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Corrosion Products Study of VVER-440 Secondary Circuit

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Abstract: The variability of the properties and the composition of the corrosion products of the stainless CrNi and mild steels in dependence on the conditions (temperature, acidity, … etc.) are of such range that, in practice, it is impossible to determine the properties of the corrosion products for an actual case from the theoretical data only. Since the decontamination processes for the materials of the water-cooled reactor (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 specimens. The corrosion layers were separated by scraping the rust off the surface and the powder samples were studied by transmission Mössbauer spectroscopy. It should be noted that the gamma spectroscopic measurements give no evidence of the presence of low-energy gamma radiation emitted from the samples. The ^{57}Co in Rh matrix was used as the radioactive Mössbauer source. Measured spectra were fitted using NORMOS SITE program. According to the results obtained from Mössbauer spectra, it is possible to establish that the main component of secondary circuit's corrosion products is magnetite Fe_3O_4. Next components are hematite alfa-Fe_2O_3 and hydroxide akagenite beta-FeOOH, which is characterized by significant paramagnetic doublet in the middle of the spectra. The sextets corresponding to base materials (martenzite and austenite steels) were identified in all measured spectra. Corrosion distribution and phase composition in form of "corrosion maps" at steam generators as well as other secondary circuit components were created for VVER-440 nuclear power plant in Jaslovske Bohunice (Slovakia). Our study was focused on the ratio magnetite/hematite and ways for operational optimization.

Keywords: Corrosion; VVER; Mössbauer spectroscopy; NPP lifetime.

I. Introduction

Steam generators (SG) are generally among 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. There are several advantages (large amount of cooling water in case of loss of coolant accidents, 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 year 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). New design of this pipeline system was performed, too. Actually, it takes time to evaluate the changes.

The variability of the properties and the composition of the corrosion products of the stainless Cr-Ni and mild steels in dependence on the NPP operating conditions (temperature, acidity, … etc.) are of such range that, in practice, it is impossible to determine the properties of the corrosion products for an actual

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case from the theoretical data only. 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 specimens [1].

II. Mössbauer spectroscopy advantages

The phenomenon of the emission and absorption of a γ-ray photon without energy losses due to recoil of the nucleus and without thermal broadening is known as the Mössbauer effect. Its unique feature is in the production of monochromatic electromagnetic radiation with a very narrowly defined energy spectrum that allows resolving minute energy differences [2, 3].

Mössbauer spectroscopy (MS) is a powerful analytical technique because of its specificity for one single element and because of its extremely high sensitivity to changes in the atomic configuration in the near vicinity of the probe isotopes (in this case ^{57}Fe). MS measures hyperfine interactions and these provide valuable and often unique information about the magnetic and electronic state of the iron species, their chemical bonding to co-ordinating ligands, the local crystal symmetry at the iron sites, structural defects, lattice-dynamical properties, elastic stresses, … etc. [1, 4]. Hyperfine interactions include the electric monopole interaction, i.e., the isomer shift, the electric quadrupole interaction, i.e., the quadrupole splitting and the magnetic dipole or nuclear Zeeman interaction, i.e., hyperfine magnetic splitting. These interactions often enable detailed insight into the structural and magnetic environment of the Mössbauer isotope. Indeed, more than four decades after its discovery (1958), Mössbauer spectroscopy still continues to develop as a sophistic scientific technique and it is often the most effective way of characterizing the range of structures, phases and metastable states.

In general, a Mössbauer spectrum shows different components if the probe atoms are located at lattice positions, which are chemically or crystalographically unequivalent. From the parameters that characterize a particular Mössbauer sub-spectrum, it can, for instance, be established whether the corresponding probe atoms reside in sites which are not affected by structural lattice defects or whether they are located at defect-correlated positions. Each compound or phase, which contains iron, has typical parameters of its Mössabuer spectrum. It means that the method is suitable for quantitative as well as qualitative analysis. Mössbauer spectroscopy is non-destructive and requires relative small quantities of samples (~100 mg) [5-8].

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 neither easy nor straightforward. Thank our more than 25 years of experience in this area, there exists already a base for the relevant evaluation of results. Optimization 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 a new feed water pipeline system. There was also a change in the type of steel of these pipelines. Instead of 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 of austenitic steel according to Czechoslovak norm ČSN, class 17. Advantages of the new construction are not only higher resistance against corrosion, but also much more comfortable visual inspection. Innovations can be seen in Figs. 3-5. Actually, experiences from the past 10 years after upgrade were evaluated.

