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

$$UO_2^{2+} + 2e = UO_{2(solid)} \quad (4)$$

$$(1-2x)UO_2^{2+} + xU_2O_5^{2+} + 2(1-x)e = UO_{2+x(solid)} \quad (5)$$

$$2(1+y)UO_2^{2+} + (1-y)U_2O_5^{2+} + 2(3-y)e = U_4O_{9-y(solid)} \quad (6)$$

$$U_3O_8^{2+} + 2e = U_3O_{8(solid)} \quad (7)$$

A difference of deposition potentials of the most electronegative 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 radionuclides in oxide melts as well as dependence of their solubility on acid-basic properties of melts and on the temperature can be great impotance 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.

REFERENCES

1.V.K.Afonichkin, V.E.Komarov, S.V.Vakarin. Russian Journal of Electrochemistry, 29 (1993) 1356.

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

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INTRODUCTION

The intersticial 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 filme formation. Although numerous works have been published in the field of iron passivity, there is litle 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 a iron oxide (Fe_3O_4 or γ-Fe_2O_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 powerfull analytical techniques to study the thickness and composition of the passive film[6,7,8]. Combination of Auger electron espectroscopy (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 ≈ 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 $\mu A/mm^2$. XPS photoelectron spectra were performed using a non-monochromated Mg anode (K_α = 1253.6 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).

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Calcium and chloride ions were also found in depth. Chloride was incorporated in the film in the outermost 15-25 nm.

For comparison, Auger profiles were also performed on samples which were immersed during two weeks in solutions with and without fly ash. In the first week solutions were chloride free. At the begining of the second week they were contaminated with NaCl 1%. The film thickness were very close to that observed for samples passivated in solutions initially contaminated with 1% of chlorides.

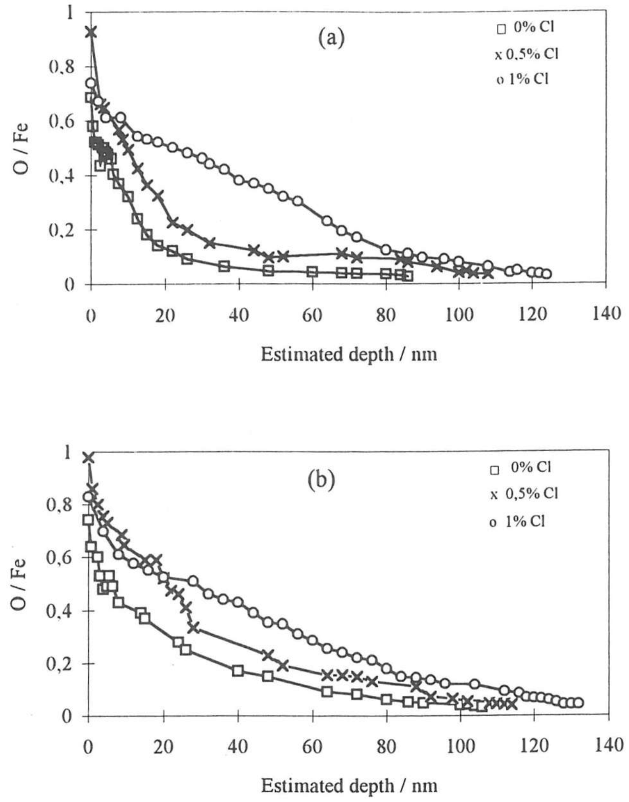

Fig. 1 - Evolution of O/Fe ratio in cement solution (a) and fly ash more cement solution (b).

XPS results were obtained from spectra deconvolution for each element present in the film. In oxygen spectra three peaks were detected: O^{-2} (530.0 eV); OH^{-} (531.4 eV); H_2O (533.0 eV); in the iron spectra five peaks were considered: the satelite peak[9,10] (at 714,6 eV and with 10% of the total peak area); FeOOH (712.0 eV); Fe^{+3} (710.4 eV); Fe^{+2} (708.8 eV); Fe^{0} (706.9 eV).

