# Influence of the Coolant Chemistry on the Structural Materials Surfaces Exposed into the CANDU NPP Primary Circuit

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## Objectives

Corrosion behavior of the structural materials from primary circuit as a function of material and environment conditions. Monitoring of operating fluid chemistry effect on the systems components corrosion and on the build-up of activity. Identification of fault types produced by the corrosion.

## Introduction

To investigate the corrosion process of some structural materials from Primary Heat Transfer System - PHTS (Zr and Ni alloys) of CANDU 6 reactor were perfomed the following activities: out of pile corrosion experiments in different conditions of water chemistry, corrosion experiments in autoclaves assembled in by-pass of CANDU 6 reactor PHTS, corrosion analysis performed on some corroded components. The gravimetric method, optical metallographic microscopy, XRD analysis, as well as electrochemical measurements have been used to evaluate the corrosion behavior of the pressure tube and steam generator tubing materials.

## Experimental Methods

The samples used in oxidation tests were cut from Zr-2.5% Nb pressure tube and Incoloy 800 Steam generator tube. Standard coupons 30 x15 x1.3 mm. The materials were in the same metallurgical condition as those used in CANDU reactors. The surface preparation of samples for testing was done by fine mechanic polishing, degreasing in ternary mixture of organic solvents, pickling in aqueous solution containing HF, $H_2SO_4$, $HNO_3$ and $H_2O$ as recommended in ASTM Standard G2-88.

The corrosion of CANDU PHTS structural materials was investigated extensively, allowing us to accumulate data and knowledge on corrosion mechanisms related to material characteristics, water chemistry and testing conditions.

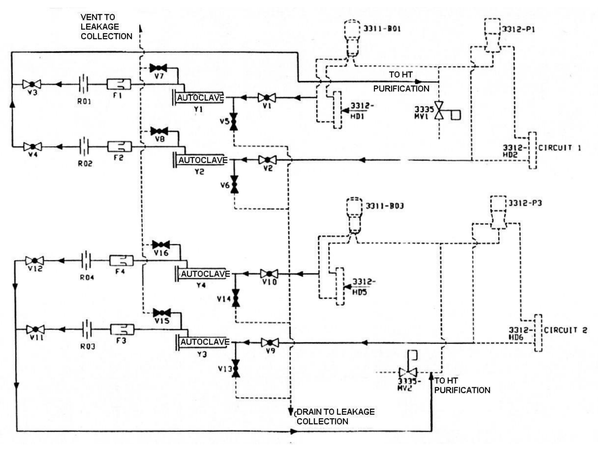
These data were obtained by analysis of specific samples tested in static autoclaves and different electrochemical methods.

On the basis of the experiments and analysis performed, have been determined:
- oxidation kinetics of zirconium alloy Zr-2.5% Nb and Incoloy 800 as a function of the initial surface state the water chemistry and testing temperature;
- corrosion of structural materials coupons exposed in PHT autoclaves at U1 NPP Cernavoda.

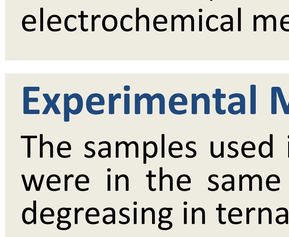
## Results and Disscussions

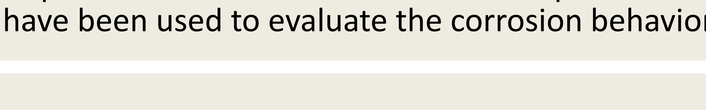
1) Assessing corrosion and analysis of crud deposits on different structural materials samples exposed in the by-pass of CANDU reactor primary circuit:
   - determination of Incoloy 800 samples corrosion (the corrosion rate, the aspect and thickness of oxide, morphology and quantity of deposits);
   - deposit activity measurement by gamma spectrometry;
   - morphological analysis of deposits by scanning electron microscopy (SEM);
   - analysis by metallographic microscopy and XPS of adherent and non-adherent deposits;
   - porosity and adherence determination of deposits by electrochemical impedance spectroscopy (EIS) measurements.
2) Comparing the results with those obtained from laboratory tests.

