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CANDU steam generator secondary side fouling characteristics

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Abstract. In the process of the equipment degradation in the secondary circuit of a CANDU plant an essential role is played by the formation, transportation and deposition of corrosion products and impurities. Minimizing the presence of these corrosion products in a key equipment, such as the steam generator, is a determining factor in ensuring optimum operation in safe conditions and without the risk of unplanned plant shutdowns resulting in direct and indirect economic costs. Through its objective, this work is an opportunity to characterize the chemical composition of the deposits removed from the Cernavoda NPP steam generator secondary side by a scheduled shutdown and to synthesize the main information from the specialty literature in the field of degradation of the steam generator tube - tubesheet joint regions.

Keywords: CANDU steam generator, deposits, corrosion products, impurities, tubesheet.

1. Introduction

Every year, the cost of repairing and inspecting of the Pressurized Water Reactor (PWR) exceeds $ 100 million. This is equivalent to about $ 1.5 million per Nuclear Power Plant (NPP) over a year.

In France, an equivalent amount is spent each year for each NPP regarding the inspection, repairing and cleaning the steam generators.

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In Canada, the recent implementation of intensive mechanical or chemical cleaning programs has resulted in tens of millions of dollars a year spent on just two nuclear power plants.

Additionally, the costs associated with the planned inspections and repairs of the steam generators that often involve forced shutdown, prolonged scheduled outages and require inspections to be carried out during the middle of the next operating period. The cost of these events in equivalent power is exorbitant. For example, over the last sixteen years, steam generator issues have caused an average of 3.6% reduction in nuclear power capacity in the US PWR plants.

During the operation of a CANDU NPP, the structural metallic components of heat transfer circuits are affected by degradations caused by environmental chemistry, operating parameters (temperature, pressure, flow rate, etc.), the structure and type of material processing, and the aging phenomenon of these components.

Therefore, a thorough knowledge of the phenomena and mechanisms underlying the processes of degradation of structural materials in nuclear installations in order to prevent or mitigate the consequences of these phenomena and to ensure the safe operation and safety of nuclear installations is a very important and permanent concern for nuclear researchers.

For this reason, the experience gained in over 50 years of operation in the CANDU nuclear units operating in Canada, Korea, Argentina, India, China, Pakistan and Romania has allowed the understanding of mechanisms for degradation of structural components and identification of factors affecting their structural integrity and, in some cases, led to the unplanned shutdown of nuclear reactors.

An important factor affecting the maintenance cost of the steam generators is the presence of deposits into the secondary side of these high capacity vertical heat exchangers. These deposits are formed by the inlet of feedwater containing hard impurities, metals and metallic oxides (corrosion products) and other materials into the secondary circuit of this equipment. The most serious consequence of the presence of deposits into the secondary side of the steam generators is the corrosion process of the tubes. For example, small amounts of corrosive species entering in the secondary side of the steam generator can be concentrated within the deposits at values that exceed their concentration in the feedwater with a factor that is well above the order of thousands. This concentration process which can increase the corrosive attack of the nickel alloys from which the tubing is made can occur under the deposits developed on the tubesheet, the oxide and corrosion products layer formed on the tubing surface and on the intermediate tubes supports on which deposits are present.

The presence of deposits in the crevices contributes to the concentration of aggressive chemical species within these crevices and therefore contributes to limiting the life of the steam generator, Fig. 1.

In recent years, a new phenomenon has been reported regarding the presence of deposits in the secondary side of the steam generator. This refers to the reduction of the heat transfer performance due to the deposition of sludge on outside surface of the tubes. This decrease in the thermal transfer performance is manifested by the reduction of the generated steam pressure acting on the turbines.

