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ASSESSMENT OF SOME IMPURITIES EFFECT ON THE CANDU STEAM GENERATOR TUBING CORROSION

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When water is converted to steam, the non-volatile impurities are left behind. As a result, the concentrations of different impurities in the water from the bulk steam generator are considerably higher. Nevertheless, the concentrations of corrosive impurities are still low and therefore the bulk water is not significantly aggressive towards steam generator materials. The purpose of this paper consists in assessment of corrosion behavior of the tubing material (Incoloy 800) at the normal secondary circuit parameters.

The testing environment was the demineralized water containing silicon compounds, sulfates and chlorides at pH=9.5 regulated with morpholine and cyclohexylamine (All Volatile Treatment – AVT). The paper presents the results of metallographic examinations and the results of electrochemical measurements. The experimental results allowed us to establish the contribution of the impurities concentration on the evolution of the corrosion processes.

Keywords: Steam generator tubing, Incoloy 800, corrosion, water chemistry, impurities concentration

1. Introduction

The concentration of the impurities and deposits developed on the steam generator structural materials can cause several types of corrosion. The failure of the steam generator as a result of tubing and tubesheet degradation by corrosion has been a major cause of Pressurized Heavy Water Reactor (PHWR) plant unavailability. Steam generator problems have caused major economic losses in terms of lost electricity production through forced unit outages and, in cases of extreme damage, as additional direct cost for large-scale repair or replacement of steam generators. Steam generator materials (especially the tubing material) are susceptible to failure by a variety of mechanisms, the most majority of which are related to corrosion in the presence of deposits containing aggressive impurities.

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The feedwater that enters the steam generators under normal operating conditions is extremely pure, but nevertheless contains low levels (generally in the μg/l concentration range) of impurities such as iron, chloride, sulphate, silicate, etc.

The excellent performance of CANDU steam generators can be attributed, in part, to their design and performance characteristics, which typically involve higher recirculation ratios and lower heat fluxes and temperatures than other PWR steam generator.

Silicon compounds are abundant both in the steam generator deposits removed from operating plants and in the hideout return analyses performed during plant operation. High concentration of SiO_2 in the crevices may react with the impurities forming different polymerized species of silicates that show retrograde solubility at the operating temperature of steam generator, which, in turn, precipitate, leaving free SiO_2 and/or impurities in the solution.
In the case of the low fluid flow rate or at the change of flow direction it generates the deposits containing silicon compounds.

The effect of the silicon compounds on the behavior of the steam generator materials has never been considered adequately. The information available is contradictory, and it is possible to encounter in the literature old results that indicate an inhibition or an aggressive effect of silicon compounds in caustic environment. Lack of understanding of the role played by silicon compounds may be caused by the complexity of their chemistry which complicates laboratory testing and interpretation of the analyses of the deposits.

The inhibition effect of silicon compounds was shown in the corrosion tests. Under all conditions of corrosion tests, the material of the steam generator tubing (Incoloy 800) demonstrates a corrosion resistance when compared to its behavior in other impurities (NaCl, Na_2SO_4). The information obtained from this work was not sufficient to appreciate if the corrosion behavior observed in the solutions containing silicon compounds was caused by the incorporation of silicon in the oxide layer, making the latter more protective or simply that it had a barrier effect preventing contact between the solution and the surface of the material. Supplementary it is important to consider the significant synergistic effect of the mixture of impurities like SiO_2, NaCl, Na_2SO_4, [1÷17]. The present work studies the effect of silicon compounds, such as silica (SiO_2), sodium sulphate (Na_2SO_4) and natrium chloride (NaCl) used together, on the corrosion susceptibility of steam generator tubing material, Incoloy 800.

2. Experimental

The corrosion experiments included in the present paper have been carried out by autoclaving at the specific parameters for the secondary circuit of the

CANDU steam generator: temperature 260ºC, pressure 5.1MPa. The preoxided samples for 10 days were from Incoloy 800, the structural material of the steam generator tubing. The chemical composition of Incoloy-800 in percent weight is: C=0.02%, Mn=0.64%, Si=0.49%, S=0.01%, Ni=33.40%, Cr=21.90%, Cu=0.01%, Al=0.24%, Ti=0.41% and Fe=42.88%. The specimens used were from Incoloy-800, steam generator tube, (15.9mm outside diameter and 1.13mm wall thickness) which was sectioned on the diameter into 15 mm long pieces polished with grit papers and cleaned ultrasonically.