Results are sumarized in fig. 2 in which it is possible to see the distribution of iron and oxygen as a function of NaCl concentration. The FeOOH content increases with chloride content and is higher in fly ash containing solutions. After surface etching the Fe^{+3} and Fe^{+2} significantly increase, essencially at the cost of FeOOH. Iron spectra evolution is

confirmed by the oxygen behaviour: OH^{-} is higher in fly ash containing solutions and increases in the presence of chlorides. After etching an increase on the O^{-2} spectra was observed.

The presence of water in the passive film was detected by XPS, its content being increased by the presence of chloride ion - fig.2.

Film characterization by XPS was also made in samples passivated in a chloride free solution, which were later contaminated with sodium chloride. The passive film behaviour is closer to that obtained in an initially contaminated solution than in a free chloride solution.

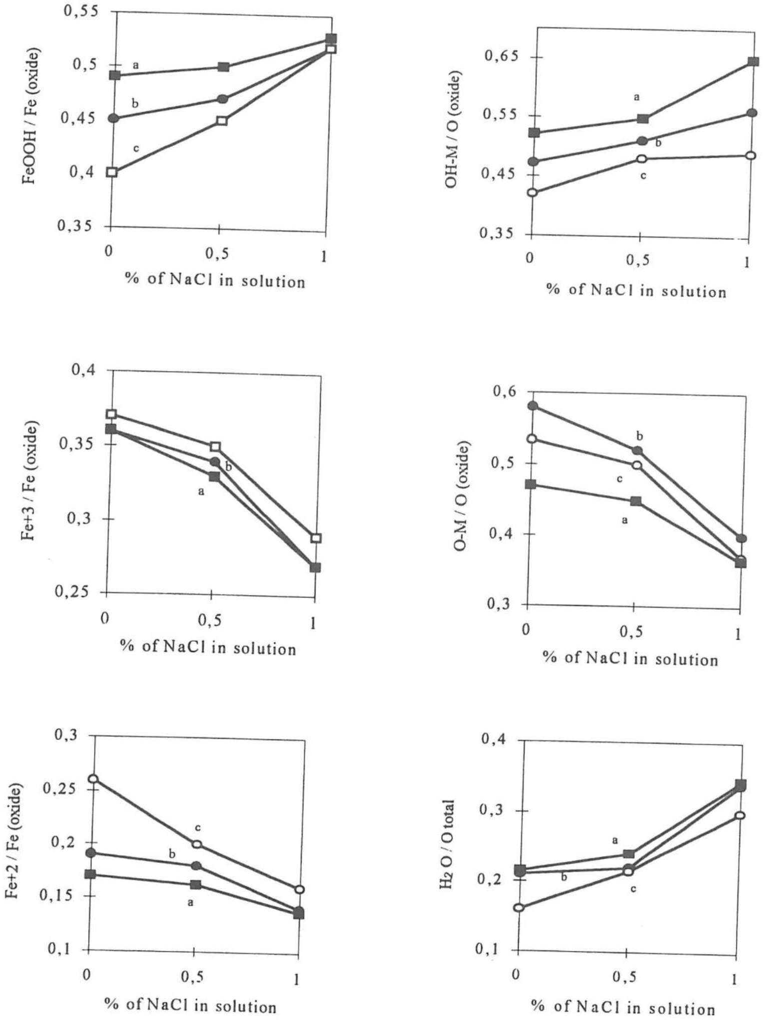

Fig. 2 - Evolution of iron, oxygen and water in the passive film before and after surface etching. a) fly ash solution without etch; b) cement solution without etch; c) fly ash solution with etch

CONCLUSIONS

The passive film formed on iron in solutions simulating the concrete intersticial solutions is composed by more than one layer. The outer layer is an iron oxi-hydroxide.

The film thickness increases both in fly ash and in chloride containing solutions. However, the degree of protection seems to decrease because larger water contents were found in fly ash containing solutions in the presence of chloride ion.