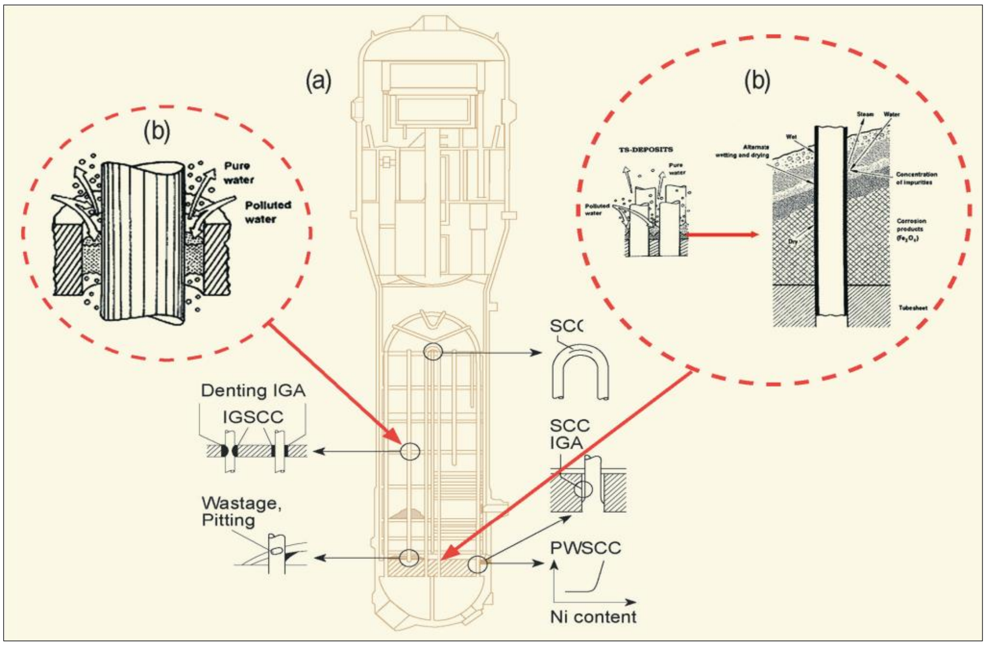


Fig. 1. The mechanism of concentration of the impurities in steam generators (a, b); areas affected by corrosion in steam generators (b).

The steam pressure drops of 10% or more have been reported. The effect of this phenomenon is to reduce the amount of energy generated. A 1% decrease in the electricity generation capacity is equivalent to a loss of $ 2.5 million.

The effects of deposits on the thermo - hydraulic performance also lead to a reduction in the power of the NPPs. In this case, the deposits present in the zones with restrictive circulation where the tubes pass through intermediate supports (plate) restrict the upward flow of the biphasic steam - water mixture over the intermediate supports and thus the level of the cooling water inside the steam generator oscillates. Continued operation under these conditions may result in a power decreasing, [1] ÷ [6].

2. Results and Discussions

At Cernavoda NPP the filtering elements that were used for retaining the deposits from the CNE Cernavoda steam generator secondary side a planned shutdown, were received.

The deposits (sludges) samples were taken by disassembling four filter elements, removing the powder deposits on a filter paper, homogenizing them and collecting them in recipients with lids. The amount of powder in each container was determined according to the type of analysis applied. The characterization of deposits consists in sampling, identification, carrying out of laboratory analyzes and the interpretation of the data that is necessary for assessing the effects of deposits developed on the structural materials of the steam generator and for the operation of this key equipment, Fig. 2.

The central activity of the deposits characterization consists in the physical and chemical analysis, examination and measurements made in the central or in the independent laboratories.