The testing solutions, with pH 9.5 regulated with morpholine and cyclohexylamine had the following compositions:

I. 1g/l NaCl+1g/l Na_2SO_4+1g/l SiO_2

II. 2g/l NaCl+2g/l Na_2SO_4+2g/l SiO_2

III. 5g/l NaCl+5g/l Na_2SO_4+5g/l SiO_2

The water pH and conductivity were measured with Multi–Channel Analyzer CONSORT C835. Experimental results included: optical microscopically analyses, electrochemical measurements (potentiodynamic and Electrochemical Impedance Spectroscopy - EIS) and Scanning Electron Microscopy - SEM. The surfaces morphologies and the cross sections of the corrosion samples were analyzed with the optical microscope OLYMPUS GX 71. The corrosion kinetic was additionally evaluated by potentiodynamic measurements using a PAR 2273 overall electrochemical potentiostat – galvanostat. Samples were examined by SEM without any preparation. SEM was performed at 30kV on TESCAN VEGA II LMU using Everhart – Tornley secondary electron detector. Energy Dispersive Spectrometry (EDS) was used to distinguish oxides particles with a Bruker Si (Li) detector coupled at SEM.

3. Results and Discussions

3.1 Incoloy 800 tested in solution containing 1g/l NaCl+1g/l Na_2SO_4+1g/l SiO_2 [I]

The sample of Incoloy 800 preoxided for 10 days, after testing for 30 days in the solution I (Fig.1a) developed on the surface a layer with a coarse granulation probably due to the previously formed oxide layer that creates the conditions for a good adhesion, but at the same time it contributes to the formation of grooves and even to the diffusion of some elements from the base metal to the superficial layer. The initial superficial layer having a thickness of 1μm is presented along with the morphology of the surface in Fig. 1b) and 1c). The mixed layer containing oxides, silicon and sodium compounds, manages to maintain its continuity.

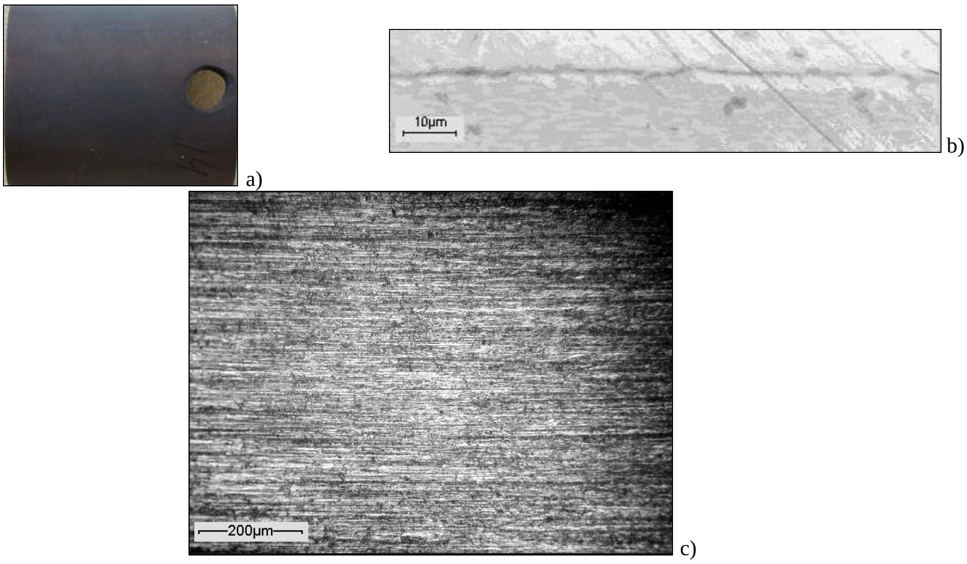


Fig.1. Aspect of the sample (a), superficial layer (b) and surface morphology (c) for the Incoloy 800 sample preoxided 10 days and then tested 30 days in solution I

From the surface morphology it is observed that the initial formed layer influences the development of non-uniform deposits both in thickness and in composition. There are portions where the surface remains only with the initially formed layer during the pre-oxidation period and portions in which it randomly forms appreciable deposits.

