

## **LONG-TERM EFFECTS OF A CHEMICAL DECONTAMINATION PROCEDURE ON THE CORROSION STATE OF THE HEAT EXCHANGER TUBES OF STEAM GENERATORS**

ANDREA SZABÓ NAGY<sup>1</sup>, KÁLMÁN VARGA<sup>2</sup>, BERNADETT  
BAJA<sup>2</sup>, ZOLTÁN NÉMETH<sup>2</sup>, DEZSŐ ORAVETZ<sup>3</sup>, ZOLTÁN  
HOMONNAY<sup>4</sup>, ERNŐ KUZMANN<sup>4</sup>, JÁNOS SCHUNK<sup>5</sup>

<sup>1</sup>*Department of Physics and Chemistry, University of István Széchenyi, H-9026 Győr,  
Hungary (nszaboa@sze.hu)*

<sup>2</sup>*Institute of Environmental Engineering and Radiochemistry, University of Pannonia,  
H-8201 Veszprém, P. O. Box: 158, Hungary (vargakl@almos.vein.hu)*

<sup>3</sup>*Institute of Materials Engineering, University of Pannonia*

<sup>4</sup>*Institute of Chemistry, Eötvös Loránd University, H-1117 Budapest, Hungary*

<sup>5</sup>*Paks NPP Ltd., H-7031 Paks, P. O. Box: 71, Hungary*

---

**Abstract:** Our previous studies have revealed that a "hybrid" structure of the amorphous and crystalline phases is formed in the outermost surface region of the austenitic stainless steel tubes of steam generators (SGs) as an undesired consequence of the industrial application of the AP-CITROX (AP: alkaline permanganate; CITROX: citric and oxalic acid) decontamination technology. The formation of this mobile oxide-layer increased the amount of the corrosion products in the primary circuit significantly, resulting in magnetite deposition on fuel assemblies.

Owing to the fact that there is no investigation method available for the in-situ monitoring of the inner surfaces of heat exchanger tubes, a research project based on sampling as well as on ex-situ electrochemical and surface analytical measurements was elaborated. Within the frame of this project, comprehensive investigation of the general corrosion state and metallographic features of 36 stainless steel specimens, cut out from various locations of the 21 steam generators of the Paks NPP in the time period of 2000-2007 has been performed. The present work gives a brief overview on the general corrosion state of the heat exchanger tubes of SGs, concerning the long-term effects of the AP-CITROX procedure on the chemical composition and structure of the protective oxide-layer.

**Key words:** steam generators, decontamination, voltammetry, SEM-EDX, CEMS

---

### **1. Introduction**

In some Soviet-made VVER-type pressurized water reactors different versions of the so-called AP-CITROX method (AP: alkaline permanganate; CITROX: citric and oxalic acid) have been widely used for the chemical decontamination of the austenitic stainless steel piping of steam generators (SGs) (VARGA, 2004; VARGA *et al.*, 2001, 2002, 2004). During the time period of 1993-2001 chemical decontamination of 24 SGs in the reactor blocks 1-3 of the Paks NPP (Hungary) were carried out by a non-regenerative version of AP-CITROX technology, sometimes in 2 or 3 consecutive cycles. The applied version of the AP-CITROX procedure is an eight-step process,

including an oxidizing pre-treatment of the surface with alkaline potassium permanganate followed by washing with a concentrated mixture of citric and oxalic acids to remove the contaminated surface layer (VARGA *et al.*, 2001, 2002, 2004).

Our previous studies have revealed that a "hybrid" structure of the amorphous and crystalline phases is formed in the outermost surface region of the austenitic stainless steel tubes as an undesired consequence of the industrial application of the AP-CITROX technology (VARGA, 2004; VARGA *et al.*, 2004; SZABÓ *et al.*, 2006; RADÓ *et al.*, 2006; VARGA *et al.*, 2006; HOMONNAY *et al.*, 2006). The formation of this mobile oxide-layer increased the amount of the corrosion products in the primary circuit significantly, resulting in magnetite deposition on fuel assemblies. As deposits blocked the cooling channels, the flow rate of water coolant through the reactor core decreased. Consequently, the power capacity of three nuclear reactor units had to be reduced, and full core fuel replacement became necessary.