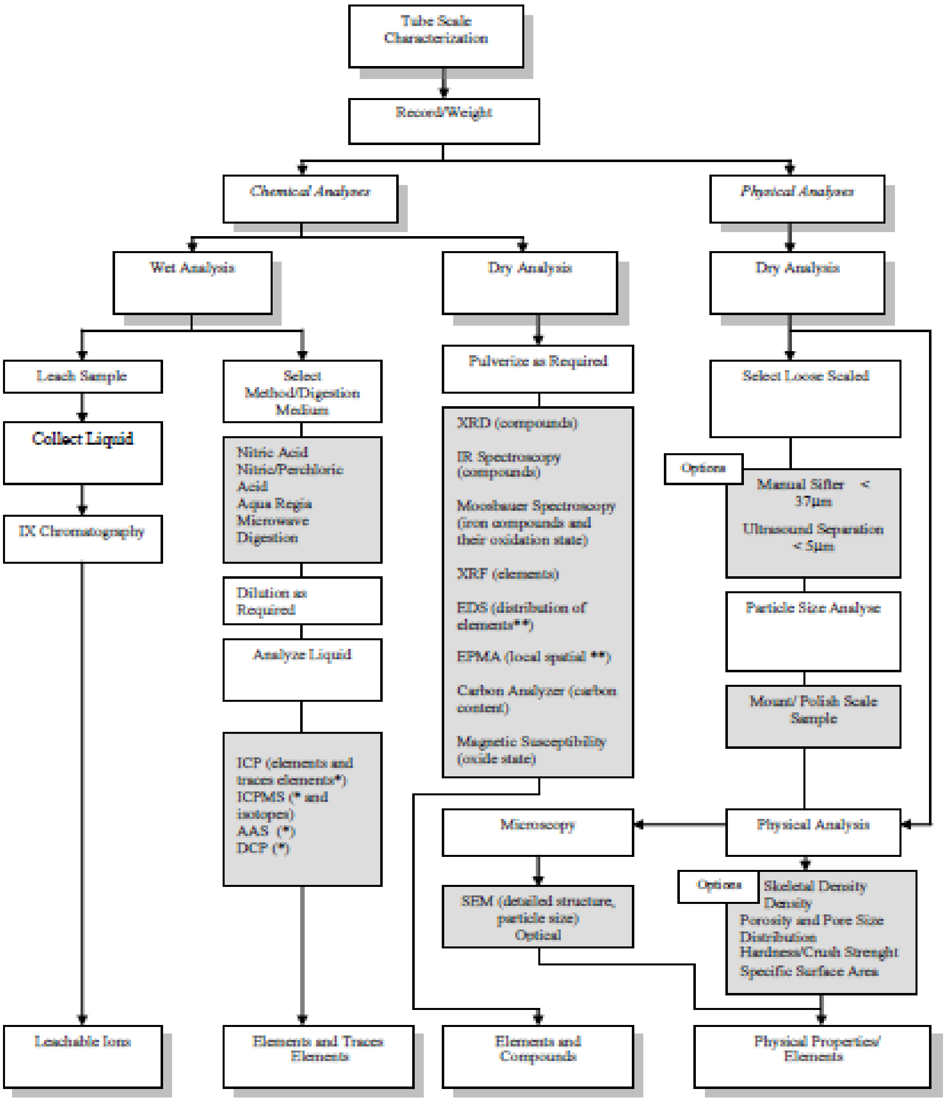


Fig. 2. Characterization of powder deposits.

The methods used to characterize the sludges resulting from the cleaning (pressure water lancing) of the steam generators secondary side from the CNE Cernavoda after a planned outage were:

1. determination of density;
2. granulometric analysis;
3. X - Ray Diffraction (XRD);
4. X - Ray Fluorescence (XRF);
5. Scanning Electron Microscopy (SEM), Energy Dispersion X-Ray Spectroscopy (EDS).

