Long-term corrosion study at nuclear power plant Bohunice (Slovakia)

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Abstract. Steam generators of four VVER-440 units at nuclear power plants V-1 and V-2 in Jaslovské Bohunice (Slovakia) were gradually changed by new original “Bohunice” design in period 1994-1998. Corrosion processes before and after these design and material changes in Bohunice secondary circuit were studied using Mössbauer spectroscopy during last 25 years. Innovations in the feed water pipeline design as well as material composition improvements were evaluated positively. Mössbauer spectroscopy studies of phase composition of corrosion products were performed on real specimens scrapped from water pipelines or in form of filter deposits. The corrosion of new feed water pipelines system (from austenitic steel) in combination to innovated operation regimes goes dominantly to magnetite. The hematite presence is mostly on the internal surface of steam generator body and its concentration increases towards the top of the body. In the results interpretation it is necessary to consider also erosion as well as scope and type of maintenance activities. The long-term study of phase composition of corrosion products at VVER reactors is one of precondition for the safe operation over the projected NPP lifetime.

1. Introduction
Steam generator (SG) is generally one of the most important components at all nuclear power plants (NPP) with close impact to safe and long-term operation. The Russian water cooled and water moderated reactors (VVER) are unique because of the horizontal position of SGs. It takes several advantages (large amount of cooling water in case of loss of coolant accident, good accessibility, large heat exchange surface, etc.) but also some disadvantages, which are important to take into account during the operation and maintenance. Material degradation and corrosion/erosion processes are serious risks for long-term reliable operation. In the period of about 10-15 years ago, the feed water pipelines were changed at all SGs in all 4 Bohunice units (V-1 and V-2, in total at 24 SGs). Also, a new design of this pipeline system was performed. Actually, there is a time to evaluate the benefit of these changes.

Application of Mössbauer spectroscopy for precise analysis of phase composition of corrosion products was performed from selected areas of secondary circuit and SGs. The interpretation of
measured results, having in vision the long-term operation and nuclear safety, is not easy, nor straightforward. Thanks to our more than 25 years of experiences in this area, there exists already a base for the relevant evaluation of results. Optimisation of operating chemical regimes as well as regimes at decontamination and passivation seems to be an excellent output.

Based on operational experiences, the mitigation of damages and leak tightness defects in pipelines or collectors require much more time and money, than prevention measures. It is necessary to keep in mind the actual development in nuclear industry towards NPP lifetime prolongation and power increase (one of essential goals of European Commission 7FP-NULIFE). Fortunately, VVER-440 steam generators were designed with the huge power reserve (possible overloading of 20%). Beside several leakages in primary pipelines (ø16 mm), which can be in case of VVER-440 SGs relatively easy solved (blended), the corrosion deposits in feed water pipeline system occurred at many VVER-440 units [1]. The identified damages were caused mostly due to corrosion/erosion processes attacking materials familiarly called “black steels” with insufficient resistance against corrosion.

2. Actual results
In the period 2007-2008 six samples for Mössbauer effect experiments collected from different parts of the NPP Bohunice unit were prepared by crushing to powder pieces (Table 1 and Fig.1).

All measured spectra contained iron in magnetic and many times also in paramagnetic phases. Magnetic phases contained iron in nonstoichiometric magnetite Fe$_{3-x}$M$_x$O$_4$ where M$_x$ are impurities and vacancies which substitute iron in octahedral (B) sites. Another magnetic fraction is hematite, α-Fe$_2$O$_3$. In one sample also the magnetic hydroxide (goethite α-FeOOH) was identified.

Paramagnetic fractions are presented in the spectra by quadrupole doublets (QS). Their parameters are close to those of hydroxides e.g. lepidocrocite γ–FeOOH or to small, so called superparamagnetic particles of iron oxides or hydroxides with the mean diameter of about 10 nm. It should be noted that there is no problem to distinguish among different magnetically ordered phases when they are present in a well crystalline form with low degree (or without) substitution. Both the substitutions and the presence of small superparamagnetic particles make the situation more complicated [2]. In such cases, it is necessary to perform other supplementary measurements at different temperatures down to liquid nitrogen or liquid helium temperatures without and with external magnetic field [3].