3.2 Incoloy 800 tested in solution containing 2g/l NaCl+2g/l Na_2SO_4+2g/l SiO_2 [II]

The Incoloy 800 sample preoxided for 10 days, tested 30 days in solution II shows on the surface a layer with a coarse granulation due to the fact that the previously formed oxide layer creates the conditions of a good adhesion, but at the same time it contributes to the formation of grooves and even to the diffusion of some elements from the base metal to the superficial layer. The formed superficial layer having an average thickness of 2µm is shown along with the surface morphology in Fig.2 b) and c). The mixed layer composed of oxides and silicon and sodium compounds has a higher thickness than in the previous case and manages to maintain its continuity. From the surface morphology it is observed that the initial formed layer influences the formation of non-uniform deposits both in thickness and in composition.

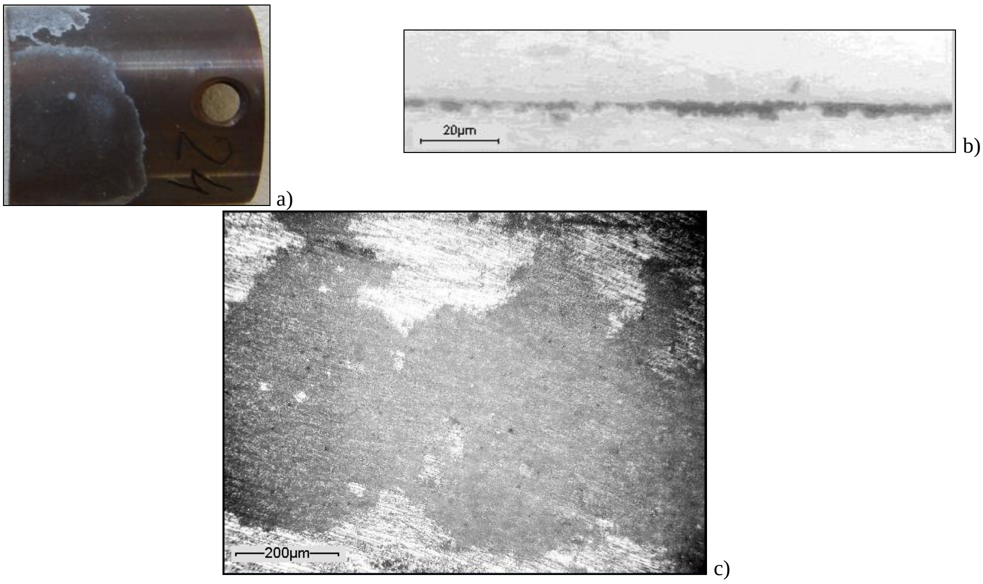


Fig.2. Aspect of the sample (a), superficial layer (b) and surface morphology (c) for the Incoloy 800 sample preoxided 10 days and then tested 30 days in solution II

There are portions where the surface remains only with the initially formed layer during the preoxidation period and portions in which randomly deposits are formed.

3.3 Incoloy 800 tested in solution containing 5g/l NaCl+5g/l Na_2SO_4+5g/l SiO_2 [III]

For the sample of Incoloy 800 preoxided for 10 days and then tested 30 days in the testing solution III, the aspect of the surface is strongly influenced by the presence of impurities in the testing solution. Fig. 3 b) and c), show the aspect of the superficial layer and surface morphology and it can be observed that the thickness of the layer is less than 3μm.

From the morphology of the surface it is observed that the initial formed layer influences the formation of non-uniform deposits both in thickness and in composition. There are portions where the surface remains only with the initially formed layer during the pre-oxidation period and the portions in which randomly deposits are formed.