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References:

1. M. Nagayama, M. Cohen; *Journal of Electrochemical Society*, **110**, (1963) p. 670

2. J. Kruger, J.P. Calvert; *Journal of Electrochemical Society* **114**, (1967) p. 43

3. H. Oranowska; Z. Szklarska-Smialowska; *Corrosion Science*, **21** (1981) p. 735

4. T. Zakroczymski; Chwei-Jer Fan; Z. Szklarska-Smialowska; *Journal of Electrochemical Society*, **132** (1985) p. 2862

5. T. Zakroczymski; Chwei-Jer Fan; Z. Szklarska-Smialowska; *Journal of Electrochemical Society*, **132** (1985) p. 2868

6. T.E.Pou; O.J. Murphy; V. Young; J.M. Bockris; *Journal of Electrochemical Society*, **131** (1984) p. 1243

7. M. Seo, M.Sato, J.B. Lumsden, R.W. Staehle; *Corros. Sci.*, **17**, (1977) p. 209

8. R.Devaux, D.Vouagner, A.M.BecDelievre, C.Duret-Thual; *Corros.Sci.*, **36**, (1994) p. 171

9. D. Briggs, M.P. Seah; " Practical Surface Analysis", Eds. Wiley & Sons; England (1990)

10. K. Asami, K. Hashimoto; *Corros. Sci.*, **17** (1977) p. 559

COMPORTAMENTO ELECTROQUÍMICO DA ESPINELA $Ni_{1-x}Cu_xCo_2O_4$ EM MEIO BÁSICO

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1. **Introdução:** A espinela $NiCo_2O_4$ é um dos materiais tipo óxido que apresenta uma melhor desempenho relativamente à reacção de evolução do oxigénio [1]. Com o objectivo de correlacionar a actividade deste material com as suas propriedades estruturais e físico-químicas, iniciou-se um estudo que consiste na preparação e caracterização electroquímica de materiais que derivam desta espinela por substituição parcial de um dos seus catiões por um terceiro [2,3]. Neste trabalho são apresentados resultados experimentais relativos ao comportamento electroquímico do sistema $Ni_{1-x}Cu_xCo_2O_4$. O estudo da actividade de eléctrodos destes óxidos foi feita através do registo de curvas de polarização I-E sob condições de estado estacionário, numa região de potencial compreendida entre 0.55 e 0.80 V *vs* Hg/HgO. Com o objectivo de estudar o comportamento destes eléctrodos após evolução prolongada de oxigénio, os eléctrodos foram submetidos a uma descarga contínua de oxigénio durante aproximadamente 17 horas. Procedeu-se mais uma vez ao registo das curvas de polarização no mesmo intervalo de potencial. A actividade dos eléctrodos foi analisada em termos de declives de Tafel, b, densidade de corrente de troca, i_0, e sobrepotencial, η. É considerada a variação destes três parâmetros em função da percentagem de cobre introduzida.

2. **Detalhes Experimentais:** Os eléctrodos foram preparados por deposição de camadas sucessivas dos óxidos obtidos por decomposição térmica de misturas estequiométricas dos respectivos nitratos ($Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ e $Cu(NO_3)_2.3H_2O$ pro-analyse, Merck), a 350°C durante 1 hora. Estudaram-se as composições nominais em cobre, x= 0, 0.05, 0.10, 0.25, 0.50 e 0.75. Em todos os ensaios electroquímicos utilizou-se uma célula de vidro de três compartimentos, uma folha de platina como eléctrodo secundário, o eléctrodo de Hg/HgO como referência e uma solução de KOH 5 $moldm^{-3}$ como electrólito.

3. **Resultados e Discussão:** Na figura 1 encontram-se representadas as curvas de polarização de dois eléctrodos com x=0.00 e 0.05 antes de serem submitidos à evolução prolongada de oxigénio. Como se pode observar, a substituição de apenas 5% de níquel por cobre provoca um aumento significativo da densidade de corrente na região de maior sobrepotencial.

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