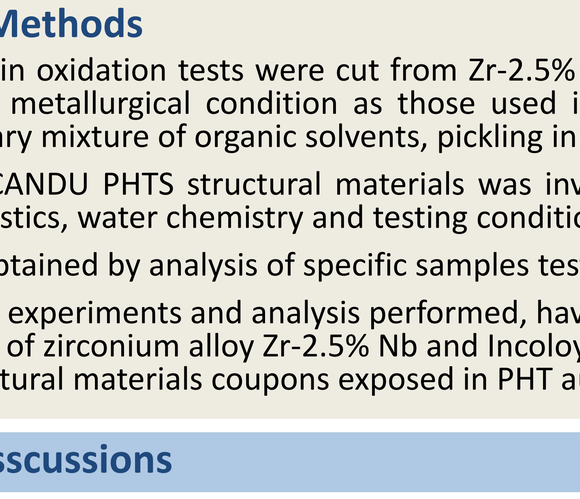
**Cernavoda NPP Unit 1 PHT Autoclaves System Diagram**



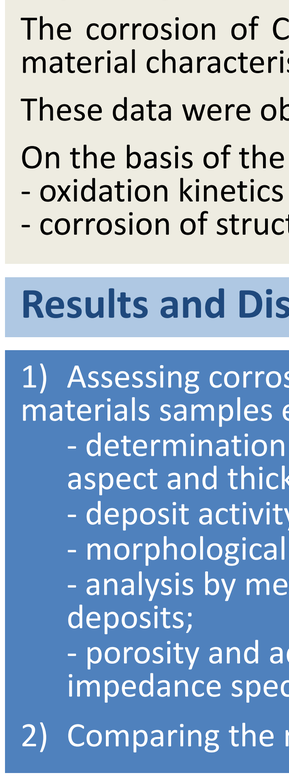

Operation history of removed samples
Working environment: heavy water
Conductivity: 8-25 S/cm
Dissolved D2: 3 -10 ml/kg
Chloride: ≤0.2mg/kg
Fluoride: ‹1mg/kg
D2: ≤2 % by vol. O2: ≤1 % by vol.
N2: ≤6 % by vol.I-131: ‹500 MBq/kg
Suspended solids:‹0.1mg/kg
Total organic carbon: ≤1.0mg/kg