2.1. Density determination

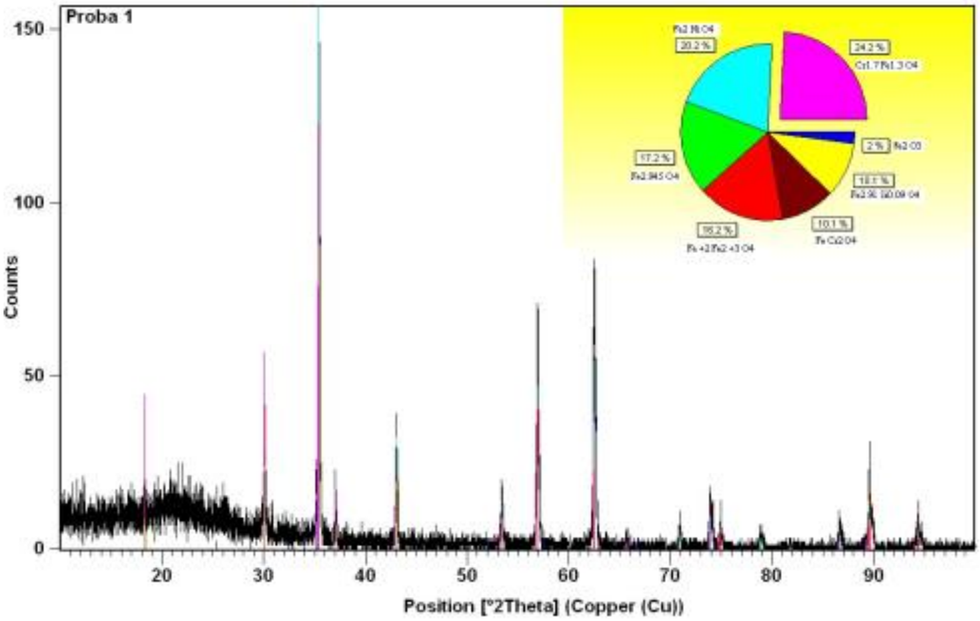
Apparent density 1.09 [g/cm^3]
Density 1.64 [g/cm^3]

2.2. Granulometric analysis

After the granulometric analysis it was noticed that for one of the samples two fractions with the approximate dimensions of 10 µm and 100 µm were identified and for the second one it was found that the homogeneity of the sample was of 10 µm.

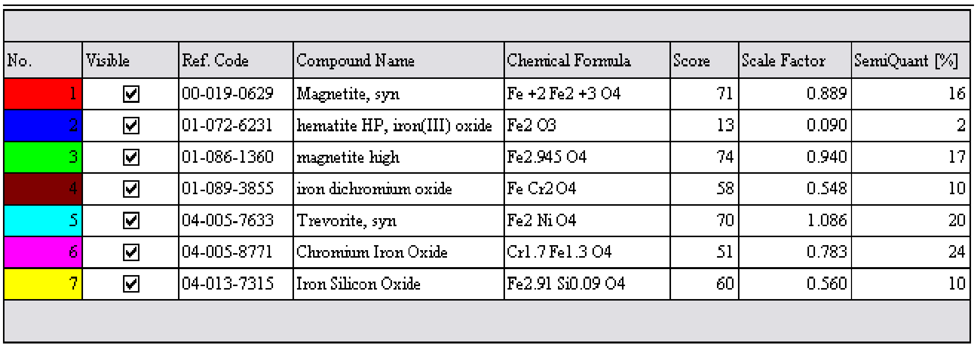
2.3. X – Ray Diffraction

X-ray diffraction analyzes were performed using the X'Pert PRO MPD X-ray diffractometer, equipped with an X-ray tube (Line Fine Focus - 12x0.4mm) with Cu anode.



a)

Fig. 3. The diffraction spectrum for sample 1 (a).



No.	Visible	Ref. Code	Compound Name	Chemical Formula	Score	Scale Factor	SemiQuant [%]
🟥 1	☑	00-019-0629	Magnetite, syn	Fe +2 Fe2 +3 O4	71	0.889	16
🟦 2	☑	01-072-6231	hematite HP, iron(III) oxide	Fe2 O3	13	0.090	2
🟩 3	☑	01-086-1360	magnetite high	Fe2.945 O4	74	0.940	17
🟫 4	☑	01-089-3855	iron dichromium oxide	Fe Cr2 O4	58	0.548	10
🟦 5	☑	04-005-7633	Trevorite, syn	Fe2 Ni O4	70	1.086	20
🟪 6	☑	04-005-8771	Chromium Iron Oxide	Cr1.7 Fe1.3 O4	51	0.783	24
🟨 7	☑	04-013-7315	Iron Silicon Oxide	Fe2.91 Si0.09 O4	60	0.560	10

b)