Besides the examination by metallographic method, the results of which were discussed above, the electrochemical methods were also used in the pursuit of through investigations of the corrosion of the steam generator tubing material in the presence of aqueous solution containing chlorides, sulphates and silicon compounds at the chemical parameters specific to the steam generator secondary side. The samples having the same initial states (preoxided for 10 days) and tested in solution I for 10 days, 20 days and 30 days were tested by potentiodynamic and Electrochemical Impedance Spectroscopy method.

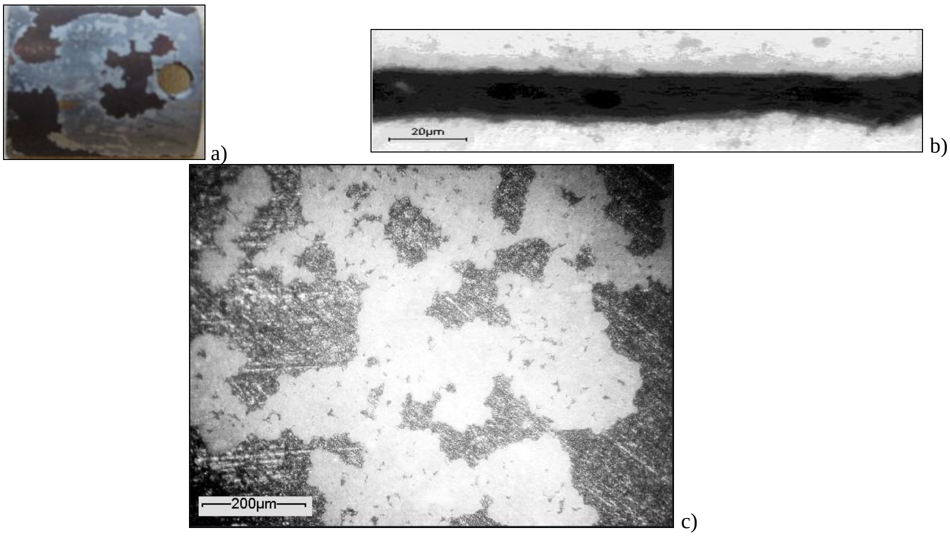


Fig.3. Aspect of the sample (a), superficial layer (b) and surface morphology (c) for the Incoloy 800 sample preoxided 10 days and then tested 30 days in solution III

Analyzing the potentiodynamic curves presented in Fig.4, can be seen that the corrosion potential for the sample I.30 has more negatively values and in the same time, the active zone of this curve is situated to the more anodic values of the corrosion currents.

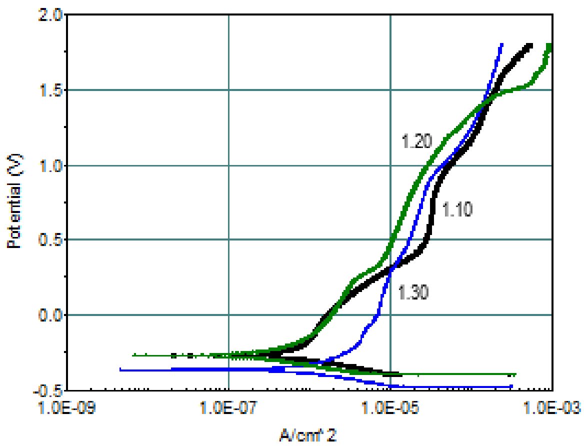


Fig.4. Potentiodynamic curves for the Incoloy 800 samples in demineralized water, pH=9.5 (AVT), initially preoxided 10 days and then tested in solution I 10 days (1.10) and 20 days (1.20) and 30 days (1.30)

The corrosion rates measured using Tafel slopes and polarization resistance (Rp) are presented in the Table1.