In the light of the above events, the present work gives a brief overview on the general corrosion state of the heat exchanger tubes of SGs, concerning the long-term effects of the AP-CITROX procedure on the chemical composition and structure of the protective oxide-layer. Owing to the fact that there is no investigation method available for the in-situ monitoring of the inner and outer surfaces of heat exchanger tubes, a research project based on sampling as well as on ex-situ electrochemical and surface analytical measurements was elaborated. Within the frame of this project, comprehensive investigation of the general corrosion state and metallographic features of 36 stainless steel specimens, cut out from various locations of the 21 steam generators of the Paks NPP in the time period of 2000-2007 has been performed. In this paper we report some voltammetric, SEM-EDX, and CEMS results that reveal the corrosion properties, morphology and chemical composition of the inner surfaces of heat exchanger tubes.

## 2. Materials and methods

The experiments have been performed on 36 austenitic stainless steel specimens (type: 08X18H10T (GOST 5632-61) which corresponds to AISI 321 and DIN 1.4541; outer diameter: 16 mm, average wall thickness: 1.6 mm) originating from different SGs of the Paks NPP. The main characteristics of the specimens obtained from the same SGs at various sampling date are given in Table 1. The surface decontamination procedure of the heat exchanger tubes was carried out at Paks NPP according to a non-regenerative version of the AP-CITROX technology (VARGA *et al.*, 2001, 2002, 2004).

The passivity of the tube samples was studied by potentiostatic polarization method. The experiments were carried out by the means of a VoltaLab 40 (RADIOMETER) type electrochemical measuring system controlled by PC. The measurements were carried out in boric acid solution ( $c=12 \text{ g}\cdot\text{dm}^{-3}$ ) in argon gas atmosphere (99.999 v/v % Ar). The schematic of the measuring system, the detailed experimental procedure and the determination of the corrosion parameters have been described in our earlier papers (VARGA *et al.*, 2001; SZABÓ *et al.*, 2006; VARGA *et al.*, 2006; HOMONNAY *et al.*, 2006).

The morphology and chemical composition of the oxide layer developed on the inner surfaces of the 36 stainless steel specimens were studied by scanning electron microscopy (SEM), equipped with an energy dispersive X-ray microanalyzer (EDX) (Type: JEOL JSM-50A, controlled with Röntec EDR 288 software). In addition, the metallographic cross sections of tube specimens were also studied (SZABÓ *et al.*, 2006; RADÓ *et al.*, 2006; VARGA *et al.*, 2006; HOMONNAY *et al.*, 2006).

In order to determine the phase composition of the surface oxide layers, the samples were measured by Conversion Electron Mössbauer Spectroscopy (CEMS). The CEMS spectra were recorded at room temperature with a conventional Mössbauer spectrometer (Wissel) in constant acceleration mode and a  $^{57}\text{Co}(\text{Rh})$  source provided the  $\gamma$ -rays (SZABÓ *et al.*, 2006; VARGA *et al.*, 2006; HOMONNAY *et al.*, 2006).

Table 1. Characteristic features of tube samples obtained from the same steam generators at various sampling date.

Number of SG sample	Year of decontamination	Time period between the last decontamination and the sampling [year]	Year of sampling	Year of investigation
I/1	1996, 1997	4	2001	2001
I/2	1996, 1997, 2001	4	2005	2005
II/1	1996	1	1997	2003
II/2	1996	4	2000	2000
II/3	1996, 2001	4	2005	2005
III/1	1999, 2001	1	2002	2002
III/2	1999, 2001	3	2004	2004
III/3	1999, 2001	5	2006	2006
IV/1	2001	1	2002	2002
IV/2	2001	5	2006	2006
V/1	2001	0	2001	2001
V/2	2001	4	2005	2005
VI/1	1993	7	2000	2000
VI/2	1993, 2001	3	2004	2004

