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Application of Mössbauer spectroscopy on corrosion products of NPP

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Abstract 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. Material degradation and corrosion/erosion processes are serious risks for long-term reliable operation. Steam generators of four VVER-440 units at nuclear power plants V-1 and V-2 in Jaslovske Bohunice (Slovakia) were gradually changed by new original "Bohunice" design in period 1994–1998, in order to improve corrosion resistance of SGs. 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 filters deposits. 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 hydrooxides. Regular observation of corrosion/erosion processes is essential for keeping NPP operation on 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 more to magnetite fraction in the corrosion products composition.

Keywords NPP · Corrosion · Mössbauer effect

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1 Introduction

Application of Mössbauer spectroscopy for precise analysis of phase composition of corrosion products was performed from selected areas of primary and secondary circuit and SG. Interpretation of measured results, having in vision the long-term operation and nuclear safety, is not easy, nor straightforward. Thank to our more than 25 years of experiences in this area, there exists already 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.

All steam generators at four VVER-440 units in Bohunice were gradually changed. The basic design from 1977 was improved after 1994 by new feed water pipeline system. There was also change in the type of steel of these pipelines. Instead conventional carbon steel, the austenite steel was used in distribution boxes as well as feed water pipelines. All components in the Bohunice innovated feed water pipeline system were made from austenitic steel according to Czechoslovak norm ČSN, class 17. Since the decontamination processes for the materials of the VVER-440 secondary circuits are in the progress of development, it is necessary to draw the needed information by the measurement and analysis of the real samples [1].

2 Experimental

For the experimental measurements, several specimens containing corrosion products were taken from different parts of NPP Bohunice and Dukovany units. The corrosion layers were separated by scraping the rust off the surface from different parts of secondary circuit components and several filter deposits were analysed as well. The room temperature Mössbauer study was performed using Wissel transmission Mössbauer spectrometer with the source ^{57}Co(Rh) matrix. Spectra were fitted using CONFIT [2] and NORMOS program.

3 Results

The advanced evaluation of phase analyses of corrosion products from different parts of VVER-440 steam generators via Mössbauer spectroscopy go over 25 years. The first period (mostly 80-ties) was important for improving Mössbauer technique. The benefit from this period is mostly in experience collection, optimization of measurement condition and evaluation programs improvement [3]. In the period 1994–1999 we focused our study on the comparison of the phase composition of corrosion products taken from the NPP Bohunice before and after changes in the feed water pipeline system. Serious damages were observed in the region of T-junction as well as of pipe-collector and outlet nozzles on many VVER440 SGs after approximately ten years of operation. Therefore, the former feed-water distributing system has been replaced by an advanced feed-water distributing system of EBO design at SGs of NPP Bohunice [4]. After five year's operation in the SG No. 35 in the NPP outage one feed water box and corresponding distributing pipelines were replaced by new ones with the aim to analyse their overall stage and corrosion products on walls. For comparison, some parts of the former feed-water -distributing