Table 1

Electrochemical parameters for Incoloy 800 sample initially preoxided 10 days and then tested in solution I 10 days (1) and 20 days (2) and 30 days (3)

	Tafel slopes	Rp
1	Vcor=9.7x10^{-4}mm/y	Vcor=5.8x10^{-4}mm/y
	Ecor=-254.4mV	Ecor=-205.0mV
	I=3.56x10^{-1}µA	I=2.13x10^{-1}µA
		Rp=102042.0ω
2	Vcor=6.9x10^{-4}mm/y	Vcor=5.7x10^{-4}mm/y
	Ecor=-257.0mV	Ecor=-211.4mV
	I=2.55x10^{-1}µA	I=2.09x10^{-1}µA
		Rp=103687.0ω
3	Vcor=1.74x10^{-3}mm/y	Vcor=1.3x10^{-3}mm/y
	Ecor=-353.04mV	Ecor=-326.3mV
	I=6.38x10^{-1}µA	I=1.79x10^{-1}µA
		Rp=45341.4ω

In Fig.5 are compared Bode curves for samples, which are representations of the impedance (in absolute value) versus frequency. In diagram are observed the highest impedance value for the sample preoxided 10 days which is a feature of the oxide layer type (protective) formed on the samples surface. Because the impedance | Z | is directly proportional to the strength of the film and inversely proportional to its capacity, a high value of impedance indicates a good resistance to corrosion. For the other samples, the impedance values decreased with the testing time in the solution I.

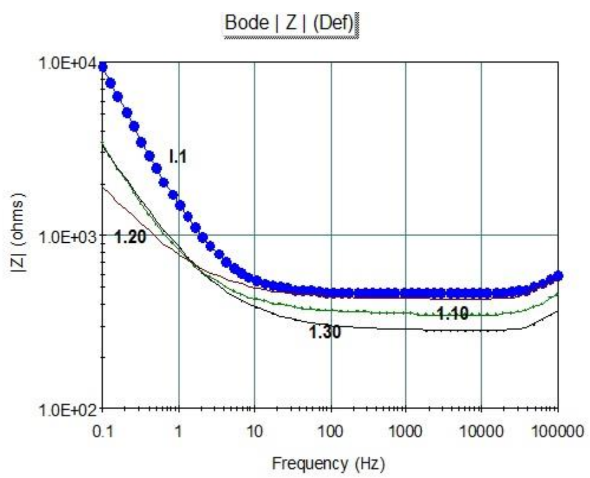


Fig.5. Bode curves for Incoloy 800 sample initially preoxided 10 days (I.1) and then tested in solution I for 10 days (1.10), 20 days (1.20) and 30 days (1.30)

In Fig. 6 are presented the phase angles recorded for the same samples. The values of the phase angles within the range 40-75^0, are lower than 90^0 (which is the specific value of the total capacitive film) which lead to the conclusion that, there are some local inhomogeneities of the oxide layers.

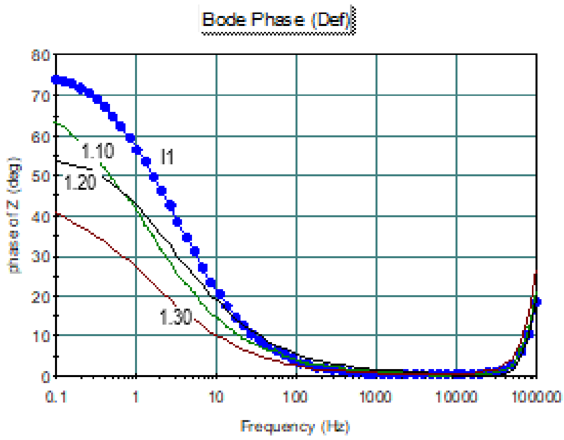


Fig.6. Angle phase curves for Incoloy 800 sample initially preoxided 10 days (I.1) and then tested in solution I 10 days (1.10) and 20 days (1.20) and 30 days (1.30)

The Nyquist curves in EIS analysis can give information about the effects of ohmic resistance (solution resistance) and polarization resistance (corrosion resistance). Diameters of semicircles described by Nyquist curves represent the polarization resistance values. As can be seen in the Fig.7 the preoxided sample has higher polarization resistance (of the order of 10^4 Ω) indicating a protective oxide layer.

