

Thesis Booklet

Adsorption of fission and corrosion products on structural materials of the  
primary circuit in nuclear power plants

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2011

## Introduction

The structural materials of the primary circuit of a nuclear power plants are contaminated by accumulated impurities which can have some negative influence on radiation hazards, operating processes and waste treatment. Impurities can generate problems under operating circumstances and during the storage of the cassettes or in case of disassemble. The surface of the structural materials can be oxidised and the corrosion products can be transported to the core by the coolant. They may be activated by neutrons forming radioactive cobalt, manganese and silver nuclei which can adsorb onto the structural materials. In the case of a malfunction or leaking of the fuel rods further impurities appear in the coolant in colloidal, gas or dissolved form. Generally, in a power plant after some operating time, the equipment or installation must be repaired or exchanged because of the erosion-corrosion processes.

In the 2<sup>nd</sup> block of the Paks Nuclear Power Plant corrosion products were deposited onto the cassettes during the operation. The reason for this is that during the annual maintenance several steam generator were decontaminated, and the process included a step of the protecting oxide layer stripping. After this the corrosion process was accelerated, and the corrosion products adsorbed on the hottest location of the circuit, which is the reactor core. In April 2003 during the annual maintenance of the stopped reactor the contaminated cassettes were cleaned (rinsing with oxalic acid) in a cleaning tank for thirty cassettes. This process was performed in shaft 1 next to the reactor. In the sixth cycle a serious malfunction occurred. Due to the unsatisfactory cooling the cassettes were overheated (about 800-900°C) afterwards opening the lid cool water quenched the cassettes suddenly. The

rigidity of the cassettes caused by the thermal shock resulted in rod breaking and the fuel debris and uranium appeared in the coolant. This time shaft 1, the reactor and the spent fuel storage pool were connected to a common cooling circuit. Thus the whole primary circuit of the 2<sup>nd</sup> block became contaminated with fission products and uranyl. After this incident came into interest the adsorption of the fission products on the structural materials. It is important to know the surface activity of the cassettes during treatments like refuelling process, storage, transport or at normal operation conditions from the point of view of radiation hazards.

## **Aims**

The goals of this study were:

- to develop a physico-chemical model which can describe the contamination of the cassettes caused by the ionic forms of the corrosion and fission products under the conditions of the spent fuel storage pool. It includes the adsorption isotherms for the main isotopes of fission and corrosion products.
- to estimate the rate of the adsorption and desorption of the fission products.

The methods used for the investigation of the surface adsorption were the quartz crystal microbalance (QCM), total X-ray fluorescence analysis (TXRF) and radiotracer technique. A combined quartz crystal microbalance - radiotracer and electrochemistry method and equipment was developed. This method is suitable for detecting simultaneously the adsorbed species ( $\beta$  - emitter), the

mass change (in microgram range) and the electrode potential variation at room temperature.

## Theses

1. According to the quartz crystal microbalance measurements the maximally adsorbed amount of the fission and corrosion products ions ( $\text{Cs}^+$ ,  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{I}^-$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Ni}^{2+}$  és  $\text{Fe}^{3+}$  and uranyl ion) – on both zirconium and steel surfaces – are in the range of the monolayer coverage calculated from the ionic radii and the geometry. The maximally adsorbed mass is independent of the temperature, in the investigated temperature range 20-60 °C. The Langmuir – Freundlich isotherm describes the experimental results adequately.

Maximal coverage can be attained by solute concentrations in the range of 3,6 - 37,4 mmol dm<sup>-3</sup> ; the saturation concentrations vary with the nature of the investigated ions and surfaces. The isotherms of the corrosion products reach maximum coverage at higher concentrations than those of the fission products. On stainless steel surfaces twice as high concentrations are required for maximum coverage than on zirconium surfaces.

2. By using a radiochemical tracer technique the investigated ions can be identified both on zirconium and steel surfaces. It was corroborated that the mass change measured by QCM is caused by the studied ions. Several elements of uncertainty result from the ex-situ nature of the method (oxidation, solution remains, partial dissolution of the adsorbed layer during rinsing etc.).

In general the divalent ions of the corrosion products saturate the surface at higher concentrations than the monovalent ions of the fission products. The mass change measured by QCM was found to be higher than

that observed by radiotracer technique. Beside ion adsorption, the QCM measures the water (in the hydration shell) and the co-adsorbed anions taking part in the accumulation on the surface, whereas the radiotracer technique detects only the traced ions.