The major fraction in all samples consists of magnetically ordered iron oxides, mainly magnetite (apart from the sample No. 1 and 2, where also goethite and hematite has appeared, respectively). Magnetite crystallizes in the cubic inverse spinel structure. The oxygen ions form a closed packed cubic structure with Fe ions localized in two different sites, octahedral and tetrahedral. The octahedral sites (A) are occupied by trivalent Fe ions. Tri- and divalent Fe ions occupying the octahedral sites (B) are randomly arranged at room temperature because of electron hopping. At room temperature, when the electron hopping process is fast, the Mössbauer spectrum is characterized by two sextets. The one with the hyperfine magnetic field $B_{hf} = 48.8$ T and the isomer shift IS = 0.27 mm/s relative to α-Fe corresponds to the Fe$^{2+}$ ions at the tetrahedral A - sites. The second one with $B_{hf} = 45.7$ T and IS = 0.65 mm/s is the Fe$^{2.5+}$ - like average signal from the cations at octahedral B sites. Fe$^{2+}$ and Fe$^{3+}$ are indistinguishable due to fast electron transfer (electron hopping), which is faster (~1 ns) than the $^{57}$Fe excited state lifetime (98 ns). The magnetite unit cell contains eight Fe$^{2+}$ ions and eight Fe$^{3+}$ ions, 16 in total at the B sites, therefore, the intensity ratio $\beta = I(B)/I(A)$ of the two spectral components is a sensitive measure of the stoichiometry. Assuming that the room temperature ratio of the recoil-free fractions $f_0/ f_A$ for the B and A sites is 0.97, the intensity ratio $\beta$ for a perfect stoichiometry should be 1.94 [4,5]. In non-stoichiometric magnetite, under an excess of oxygen, cation vacancies and substitutions at the B sites are created. The vacancies screen the charge transfer and isolate the hopping process. For each vacancy, five Fe$^{3+}$ ions in octahedral sites become trapped. In the Mössbauer spectrum these trapped Fe$^{3+}$ ions at the octahedral sites and Fe$^{3+}$ ions at tetrahedral sites are indistinguishable without applying an external magnetic field. Therefore, in the spectrum of non-stoichiometric magnetite, intensity transfer from the Fe$^{2.5+}$ to Fe$^{3+}$-like components is observed. Thus, the intensity ratio $\beta$ decreases markedly with the oxidation process, until the stoichiometry reaches the
γ-Fe₂O₃ phase. It should be noted that in our samples the intensity ratio \( \beta \) is far from 1.94 (for perfect stoichiometry), it varies from 0.97 up to 1.85.

**Table 1.** Spectral parameters of individual components including spectral area \( (A_{\text{rel}}) \), isomer shift (IS), quadrupole splitting (QS), as well as hyperfine magnetic field \( (B_{\text{hf}}) \) for each sample with according components.