### 3. Results and discussion

#### 3.1 General corrosion state and morphology

As illustration, potentiostatic polarization curves measured in boric acid solution at the inner surface of the stainless steel specimens cut out from the same steam generators of the Paks NPP at various sampling date are shown in Figs. 1-2. As may be seen in Figs. 1-2, the inner surfaces of the samples have a passive character in a wide potential interval next to the corrosion potential. The average corrosion rates for the samples, independently of the time period spent between the last decontamination and the sampling are very low ( $v_c \leq 3.5 \mu\text{m}/\text{year}$ ). The measured corrosion rates are as low as that of the inactive reference sample and even better than the literature data which were measured for the stainless steels type 08X18H10T and AISI 321 in aqueous solutions (0.3 - 4  $\mu\text{m}/\text{year}$ ) (GERASZIMOV and MONAHOV, 1991; LISTER 2003, and references therein). The results imply that the average corrosion

rate of decontaminated steel surfaces in the long run exhibits favorable trend under normal operation conditions of VVER-type nuclear reactor.

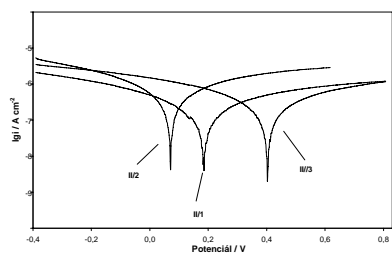


Fig. 1.

Potentiostatic polarization curves measured at the inner surface of the samples No. II in boric acid solution ( $c = 12 \text{ g}\cdot\text{dm}^{-3}$ ). Scan rate:  $10 \text{ mV}\cdot\text{min}^{-1}$ .

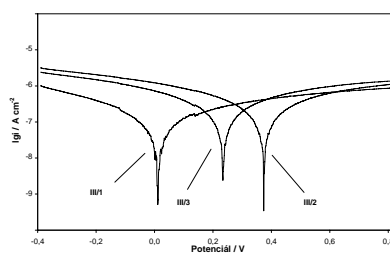


Fig. 2.

Potentiostatic polarization curves measured at the inner surface of the samples No. III in boric acid solution ( $c = 12 \text{ g}\cdot\text{dm}^{-3}$ ). Scan rate:  $10 \text{ mV}\cdot\text{min}^{-1}$ .

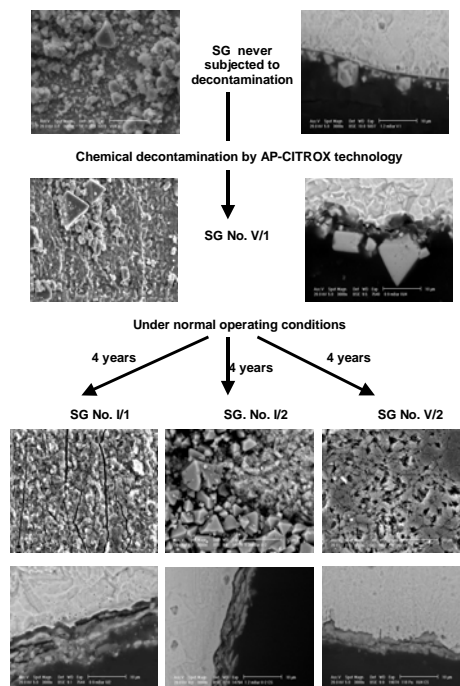
The morphology and chemical composition of the inner surfaces of the specimens were studied by SEM-EDX method. Some typical SEM micrographs of the steel samples studied are shown in Fig. 3. On the surfaces of samples never-decontaminated a thin film of the grown-on oxides with excellent protective character can be detected. Cracks in these oxide-films can not be identified; however, large amounts of less-adherent crystalline phases (presumably magnetite, hematite and non-stoichiometric mixed oxide of spinel structure) are found on the top of the grown-on oxide-layer. It is of special interest to note that some large crystals can be observed sparsely on the surface of the samples decontaminated immediately before the cutting procedure, too. The protective oxide-layers formed on the surfaces of the samples decontaminated a few (3-4) years before the sampling are compact, thick (up to  $11 \mu\text{m}$ ), and contain many cracks and scattered deep failures. The surface region exhibits amorphous character and are rich in chromium and nickel.