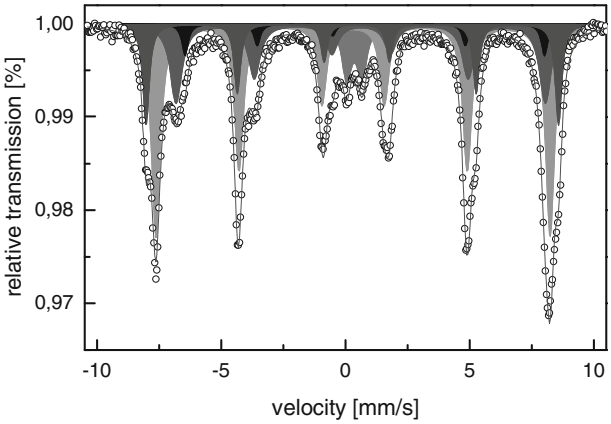

Fig. 1 Mössbauer spectrum of sample 2

system from the SG Number 46 were cut out and analysed. In the period 2002–2003 we focused on the phase analyses of corrosion induced damage of feed water pipelines of SG 16 near the heterogenic weld. In frame of this study visual inspections as well as original "in situ" specimens scrapping was performed. The SG16 was in excellent status with minimal thickness of corrosion layer or other deposits. The dominant phase composition of the studied corrosion products taken from SG11 was magnetite (66,4 % at hot collector, 80,8 % at cold collector). The rest of the magnetic phase is formed by hematite. Minor contribution of paramagnetic doublet was observed, which was assumed to be iron hydrooxides – high probably lepidocrockite. The magnetite presence in all samples is almost stoichiometric (ratio Fe^{3+}/ Fe^{2+} tends to 2.0). Results of these analyses are summarized in our previous work [5].

Recently, six filter deposits from NPP Dukovany were analysed using MS. All measured spectra contains iron in magnetic and also in paramagnetic phases. Another magnetic fraction is hematite. Paramagnetic fractions are presented in the spectra by quadrupole doublets. Their parameters are close to hydroxides (FeOOH) or small, so-called superparamagnetic, particles of iron oxides or hydroxides with the mean diameter of about 10 nm (Fig. 1).

Magnetic phases contain iron in form of nonstoichiometric magnetite $Fe_{3-x}M_xO_4$, where M_x represents impurities and vacancies which substitute iron in octahedral (B) sites. Assuming that the room temperature ratio of the recoil-free fractions f_B/f_A for the B and A sites is 0.97, the intensity ratio β for a perfect stoichiometry should be 1.94 [6].

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. Therefore, the intensity ratio β decreases markedly with the oxidation process, until the stoichiometry reaches the γ-Fe_2O_3 phase. In our samples the intensity ratio β is far from 1.94 (for perfect stoichiometry), varies from 0.47 up to 0.83. On the

other hand, B sites of the magnetite exhibit broad, asymmetric line shape. These observations can be explained by high level of impurities at B sites, probably Cr and Ni, since base steel material contains significant amount of these elements [7]. In order to cover broad, asymmetric line shape of B sites, more than one sextet (1–3) was used in fitting model for B sites.

4 Conclusion

Material degradation and corrosion are serious risks for long-term and reliable operation of NPP. The paper summarises results of long-term measurements of corrosion products phase composition using MS.

The replacement of STN 12022 steel (in Russian NPP marked as GOST 20K) used in the steam generator feed water systems is necessary and very important from the operational as well as nuclear safety point of view. Steel STN 17 247 seems to be optimal solution of this problem.

Regular observation of corrosion/erosion processes is essential for keeping NPP operation on 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 more to magnetite fraction in the corrosion products composition.

Basically, the corrosion of new feed water pipelines system (from austenitic steel) in combination with operation regimes goes to magnetite. The hematite presence is mostly on the internal surface of SG body (constructed from "carbon steel" according to GOST20K).

Recently, filter deposits from NPP Dukovany were analysed using MS. Magnetic phases contain iron in form of nonstoichiometric magnetite (64–81 %) and haematite (15–27 %), parameters of paramagnetic fractions are close to hydroxides or superparamagnetic particles of iron oxides or hydroxides (3–9 %). The intensity ratio β of magnetite is far from 1.94, varies from 0.47 up to 0.83. Also, B sites of the magnetite exhibit broad, asymmetric line shape. High level of impurities is possible explanation, for instance Cr or Ni, since base steel material contains significant amount of these elements. Our results confirm good operational experiences and suitable chemical regimes (reduction environment) which results mostly to creation of magnetite (on the level 64 % or higher) and small portions of haematite and hydroxides. Additional analyses should be performed in order to better describe and explain nonstoichiometry of magnetite observed in Dukovany samples in future.

The long-term study of phase composition of corrosion products at VVER reactors is one of precondition to the safe operation over the projected NPP lifetime. The long-term observation of corrosion situation by Mössbauer spectroscopy is in favour of utility and is not costly.

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