III. Experimental

For the experimental measurements, several specimens containing corrosion products were taken from different parts of all of the 4 NPP Bohunice units. In the first step, the corrosion process at the steam generators was studied. The corrosion layers were separated by scraping the rust off the surface and the powder samples were studied by transmission Mössbauer spectroscopy. It should be noted that the gamma spectroscopic measurements give no evidence of the presence of low-energy gamma radiation emitted from the samples. Later, the corrosion products were collected also from different parts of secondary circuit components and several filter deposits were analyzed as well.

The room temperature Mössabuer study was performed at two different steam generator materials using conventional transmission Mössbauer spectrometer with the source ^{57}Co in Rh matrix. Spectra were fitted using NORMOS program.

The original STN 12022 material used at the 4th (SG46) over 13 years was compared to STN 17247 steel used at the 3rd unit (SG35) for about 5 years (1994-1998). The chemical composition of both materials is shown in Table 1.

Samples of corrosion products scrapped from different parts of the steam generators SG 35 and SG46 were analyzed. The scrapped corrosion particles were homogenized by granulation and sieved in the wire of 50μm.

TABLE 1. Chemical composition of the investigated base materials.

Steam generator	Type of the steel	Chemical composition [weight %]							
		C	Mn	Si	Cr	Ni	Ti	P	Cu
SG35	STN 17247	max. 0,08	max. 0,08	max. 1,0	17,0 -19,0	9,5 - 12,0	min. 5x%C	max. 0,045	-
SG46	STN 12022 (GOST 20K)	0,16-0,24	0,35-0,65	0,15-0,30	max. 0,25	max. 0,25	-	0,04	max. 0,3

IV. Results from Mössbauer spectroscopy analyses

The advanced evaluation of phase analyses of corrosion products from different parts of VVER-440 steam generators via Mössbauer spectroscopy is our active and unique contribution in this area. The scientific works go over 25 years. The first period (mostly 80-ies) was important for proper Mössbauer technique improving. The benefit from this period is mostly in experience collection, optimization of measurement condition and evaluation programs improvement [5]. Unfortunately, not all specimens were well defined. Having in mind also different levels of techniques and evaluation procedures, it would be not serious to compare results from this period to results obtained from measurements after 1998.

IV.1. Comparison of the phase composition of corrosion products taken from the NPP Bohunice before and after changes in the feed water pipeline system, 1998-1999

In the period 1998-1999, 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.

Schematic drawings of VVER steam generators (SGs) with indicated places of scrapped corrosion specimens are presented in Fig.1.

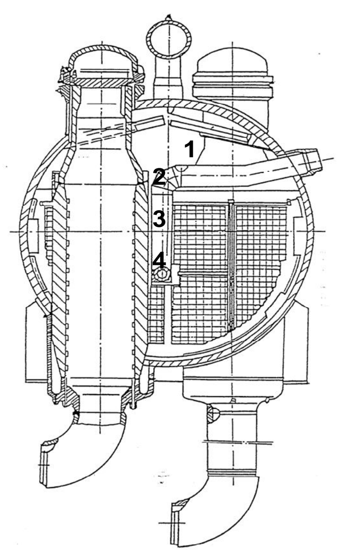

FIG. 1. Cross-section of SG46 (Numbers indicate the places, where the specimens were scrapped).

Serious damages were observed in the region of T-junction (position 4 in Fig.1) as well as of pipe-collector and outlet nozzles on many VVER440 SGs after approximately ten years of operation [9, 17]. Therefore, the former feed water-distributing system has been replaced by an advanced feed water distributing system of EBO design at SGs of NPP Jaslovske Bohunice [18, 19]. The advanced system consists of a V-shaped junction connected to the left and the right part water distributing chambers both located above the tube bundle and few feed water boxes with water ejectors inserted into the tube bundle and connected to the distributing chamber by distributing pipelines.

After five year operation in the SG 35 in the NPP outage one feed water box and the corresponding distributing pipelines were replaced by new ones with the aim to analyze their overall stage and corrosion products on the walls. For comparison, some parts of the former feed water distributing system from the SG 46 were cut out and analyzed.