### 3.2 Phase analysis of the surface oxide-layers

Due to the absorption of the conversion electrons, information can be obtained from the  $\sim 300 \text{ nm}$  thick layer of the sample surfaces. The percent rates refer to the iron content involved in the indicated phases relative to the total iron content of the sample detectable by the conversion electrons.

On analyzing the CEMS spectra it has become obvious that a common phase on the inner surface of all tube specimens is the amorphous iron-hydroxide ( $\text{Fe}(\text{OH})_3$  and/or  $\text{FeO}(\text{OH})$ ). Its dominance is most characteristic for the decontaminated samples, especially for those steel tubes which were decontaminated by the AP-CITROX procedure a few years before the sampling. At the same time, it is difficult to understand the slight amount of amorphous  $\text{Fe}(\text{OH})_3$  detected on the samples never-decontaminated. This conspicuous oxide-layer may most likely be formed in either the transient and shut-down periods of the reactor operation or under the storage conditions of the steel specimens (as a consequence of the humid air).

In accordance with the literature data (see e.g. SZABÓ *et al.*, 2006; VARGA *et al.*, 2006 and references cited therein), magnetite and/or hematite are dominant on the inner surfaces of samples that were never subjected to decontamination. Magnetite is represented by two sextets in the Mössbauer spectra due to two different cationic sites for iron in the inverse spinel structure, while hematite can be described with one sextet only. The Mössbauer parameters obtained for these phases (especially for magnetite) were slightly different from the literature data on the pure compounds, which can be attributed to the effect of Cr- and Ni-substitution. It is especially noteworthy that the approximate intensity ratio of the two sextets of magnetite is normally  $I_H:I_L = 1:2$ , where  $I_H$  is the intensity of the sextet with higher magnetic field (representing  $Fe^{3+}$  at the tetrahedral site of the unit cell of magnetite  $Fe^{3+}_{tet}(Fe^{3+}Fe^{2+})_{oct}O_4$ ) and  $I_L$  is the intensity of the sextet with lower magnetic field (representing  $Fe^{3+}$  and  $Fe^{2+}$  coupled by rapid electron hopping at the octahedral site), but we have found in our samples roughly the opposite ratio. Since it is well known that  $Cr^{3+}$  and  $Ni^{2+}$  is ready to substitute for iron at the octahedral site, it is logical to assume such substitution in our case, on the surface of a Cr-Ni-steel. A formal calculation results in a possible composition of  $Fe^{3+}_{tet}(Fe^{3+}_{1/4}Cr^{3+}_{3/4}Fe^{2+}_{1/4}Ni^{2+}_{3/4})_{oct}O_4$  for  $I_H:I_L = 2:1$ .



**Fig. 3.** The long-term effects of the AP-CITROX procedure on the surface structure and morphology of the heat exchanger tubes of SGs.

It is important to return to the detection efficiency of the different phases by CEMS. Since it is experimentally demonstrated (SZABÓ *et al.*, 2006; VARGA *et al.*,

2006) that, as a tendency, the spinel phases (substituted magnetite) directly cover the bulk steel, and amorphous  $\text{Fe}(\text{OH})_3$  may be formed only on the outermost surface; the amount of the former is underestimated, while that of the latter is overestimated. The relative amount of the spinel phase can be even further reduced (may become practically invisible at the statistics of the particular Mössbauer spectrum) if the substitution of Fe by Cr and Ni is very significant.

#### 4. Conclusions

Within the frame of a comprehensive program to qualify the general corrosion state of heat exchanger tubes, corrosion and metallographic features of 36 specimens originating from different SGs of the Paks NPP were studied by electrochemical (voltammetry) and surface analyzing (SEM-EDX, CEMS) methods. Despite the limited number of tube samples, some general conclusions can be drawn.