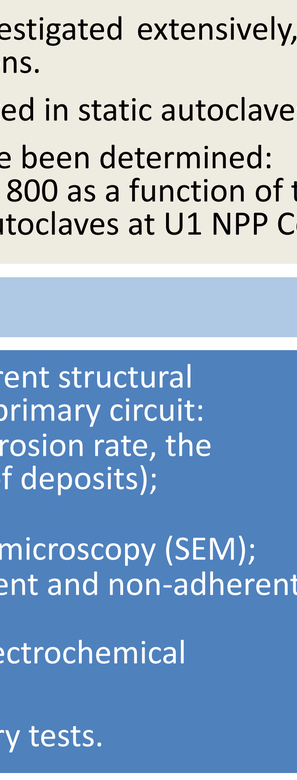


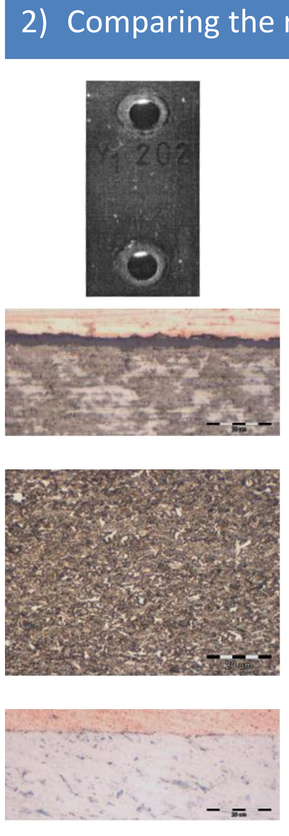



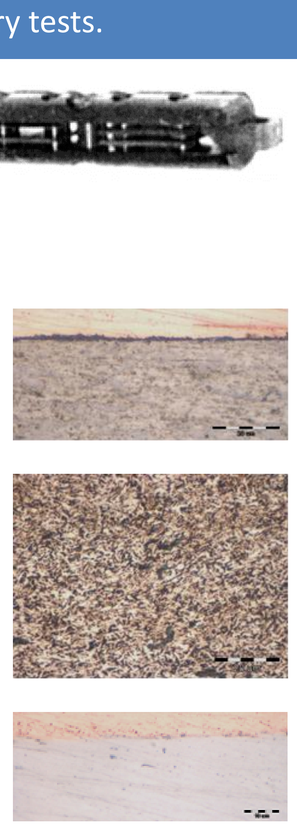



**Corrosion kinetics of Zr-2.5% Nb samples as a function of temperature**







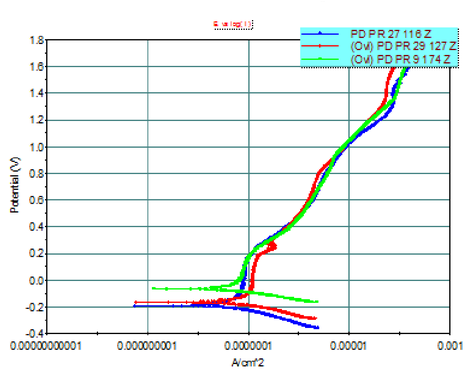










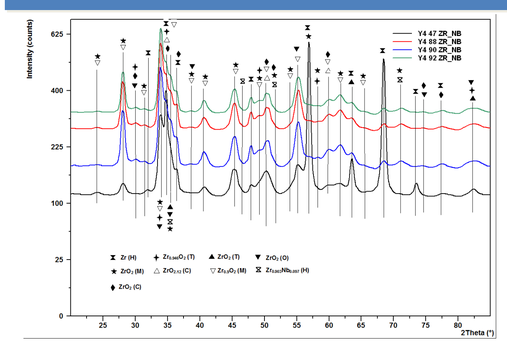



**Potentiodynamic curves in demineralized water, pH 10.5 (LiOH), Iy-800 initially tested for 116 days, 127 days and 174 days in the specific conditions of the primary circuit**

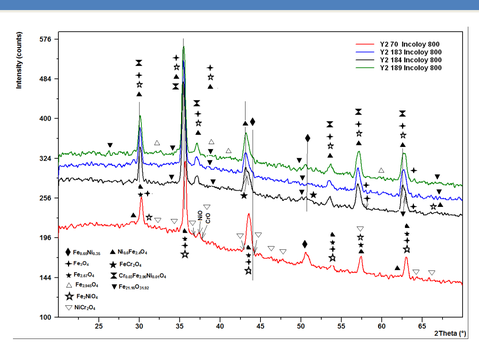
**The aspect of the Zr-2.5%Nb and Incoloy 800 oxide films after different testing periods at 310°C, evidenced through metallography**

**Chemistry control of the PHT System and Auxiliaries is required to:**

1) Minimise the corrosion of system components;
2) Limit the production rate of radioactive corrosion products;
3) Minimise the fouling of the heat transfer surfaces by controlling the crud movement and removal;
4) Maintain heat transport storage tank cover gas deuterium and oxygen concentration below explosive limits.




**Superposition of diffraction spectra obtained for Zr-2.5%Nb coupons exposed in the autoclave Y 4**




**Superposition of diffraction spectra obtained for Incoloy 800 coupons exposed in the Y 2 autoclave**

**The results of examinations obtained will be used in order to determine:**

a) Characteristics of structural materials samples extracted from Cernavoda NPP autoclaves placed in the by-pass of the primary circuit (chemical composition, morphology, aspect in section, thickness, porosity and activity of radionuclides);
b) The oxidation rate, characteristics of oxide layer formed on the structural materials surface (morphology, aspect in section, thickness, adherence and porosity);
c) After the samples characterization one can compare the results obtained on the samples removed from Cernavoda autoclaves with the experimental results obtained in the laboratory on the samples tested in the same conditions.

## Conclusions

- The testing and analysis of numerous samples from CANDU PHT structural materials allowed their behavior characterization in normal and abnormal conditions of operation.
- The analysis of coupons exposed in the autoclaves from Cernavoda Unit 1 show a normal corrosion behavior of structural materials, till now.
- Reactor coolant aggressiveness is controlled by monitoring the dissolved oxygen content, pH and the level of impurities, crud and fission products.
- The oxidation of Zr-2.5%Nb alloys was strong dependent of temperature. Thus the constants of corrosion kinetics at pre and post-transition (k1 and k2) increased significantly with temperature. Generally, the formed oxides were continuous and uniform, but, at temperatures more than 310°C increased the porous character of oxides and appeared fissures at exterior surface oxides which increased of time, advancing to oxide/metal interface.
- In normal conditions of the operation and water chemistry, the general corrosion did not limit life of structural components. But, localized corrosion processes can conduct to failure of some components and leakages of the coolant.
- After a period of exposure of samples exceeding five years not seen an influence of irradiation on NPP PHT structural materials.