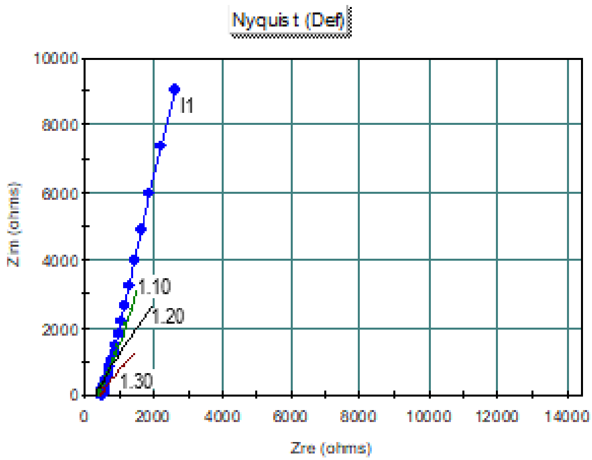


Fig.7. Nyquist curves for Incoloy 800 sample initially preoxided 10 days (I10) and then tested in solution I 10 days (1.10) and 20 days (1.20) and 30 days (1.30)

The diameters of Nyquist curves ploted for samples tested in solution I decreased with the testing time, so the sample tested for 30 days even has a thicker oxide layer, this can be unprotective.

The surface of Incoloy 800 samples initially preoxided 10 days and then tested 10 days in solution I (1.10) was examined by Scanning Electron Microscopy. A scanning electron image from sample surface is displayed in Fig.8 and Fig.9. The image from Fig.8 reveals groups formed from very small particles. These particles prove that the silicon compounds are present on the surface. At a higher magnify (Fig.9) it can be observed that the groups of crystallites are made of needles having the dimensions below 2µm. The silicon compounds are also revealed on the surface in EDS maps from Fig.10 ÷ Fig.13. The maps of silicon compounds from Fig.10 put in evidence same groups like SEM image, and Fig.14 shows the EDS spectrum and quantitative composition of the layer formed on surface sample 1.10.