Some adverse effects (general attack, formation of “hybrid” layer with accelerated corrosion rate and greater mobility) have been detected promptly after applying the AP-CITROX procedure. Process restrictions and modifications to minimize corrosion damages should be defined, and there is ample data available now for utilities to select a CITROX based process for particular application. It is, however, of special importance to highlight that significant beneficial change in the corrosion properties, mobility and chemical composition of the inner oxide layers of heat exchanger tubes can be observed in the time period of 2000-2007, as a consequence of the normal operation of the VVER type reactors.

#### Acknowledgements

This work was supported by the Paks NPP Co. Ltd (Paks, Hungary) and the Hungarian Science Foundation (Grant No. T047219).

#### References

- GERASZIMOV V. V., MONAHOV Sz.: *Materiali Jadernoj Techniki*, Atomizdat, Moskva, 1981. (Hungarian translation).
- HOMONNAY, Z., KUZMANN, E., STICHLAUTNER, S., VARGA, K., NÉMETH, Z., SZABÓ, A., RADÓ, K., MAKÓ, K. É., KÖVÉR, L., CSERNY, I., VARGA, D., TÓTH, J., SCHUNK, J., TILKY, P., PATEK, G., OSZVALD, F.: Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators. Part II. Chemical composition and structure of tube surfaces. *J. Nucl. Mater.*, 348, 2006, 191-204.
- LISTER, D. H.: Some aspects of corrosion in cooling water systems and their effects on corrosion product transport. *Proceedings of the EUROCORR 2003*, Budapest, Hungary, 28 September – 2 October, 2003.
- RADÓ, K., NÉMETH, Z., VARGA, K., SCHUNK, J., KÖRÖSI, F.: Fundamental issues of the effective decontamination of the steam generators of Paks NPP. *J. Radioanal. Nucl. Chem.*, 268(2), 2006, 313-322.

- SZABÓ, A., VARGA, K., NÉMETH, Z., RADÓ, K., ORAVETZ, D., MAKÓ, K. É., HOMONNAY, Z., KUZMANN, E., TILKY, P., SCHUNK, J., PATEK, G.: Effect of a chemical decontamination procedure on the corrosion state of the heat exchanger tubes of steam generators. *Corrosion Sci.*, 48, 2006, 2727-2749.
- VARGA, K.: The role of interfacial phenomena in the contamination and decontamination of nuclear reactors. In: *Radiotracer Studies of Interfaces* (Ed. by G. Horányi), Interface Science and Technology, Elsevier B.V., Amsterdam, 2004, Vol. 3, 313-358.
- VARGA, K., NÉMETH, Z., SOMLAI, J., VARGA, I., SZÁNTHÓ, R., BORSZÉKI, J., HALMOS, P., SCHUNK, J., TILKY, P.: Hydrodynamics of the effectiveness of the AP-CITROX decontamination technology. *J. Radioanal. Nucl. Chem.*, 254(3), 2002, 589-596.
- VARGA, K., BARADLAI, P., HIRSCHBERG, G., NÉMETH, Z., ORAVETZ, D., SCHUNK, J., TILKY, P.: Corrosion behaviour of stainless steel surfaces formed upon chemical decontamination. *Electrochim. Acta*, 46, 2001, 3783-3790.
- VARGA, K., NÉMETH, Z., SZABÓ, A., RADÓ, K., ORAVETZ, D., MAKÓ, K. É., HOMONNAY, Z., KUZMANN, E., STICHLAUTNER, S., TILKY, P., SCHUNK, J., OSZVALD, F., PATEK, G.: Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators. *Proceedings of the WANO-MC Workshop: "Experiences and techniques of SG Decontamination in VVER Plants"*, Paks NPP, Paks, Hungary, April 5-9, 2004.
- VARGA, K., NÉMETH, Z., HOMONNAY, Z., SZABÓ, A., RADÓ, K., ORAVETZ, D., SCHUNK, J., TILKY, P., OSZVALD, F.: Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators. Part I. General corrosion state and morphology. *J. Nucl. Mater.*, 348, 2006, 181-190.