxides can take part in the exchange chemical reactions with dissolved radionuclides during the electrolysis. They have to behave in these in different ways depending on oxygen coefficient and on the crystal lattice type. A limited solubility of some radio-nuclides in oxide melts as well as dependence of their solubility on acid-basic properties of melts and on the temperature can be great importance for the radiochemists.

These particularities of uranium electrodeposition from the oxide melts as well as an absence of chlorine at the stages of the irradiated fuel dissolution and of the electrolysis can be used during production of the new radiochemical processes.

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ANALYTICAL CHARACTERIZATION OF THE PASSIVE FILM FORMED ON STEEL IN CEMENT PASTE INTERSTITIAL SOLUTIONS

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INTRODUCTION

The interstitial solution existing in concrete pores is characterized by a very high pH (12.5 - 13.5) which prevents reinforcing steel corrosion due to a passive film formation. Although numerous works have been published in the field of iron passivity, there is little comprehension of some fundamental aspects of the passivation phenomena particularly in very alkaline solutions. The first works on this field^{1,2} found that the passive film was composed of an iron oxide (Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$). Later, *Smialowska et al.*³⁻⁵ concluded that the passive film is closer to an iron oxide-hydroxide (FeOOH) than to Fe_3O_4 or Fe_2O_3 and observed that the presence of chlorides in solution seemed to change the composition, thickness and density of the passive film. According *Pou et al.*⁶, the incorporation of water in the film decreases its protective nature, because the water "paths" facilitates chloride ion penetration and consequently the passive film breakdown. Auger and XPS electron spectroscopy are powerful analytical techniques to study the thickness and composition of the passive film^{6,7,8}. Combination of Auger electron spectroscopy (AES) and ion sputtering of surface has made possible the measurement of the composition profile of the surface layers in depth. By using XPS spectroscopy it is possible to characterize the oxidation state of iron compounds present in the film.

EXPERIMENTAL PROCEDURE

Steel samples previously polished with a 2400 SiC grit were spontaneously passivated by immersion in solutions (pH \approx 13) obtained from a mortar prepared with portland cement (w/c = 1) and from a mortar prepared with addition of fly ash [w/(c + f) = 1]. Three different sets of solutions were prepared: without chloride and with 0.5% and 1% of NaCl. A *Microlab 310F* from *VG Scientific* with a concentric hemispherical analyser and a Field Emission Type electron gun (35 nm spatial resolution)

was used. Spectra was taken using a 10 keV, 50 nF primary electron beam. Ion etching was performed at a current density of 0.3 - 0.5 $\mu\text{A}/\text{mm}^2$. XPS photoelectron spectra were performed using a non-monochromated Mg anode ($K_\alpha = 1253.6 \text{ eV}$) with a resolution of 0.83 eV.

RESULTS AND DISCUSSION

Results have shown that the presence of the chloride ion in solution results in a thicker film - fig.1. The film thickness also increases in flyash containing solutions. According fig.1, the estimated film thickness is about 80 - 90 nm for samples passivated in cement solution (without chloride) and 100-110 nm for samples passivated in fly ash solutions (without chloride).