| Sample | Component | Area [%] | Isomer shift [mm/s] | Quadrupole shift/splitting [mm/s] | Hyperfine field [T] |
|--------|-----------|----------|---------------------|-----------------------------------|---------------------|
| Sample no. 1. | Magnetite A-site | 36.3 | 0.28 | 0.00 | 48.90 |
| Surface deposit at small coolant circuit of pumps 17. 10. 2007 | Magnetite B-site | 37.2 | 0.64 | 0.00 | 45.60 |
| | Goethite | 14.4 | 0.36 | -0.25 | 35.80 |
| | Hydroxide | 12.1 | 0.36 | 0.70 | - |
| Sample no. 2. | Hematite | 15.8 | 0.38 | -0.23 | 51.56 |
| Deposites scraped from filters after filtration of SG - feed water during operation | Magnetite A-site | 32.6 | 0.28 | 0.00 | 49.14 |
| | Magnetite B-site | 41.8 | 0.65 | 0.00 | 45.91 |
| | Hydroxide | 9.7 | 0.38 | 0.56 | - |
| Sample no. 3. | Magnetite A-site | 34.6 | 0.28 | 0.00 | 49.14 |
| SG42 pipelines - low level | Magnetite B-site | 65.4 | 0.65 | 0.00 | 45.83 |
| Sample no. 4. | Hematite | 9.2 | 0.38 | -0.22 | 51.29 |
| Mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42 | Magnetite A-site | 45.4 | 0.28 | 0.00 | 49.20 |
| | Magnetite B-site | 40.7 | 0.66 | 0.00 | 45.87 |
| | Hydroxide | 4.7 | 0.37 | 0.56 | - |
| Sample no. 5. | Hematite | 8.3 | 0.36 | -0.22 | 51.33 |
| Deposit from filters after 340 l of feed water of SG S3-09 during pasivation 27. and 28. 5. 08 | Magnetite A-site | 49.3 | 0.30 | 0.00 | 49.11 |
| | Magnetite B-site | 38.5 | 0.61 | 0.00 | 45.51 |
| | Hydroxide | 3.9 | 0.37 | 0.55 | - |
| Sample no. 6. | Hematite | 6.4 | 0.38 | -0.25 | 51.26 |
| Deposit from filters after 367 l of feed water of SG S4-09 during pasivation 27. and 28. 5. 08 | Magnetite A-site | 50.3 | 0.29 | 0.00 | 49.14 |
| | Magnetite B-site | 40.7 | 0.66 | 0.00 | 45.61 |
| | Hydroxide | 2.6 | 0.37 | 0.54 | - |

**Figure 1.** Mössbauer spectrum of sample no. 1. A-site (red), B-site (dark red) magnetite, goethite (pink) and hydroxide (green) were identified.
3. Conclusion
Newest results in our long-term corrosion study confirm good operational experiences and suitable chemical regimes (reduction environment) which results mostly in creation of magnetite (on the level 70% or higher) and small portions of hematite, goethite or hydroxides.

Regular observation of corrosion/erosion processes is essential for keeping NPP operation on a high safety level. The output from performed material analyses influences the optimisation of operating chemical regimes and it can be used in optimisation of regimes at decontamination and passivation of pipelines or secondary circuit components. It can be concluded that a longer passivation time leads to a higher magnetite fraction in the corrosion products composition.

The long-term study of the phase composition of corrosion products at VVER reactors is one of the precondition to the safe operation over the projected NPP lifetime. The long-term observation of the corrosion situation by Mössbauer spectroscopy is in favour of utility and is not costly. Based on the achieved results, the following points could be established as an outlook for the next period:

A) In collaboration with NPP-Bohunice experts for operation as well as for chemical regimes, several new additional samples from places not studied up to now should be extracted and measured by Mössbauer spectroscopy with the aim to complete the existing “corrosion map” of the VVER-440 secondary circuit.

B) Optimisation of chemical regimes (having in mind the measured phase composition of measured corrosion specimens from the past) could be discussed and perhaps improved.

C) Optimisation and re-evaluation of chemical solutions used in cleaning and/or decommissioning processes during the NPP operation can be considered.

D) In connection to the planned NPP Mochovce 3, 4 commissioning (announced officially at 3.10.2008) it is recommended that all feed water pipelines and water distribution systems in steam generators should be replaced immediately before putting in operation by new ones constructed from austenitic steels. The Bohunice design with feed water distribution boxes is highly recommended and it seems to be accepted from the utility side.

Acknowledgement
This work was supported by company ENEL Produzione, Pisa and by VEGA 1/0129/09.

References
[1] Slugen V 1999 Mössbauer spectroscopy in material science ed. M Miglierini and D Petridis, (Amsterdam: Kluwer) 119-130.
[2] Lipka J and Miglierini M 1994 J. of El. Eng. 45 15
[3] Morup S, Topsoe H and Lipka J 1976 J. de Phys. 37 287
[4] Korecki J et al. 2002 Thin Solid Films 412 14
[5] Cornell RM, Schwertmann U 1996 The Iron Oxides ISBN 3-527-28576-8