More than 50 specimens were collected from the NPP Bohunice secondary circuit in 1998-2000. The investigation was focused mainly on the corrosion process going on in steam generators SG35 with new design and SG46 with old design. Nevertheless, additional measurements performed on the corrosion products from SG31 and SG32 confirmed that the corrosion process in all 6 steam generators of one reactor unit is the same and the corrosion layers are on the same places altogether identical.

All measured specimens comprise iron in magnetic and many times also in paramagnetic phases. Magnetic phases consist in form of nearly stoichiometric magnetite (γ-Fe_3O_4), hematite (α-Fe_2O_3), and in some cases also iron carbides. The paramagnetic fractions are presented in Mössbauer spectra by doublets and singlets. Its parameters are close to hydro-oxide (FeOOH) parameters or to parameters of small so-called superparamagnetic particles of iron oxides (hydroxides) with the mean diameter of about 10 nm (see Table 2 and Table 3).

MS confirmed its excellent ability to identify steel specimens phase composition in spite of their sawdust form and relative small amount (~ 100 mg). Our experiences with such measurements were published in [16, 20-22]. MS confirmed an austenitic structure of STN 17247 steel and ferrite structure of STN 12022 steel.

Results confirmed that during operation time a very weak oxidation surrounding was in the observed steam generator SG35 after 5 years of operation time and the corrosion specimens were fully without base material particles.

Magnetite was identified as dominant component in all studied specimens (see Table 2). Mössbauer spectrum of the steam generators (both SG35 and SG46) surface layer is the superposition of two sextets with hyperfine magnetic field H_{efA} = 49,4T and H_{efB} = 45.8T. Sextet H_{efA} corresponds to the Fe^{3+} ions in tetrahedral (A) sites and sextet H_{efB} corresponds to Fe^{2+} and Fe^{3+} ions in octahedral (B) sites in magnetite spinel structure (Fe_3O_4).

TABLE 2. MS parameters of corrosion products taken from the steam generator SG35.

	Magnetite					Doublet			Singlet	
Sample	H_A	A_{rel}	H_B	A_{rel}	r_{AB}	IS	QS	A_{rel}	IS	A_{rel}
	(T)	(%)	(T)	(%)	(a.u.)	(mm/s)	(mm/s)	(%)	(mm/s)	(%)
L754	49.0	35.0	45.9	65.0	0.538					
L755	49.0	35.3	45.9	64.7	0.546					
L757	49.0	34.8	45.9	65.2	0.534					
L758	49.0	34.1	45.9	62.3	0.547				-0.20	3.6
L789	49.0	34.4	46.0	65.6	0.535					
L790	49.0	34.9	46.0	64.3	0.543				-0.18	0.8
L759	49.0	35.4	45.9	63.9	0.534				-0.20	0.7
L777	49.0	35.0	45.9	65.0	0.538					
L786	49.0	35.2	46.0	64.8	0.545					
L787	49.1	36.5	46.0	56.1	0.651	0.22	0.67	2.0	-0.20	5.4
L760	49.0	34.1	45.9	64.3	0.530				-0.17	1.6
L761	49.0	35.0	45.9	63.9	0.547				-0.23	1.1
L762	49.1	34.8	46.0	56.4	0.617				-0.20	8.8
L779	49.0	33.4	45.9	62.9	0.531				0.10	3.7
Accuracy	±0,1	±0,5	±0,1	±0,5		±0,04	±0,04	±0,5	±0,04	±0,5

In contrast to magnetite, whose spectrum is characterized by two sextets, the hematite phase present in the powders produces one sextet. The relatively narrow line width (Γ) of the α-Fe_2O_3 (mainly 0, 24 ÷ 0, 26 mm/s) indicates the presence of a well-crystallized phase with few, if any, substitutions of other elements for Fe. However, in some spectra (mainly from filter deposits studied later) both the lower hyperfine field and the larger width (about 0.33 – 0.34 mm/s) could indicate a poorer crystallinity and/or a higher degree of substitution. These findings are in good agreement with those obtained by E. De Grave [23].