Fig. 3. The list of compounds identified by X-ray diffraction (b)

2.4. X – Ray Fluorescence

The method of analysis used was the predefined method for He-UQ_Helium atmospheric assays - a method used when analyses are in the form of powders or liquid samples. Using the OXSAS program and the UQ_Helium method, all elements are scanned to perform the semi-quantitative sample analysis, Table1.
The results obtained from the scan were processed using the UniQuant software that allows for unambiguous analysis of the samples. X-ray fluorescence confirmed the majority of iron oxides.

Table 1. Semicantitative analysis
using the Uniquant program

Element	% masic	STDErr
Fe	42.18	0.58
Rh	4.61	0.11
Zn	0.539	0.027
Mn	0.320	0.016
Cr	0.269	0.013
Ni	0.196	0.010
Ti	0.177	0.009
Al	0.0826	0.0041
Cu	0.0784	0.0039
Co	0.0725	0.0036
Si	0.0582	0.0029
Zr	0.0242	0.0012
Ca	0.0202	0.0010
La	0.0133	0.0011
Sn	0.0122	0.0008
Rest Oxygen	51.31	

2.5. Scanning Electron Microscopy, X-ray Dispersion Spectroscopy (EDS)

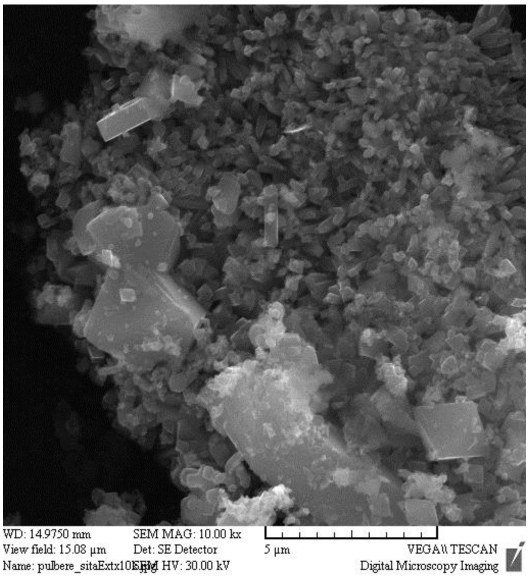
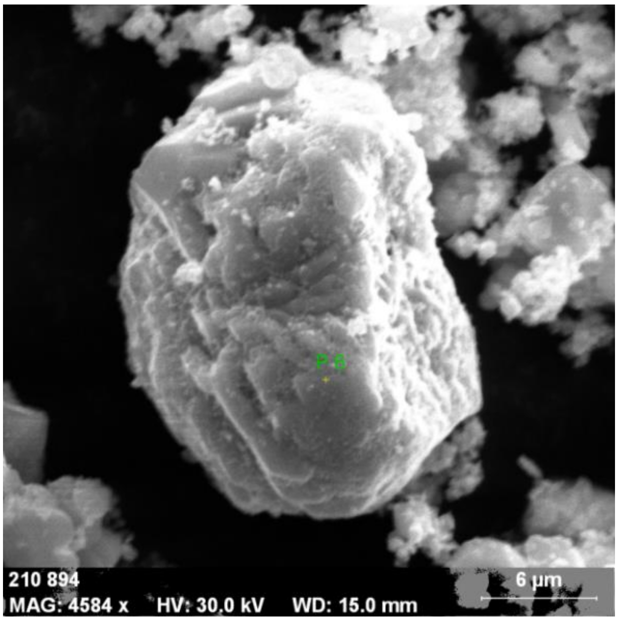
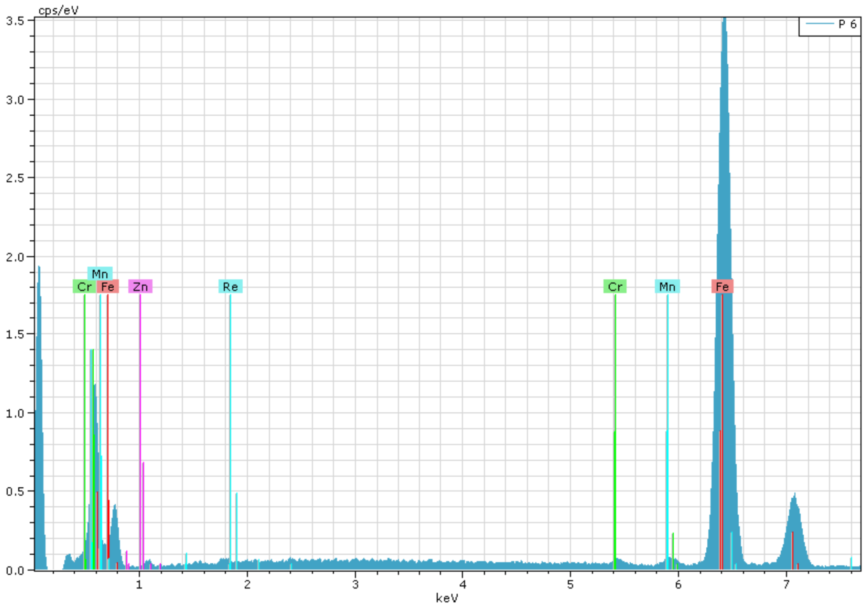