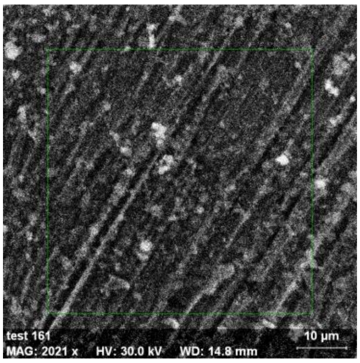


Fig.8. SEM images of 1.10 sample surface

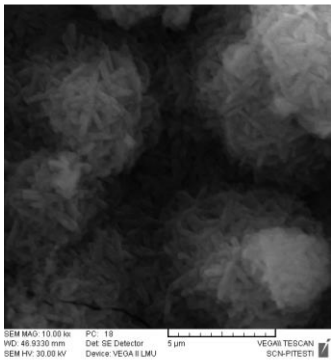


Fig.9. SEM images of 1.10 sample surface

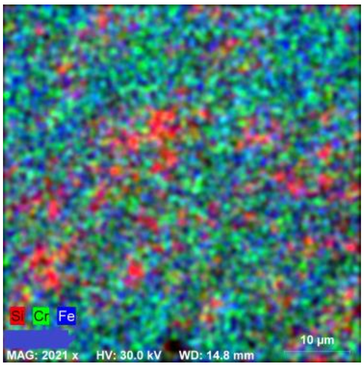


Fig.10. EDS mapping for Si, Cr and Fe

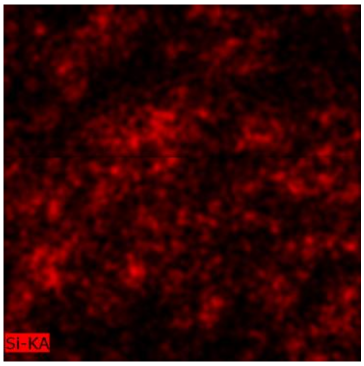


Fig.11. EDS mapping for Si - sample 1.10

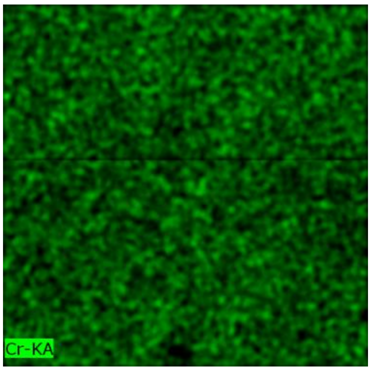


Fig.12. EDS mapping for Cr - sample 1.10

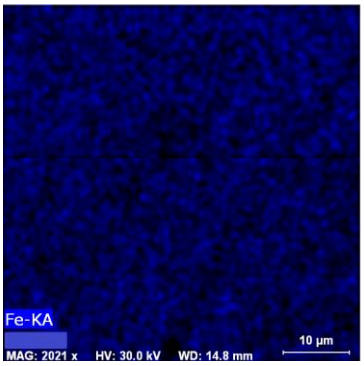
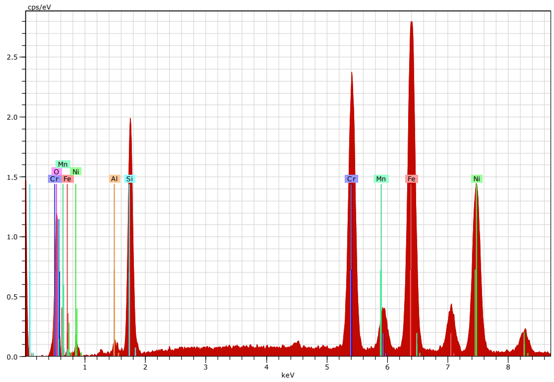
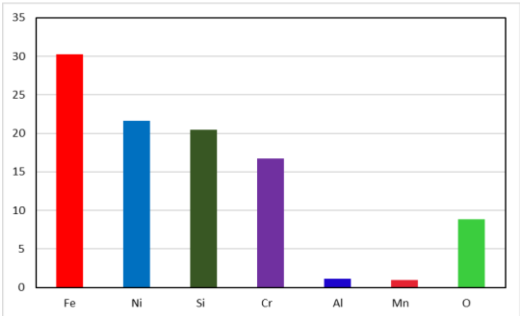


Fig.13. EDS mapping for Fe - sample 1.10



a)



b)

Elements	Masic %
Si	33.01
O	25.48
Fe	19.01
Ni	12.06
Cr	10.10
Mn	0.43

c)

Fig.14. EDS spectrum (a) and quantitative composition (b and c) of the layer formed on surface sample 1.10

4. Conclusions

By optical microscopy the thickness layers of oxides, sodium and silicon compounds are determined for samples preoxided 10 days and then tested for 30 days in solution I, II or III have the next values: 1µm, 2µm and 3µm respectively.

The corrosion behavior of samples after they were exposed to solutions containing a complex combination of impurities determined by electrochemical measurements performed in an aqueous medium with parameters specific to the secondary steam generator circuit highlights the fact that the most protective layer is the one obtained by pre-oxidation and the least protective is the layer remaining after 30 days of testing in solution I. The tests from the experimental program were made in terms of high aggressiveness testing solutions that can be found rarely in the steam generator after long periods of operation, the main aim being to enable specialists to judge this type of processes when the technical expertise of the components extracted from equipment operated in an NPP is necessary.

The research activity in this field will continue through the experimental study of the synergistic effect of several types of impurities (Si, Pb, and Na) on the corrosion of the main structural materials of the steam generator. Another direction of research would be to identify the factors that contribute to the consolidation of deposits on the CANDU steam generator tubesheet.

R E F E R E N C E S

[1]. *N. Fujita, C. Matsuura and K. Ishigure,* "Encyclopedia of Polymer Science and Engineering, 'Silicates'", 2nd Ed., 15, 178, 1988.

[2]. *M. Navas, D. Gómez-Briceño, M. García-Mazario and A. R. Mcllree,* "Effect of Silicon Compounds on Stress Corrosion Cracking of Alloy 600 in Caustic Solutions", Corrosion, Vol. 55, No. 7, 674-685, 1999.

[3]. *D. Lucan,* Diminuarea coroziunii prin optimizarea chimiei apei in echipamentele de transfer termic (Corrosion Mitigation by Water Chemistry Optimization in Heat Transfer Equipment), Editura Universitatii din Pitesti, Pitesti, Romania, 2012.