For the ideal stoichiometric Fe_3O_4, the quantity r_{AB} (ratio between A and B sub-component areas) is equal to 0.535. In the case that magnetite is the dominant (sole) phase in the specimen, the deviation from the ideal value of r_{AB} is minimal (see Table 3). Significant deviations could be explained by a small degree of oxidation of magnetite, resulting in the presence of vacancies or substitution by non/magnetic irons in the octahedral sub-lattice. Slight substitution of other elements (Mg, Ni, Cu, …) for Fe in the magnetite lattice is not unlikely, and this has a similar effect on the A- to B-site area ratio. Therefore, it is not feasible to conclude anything quantitatively about the degree of oxidation. Qualitatively, it can be inferred that this degree must be very low.

During visual inspection of the removed feed water dispersion box (1998, Fig. 2.), 2 disturbing undefined metallic particles, fixed in one of the outlet nozzles, were found. Both were homogenized and analyzed by MS. It has been shown that these high-corroded parts ("loose parts" found in the outlet nozzle of the ejector) originate not from the 17247 steel but high probably from GOST 20K steel (probably some particles from the corrosion deposit from the bottom part of the steam generator moved by flow and ejection effect into the nozzle).

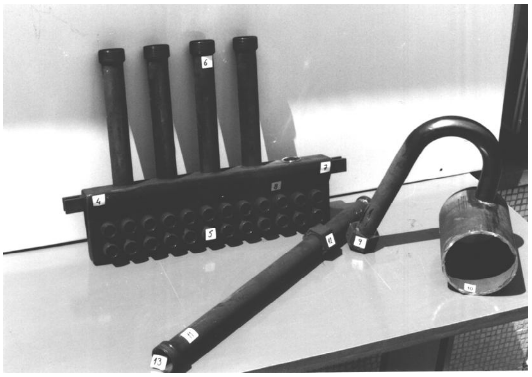

FIG. 2. Position of corrosion product scraps from the feed water dispersion box (SG35).

TABLE 3. MS parameters of corrosion products taken from the steam generator SG46.

CODE	Hematite		Magnetite				Base material				Doublet 1		Doublet 2	
	H1	A_{rel}	H_A	A_{rel}	H_B	A_{rel}	H4	A_{rel}	H5	A_{rel}	IS1	A_{rel}	IS2	A_{rel}
	(T)	%	(T)	%	(T)	%	(T)	%	(T)	%	(mm/s)	%	(mm/s	%
M005			49.0	35.4	45.8	64.6								
M006			49.1	36.5	45.9	63.5								
M007	50.0	16.9	49.2	25.6	45.8	38.2	33.0	1.6					0.84	17.7
M008			49.0	35.6	45.9	64.1								
M009	51.5	13.4	49.1	32.1	45.9	54.5								
M010			49.1	36.5	45.8	63.5								
M012	51.5	12.5	49.2	31.9	46.0	55.6								
M013			48.8	25.3	45.7	40.5	33.0	30.2	30.8	4.0				
M014			49.0	9.9	45.8	13.6	33.0	66.6	30.7	9.9				
M015			48.5	6.0	45.6	8.6	33.0	73.1	30.6	12.3				
Accuracy	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5

Mössbauer measurements on the corrosion specimens scrapped from different positions of the feed water distributing system (see Fig.10) have shown that the outside layer consists exclusively from magnetite but the inside layer contains also hematite. Its amount decreases in successive steps towards into the steam generator. The origin of this result is probably the fact that outside the system there is boiling water at a temperature of approximately 260 °C with higher salt concentration and inside there is the feed water at a temperature up to 225 °C. Changes in the inside temperature in the region (158-225 °C) can occur in dependence on the operation regime of high-pressure pumps in the NPP secondary circuit.

The most corroded areas of the former feed water distributing system are welds in the T-junction (see Fig. 3). Due to dynamic effects of the feed water flow with local dynamic overpressures of 20 to 30 kPa or local dynamic forces up to 1000 N (in the water at the pressure of about 4,4 MPa) on the inner pipe wall in the region of T-junction, the content of corrosion products was reduced and moved into the whole secondary circuit. Particles of the feed water tube of SG46 base material were identified also in sediments.