Fig. 4. The deposits morphology determined by SEM.

Fig. 4 shows the morphology of deposits determined by Scanning Electron Microscopy.



a)



b)

No.	**Elements**	**P6**
1	Fe	85.63
2	Mn	10.15
3	Si	3.19
4	Cr	0.79
5	Zn	0.24

c)

Fig. 5. Point microanalysis (a), spectrum
and quantitative composition of deposits (b) and (c).

The magnetite crystals have rounded edges and this is being explained by the fact that they have not formed inside the steam generator but inside the secondary circuit from where they were transported to the steam generator and because of the flow, the edges have been rounded. Iron is in different oxidation states, darker crystals contain more oxygen in the formula, while lighter crystals contain less oxygen. Particle sizes range from a few microns to tens of microns. In Fig. 5 are presented the point microanalysis (a), the spectra and the quantitative composition of the deposit (b) and (c), which show the presence of Fe – 85.63%, Mn – 10.15% (this may come from the austenitic steels corrosion process) and Si - 3.19%. The presence of silicon in deposits must be followed with great care as it gives hardness to deposits and therefore deposits will be more difficult or impossible to remove from the steam generator by simply cleaning with a pressure water jet, [7] ÷ [23]. The form of the deposits constituents confirms the presence of both magnetite and hematite and rarely the presence of chromium compounds (oxides and carbides). There are several types of oxides that differ in atomic form and number.

3. Conclusions

In all Nuclear Power Plants, a special emphasis is placed on the activity related to the characterization of the deposits developed into the steam generator secondary side.

In the process of the CANDU steam generator secondary circuit degradation an essential role plays the formation, transportation and deposition of the corrosion products and impurities. Minimizing the presence of these corrosion products is a determining factor in ensuring optimal operation in safe conditions and without the risk of unplanned plant shutdowns resulting in both direct and indirect considerable economic costs.

The paper describes the characterization of the removed from the the CNE Cernavoda steam generators tubesheets after a planned shutdown and summarizes the main information from the specialty literature concerning the degradation of the structural materials placed in the tube – tubesheet joint regions of the steam generators.

Considerations are made regarding the deposits in the secondary circuit of the steam generator and the consequences of the presence of these deposits, the most serious of which beeing the corrosion process of the tubing.