[4]. *D. Lucan,* "Corrosion of the Secondary Side Steam Generator in the Presence of Impurities", in Nuclear Power Plants (Book), Editors: George Petridis and Dimitrios Nicolau, Nova Science Publishing, New York, Series: Nuclear Materials and Disaster Research Physics, Research and Technology, ISBN: 978-1-61470-150-7, 197-226, 2012.

[5]. *D. Lucan,* "Degradations of Incoloy 800 Steam Generator Tubing" in Steam Generator Systems: Operational Reliability and Efficiency (Book), edited by Valentin Uchanin, ISBN 978-953-307-303-3, InTech - Open Access Publisher - Viena, Austria, 2-20, 2011.

[6]. *D. Lucan,* Procese specifice generatorului de abur (Steam Generators's Specific Processes), ISBN 978-973-47-0813-0, Paralela 45, Pitesti, Romania, 2009.

[7]. *D. Lucan, L. Velciu, M. Mihalache, A. Dinu, M. Fulger and D. Astefanesei,* "Corrosion Kinetics of the Carbon Steel SA 508 Cl.2 in High Pressure and Temperature Water with Ph 9.5", Journal of Nuclear Research and Development, (1), 27-34, 2011.

[8]. *D. Lucan,* "Behaviour of the Steam Generator Tubing in Water with Different pH Values", Nuclear Engineering and Design, 241-4, 1172-1176, 2011.

[9]. *D. Lucan, L. Velciu, A. Dinu and M. Pantiru,* “Analysis and Diagnosis of the Corroded Tubes from Steam Generator”, International Symposium for Nuclear Energy, SIEN, Bucharest, Romania, CD-ROM Proceedings, 2013.

[10]. *D. Lucan and L. Velciu,* “How to Estimate the Impurities Concentration into Crevices and their Effects on the Steam Generator Integrity”, Proceedings of the 6-th Annual International Conference on Sustainable Development through Nuclear Research and Education, NUCLEAR 2013, Pitesti, Romania, 2013.

[11]. *D. Lucan and L. Velciu,* “Experimental Research Concerning the Degradations of CANDU Steam Generator”, Proceedings of the 8-th Annual International Conference on Sustainable Development through Nuclear Research and Education, NUCLEAR 2015, Pitesti, Romania, 2015.

[12]. *D. Lucan, L. Velciu and D. Petrescu,* “Factors Affecting Deposits Consolidation into CANDU Steam Generator Secondary Circuit”, Proceedings of the 9-th Annual International Conference on Sustainable Development through Nuclear Research and Education, NUCLEAR 2016, Pitesti, Romania, 2016.

[13]. *D. Lucan, L. Velciu and Ghe. Jinescu* “The Synergistic Impurities Effect on the CANDU Steam Generator Corrosion”, Rev. Chim., 67 - 4, 603-608, 2016.

[14]. *D. Lucan and Ghe. Jinescu* “Corrosion Analysis and Diagnosis – Useful Tools for Plant Life Management and Long-Term Operation Programmes in Nuclear Power Plant”, Journal of Engineering Sciences and Innovation, 2 - 3, 80-92, 2017.

[15]. *D. Lucan,* “CANDU Steam Generator Corrosion Due to the Impurities Concentration and Deposition”, in Steam Generators: Design, Types and Applications (Book), Editor: Clayson Schellenberg, Nova Science Publishing, New York, Series: Energy Science, Engineering and Technology, ISBN: 978-1-53612-510-8, 197-226, 2017.

[16]. *D. Lucan,* Factori care contribuie la degradarea materialelor structural ale generatorului de abur (Factors Contributing to the Degradation of the Steam Generator’s Structural Materials), Editura SITECH, Craiova, 2018.

[17]. *D. Lucan Ghe. Jinescu A. Dinu, M. Stanciulescu and M. Mihalache* “CANDU Steam Generator Secondary Fouling Characteristics”, Journal of Engineering Sciences and Innovation, Vol.4, Iss.1, 31-92, 2019.