3. It was demonstrated that the use of the total X-ray fluorescence analysis (TXRFA) is applicable for studies of the adsorbed layers. On zirconium covered quartz samples  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ni}^{2+}$  ions were measured as well as the co-adsorption of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{Ce}^{3+}$ ,  $\Gamma^-$  és  $\text{UO}_2^{2+}$  ions in the solution. The surface concentrations from the TXRF measurements in case of Fe and Co are much lower than the results of the QCM measurements. The difference might be originated from the heterogeneity of the ion distribution. QCM technique measures the mass change on the whole surface of the crystal, but in case of TXRF only a  $10\text{mm}^2$  portion of the crystal area is investigated.

4. Besides the equilibrium adsorption on a zirconium sample measured, a new method was developed and tested in a model system which combined the quartz crystal microbalance, the radiotracer and electrochemical techniques. This method is capable of detecting simultaneously the adsorbed species ( $\beta$  emitter), the mass change (in microgram range) and the electrode potential change. The main advantage of the method is its in-situ nature, in addition to the measuring of the mass change and the  $\beta$  detecting the metal surface, the crystal can be used as a working electrode for performing potential dependent measurements. The disadvantage of the method is that the radiation below 0,5 MeV energy is fully absorbed in the quartz therefore only certain  $\beta$  emitter ( $^{36}\text{Cl}$ ,  $^{90}\text{Sr}$  és  $^{32}\text{P}$ ) nuclides can be measured.

The method is suitable for studying the adsorption in the concentration range of  $10^{-6}$ - $10^{-4}$  mol dm $^{-3}$  below 1% surface coverage. Only estimated results

can be obtained in this concentration range by extrapolation from other methods.

5. The kinetics of the adsorption and desorption of the fission products ( $I^-$ ,  $Cs^+$ ,  $Ce^{3+}$ ,  $Ce^{4+}$  ions) and  $UO_2^{2+}$  ion can be described in terms of a simplified model. The rate constants of the adsorption are in the range of  $11 - 34 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and the empirical time constants are  $2,9-7,3 \text{ s}$  and  $1,5-3,5 \text{ s}$  for adsorption process, and for desorption respectively.

The  $Cs^+$ ,  $Ce^{3+}$ ,  $I^-$  és  $UO_2^{2+}$  ions adsorb reversibly onto the zirconium and steel surfaces: both adsorption and desorption are fast, the time constants are several seconds in the concentration range of  $10-20 \text{ mmol dm}^{-3}$ .  $Ce^{4+}$  ions adsorb quickly onto the zirconium surface but the desorption is very slow. During the time of the experiment (24hours) no measurable desorption could be detected.

### Publications from the topic of the thesis

1. R. Répánszki, Zs. Kerner, G. Nagy: Adsorption of fission products on stainless steel and zirconium, *Adsorption* (2007) **13**, Number 3, 201-207
2. R. Répánszki, Zs. Kerner: Kinetics of fission products accumulation on structural materials, *Journal of Radioanalytical and Nuclear Chemistry* (2011) **288**: 729-733
3. R. Répánszki, Zs. Kerner, G. Nagy: Adsorption of fission products on stainless steel and zirconium; IAEA Technical Meeting on Water chemistry of NPP's (2007), Moscow, Russia, Proceeding Book, p17
4. Répánszki Réka, Kerner Zsolt, Nagy Gábor: Hasadvány termékek és urán adszorpciója atomreaktorok szerkezeti anyagain; Őszi Radiokémiai Napok 2006, Siófok, Abstract Book, p28 (ISBN 978-963-9970-01-4)
5. R. Répánszki, Zs. Kerner, G. Nagy: Investigation of the adsorption of fission products on iron, stainless steel and Zr1%Nb by EQCM; 57th Annual

Meeting of the International Society of Electrochemistry 2006, Edinburgh, UK, Book of Abstracts, S8-P68

6. R. Répánszki, Zs. Kerner, G. Nagy: Adsorption of fission products on stainless steel and Zr, 59th Annual Meeting of the International Society of Electrochemistry 2008, Seville, Spain, Book of Abstracts, S03-P-047

### Further publications

- R. Székely, J. Dobránszky, Á. Horváth, R. Répánszki: Electrochemical study of welded aisi 304 and 904l stainless steels in seawater in view of corrosion, *Gépészet 2010*, (ISBN 978-963-313-007-0)
- R. Székely, R. Répánszki, A. Somogyi, Á. Horváth, J. Dobránszky: Electrochemical study of welded AISI 304 and 904l stainless steels in seawater in view of corrosion, *International Journal of Industrial Chemistry* (2010) **1**, No. 1, 52-60
- M. Gnahn, C. Müller, R. Répánszki, T. Pajkossy, D.M. Kolb: The interface between Au(100) and 1-butyl-3-methyl-imidazolium-hexafluorophosphate, *Physical Chemistry Chemical Physics* (2011) DOI: 10.1039/C1CP20562E