The benefits of the deposits characterization are the follows:
a) Determination of the physical and chemical properties of deposits from the steam generator as an integral part of the chemical or mechanical cleaning program. As it is well known, the approximate evaluations of the deposits composition, quantity and distribution are based on the studies concerning the transport of corrosion products, which may be inadequate to plan the maintenance activities of this magnitude, which involve significant costs. This is mainly due to the uncertainty in the assessment of blowdown efficiency, the different efficiency of blowdown for different chemical species, the unavailability of data regarding the transport of corrosion products for the initial operation periods of the older plants and the difficulty of estimating the corrosion products during the NPP starting and operation under transient regimes.
b) Chemical analyses may indicate the presence of aggressive species such as lead or copper. The presence and concentration of these species is an important part of the process of assessing the status of the secondary circuit for making decisions on chemical or mechanical cleaning.
c) Measuring the thickness of deposits layers developed on the tubes, the composition and morphology of these deposits contributes to a better knowledge and evaluation by calculation of the steam generators thermal transfer performance, in general and deposits concentration factors, in particular .
d) Evaluations of the physical properties of deposits, such as density and thickness of the deposits layer, can be used in order to estimate total corrosion product transport and the blowdown efficiency. As a rule, the estimated loading values

based on the steady state corrosion products transport are lower than those obtained by direct examination of the deposits properties.

e) Knowledge of the oxidation state of deposit constituents can contribute to assessing the integrity of the condenser and the effectiveness of the reagents used to remove oxygen because oxygen in the water can enhance the formation of copper oxides and iron oxides other than magnetite.

f) Chemical characterization of deposits contributes to the assessment of cooling water chemistry strategies and control by using alternative treatment with amines that can modify the deposits structure and by using an excess concentration of hydrazine (>100 ppb) that promotes the formation of magnetite.

g) Identification of copper in the deposits on the tubes blocking the flow paths between the tubes and the intermediate supports can explain the signal deviations obtained during the eddy current inspection.

h) Discovery of foreign objects or portions of secondary circuit materials in deposits can be used as information in assessing the possible tube degradation mechanism over the next period.

i) Knowledge of the composition of deposits will contribute to a better control of cooling water, condensation and blowdown since these systems may contain different elements that are incorporated into deposits and that can be identified during laboratory analyzes.

The methods used for the deposits characterization were: density determination, granulometric analysis, X-ray diffraction, X-ray fluorescence, scanning electron microscopy and energy dispersion X-ray spectrometry.

The average deposit density was of 1.64 g/cm^3.

By granulometric analysis for one of the samples two fractions with approximate dimensions of 10 μm and 100 μm were identified and in the second one it was found a higher homogeneity, the particle size being of 10 μm.

By X-ray diffraction it was found that a high percentage of Fe_3O_4 (~ 16%), $Fe_{2.945}O_4$ (~17%), $FeCr_2O_4$ (~ 10%), Fe_2NiO_4 (~ 20%), $Cr_{1.3}Fe_{1.7}O_4$ (~ 24%). Also, $Fe_{2.91}Si_{0.09}O_4$ was found to be about 10%. The deposit also contains a very small amount of hematite - Fe_2O_3 (~ 2%).

X-ray fluorescence confirmed the majority of iron oxides.

Scanning electron microscopy, X-ray spectrometry with energy dispersion and point microanalysis revealed: deposit morphology, spectra and quantitative composition of deposit.

The form of deposit constituents confirms the presence of both magnetite and hematite and rarely the presence of chromium compounds (oxides and carbides). There are several types of oxides (especially iron oxides) that differ in atomic form and number.

From the point microanalysis, the spectra and the quantitative composition of the deposits, the majority of the iron compounds, especially in the form of oxides, are highlighted. It is noted that in very small amounts of Cr and Ni due to corrosion of the steam generator tubing material (Incoloy 800), the low corrosion rate of this material explains the presence the small quantities of these elements.

By comparing the results obtained in this paper with data made public by the operators of other similar NPP, there are no significant differences regarding the chemical composition of the deposits removed from the steam generator secondary side, [5].

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