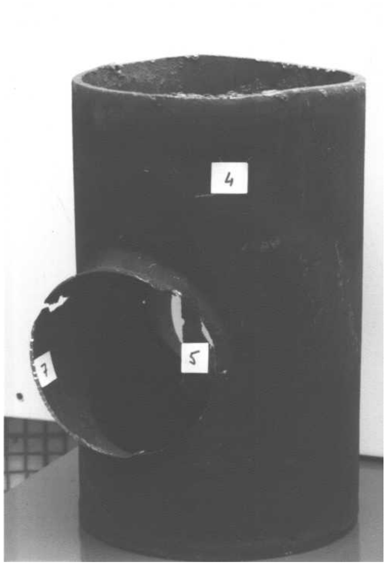

FIG. 3. Position of corrosion product scraps from the feed water dispersion tube (SG46).

IV.2. Results from visual inspection of heterogenic weld at SG16 from April 2002

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 the frame of this study, visual inspections as well as original "in situ" specimens scrapping were performed. Conclusions from visual inspections (performed at 19.4.2002 and 29.4.2002 at SG16) were as follows:

SG16 was dried under the level of primary pipelines bundle. The whole SG was decontaminated as there were lead plates on the upper part of the pipelines bundle due to maximal shielding effect. During the visual inspection of SG16 internal surface as well as hot and cold collectors (after 23 years of operation), no defects or cracks were identified. SG16 was in excellent status with minimal thickness of corrosion layer or other deposits. For comparison to our previous experiences from visual inspections from 1998, SG16 was in better condition than SG35 or SG46 (14 and 13 years in operation, respectively). Beside this, the radiation situation after decommissioning procedures was twice better.

Visual inspection on 29.4.2002 was focused on heterogenic weld, which connects the feed water pipeline from carbon steel (GOST 20K) to the new feed water pipeline system designed from austenitic steel (CSN17248). Several specimens were taken for MS analysis from the weld as well as the surrounding area in the from of powder or small particles (samples description is in Table 4). The heterogenic weld was well polished.

After visual inspection, the evaluation of corrosion phase composition of specimens close to heterogenic weld was performed. Places, where specimens were taken are shown in Fig. 4. Specimens description and MS results are summarized in Tables 4 and 5.

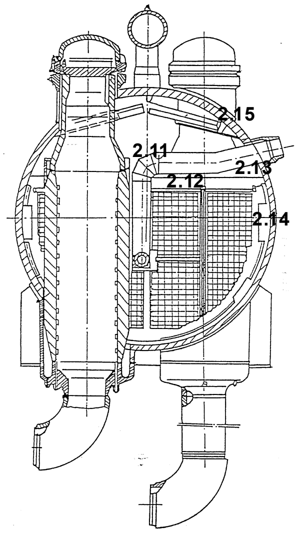

FIG. 4. SG16 cross-section with indicated places where specimens were taken.

TABLE 4. Specimens description.

Number of sample	Sample description
2.11	Heterogenic weld.
2.12	Feed water pipeline (GOST 20), 10 cm from the heterogenic weld.
2.13	Feed water pipeline (GOST 20), about 40 cm from the heterogenic weld, just close to the SG16 internal body surface.
2.14	Internal body surface, about 1 m under the place of feed water pipeline inlet.
2.15	Internal body surface, about 50 cm over the place of feed water pipeline inlet.

TABLE 5. Mössbauer spectra parameters.

	Haematite				Magnetite					
Sample	H_1 (T)	QS_1 (mm/s)	IS_1 (mm/s)	A_{rel1} (%)	H_2 (T)	IS_2 (mm/s)	A_{rel2} (%)	H_3 (T)	IS_3 (mm/s)	A_{rel3} (%)
2.11	51,9	-0,18	0,25	8,0	49,0	0,17	3,8	45,9	0,57	8,0
2.12	51,6	-0,21	0,26	75,9	49,0	0,16	9,1	45,8	0,56	14,1
2.13	51,6	-0,21	0,26	77,2	49,0	0,17	9,2	45,9	0,57	12,9
2.14	51,6	-0,21	0,26	41,1	49,0	0,16	22,0	45,8	0,55	36,9
2.15	51,8	-0,21	0,26	51,7	49,1	0,17	18,3	45,9	0,54	29,2
Accuracy	±0,1	±0,04	±0,04	±2	±0,1	±0,04	±0,1	±0,1	±0,04	±2

	Metallic iron			Doublet/singlet		
Sample	H_4 (T)	IS_4 (mm/s)	A_{rel4} (%)	QS_4 (mm/s)	IS_4 (mm/s)	A_{rel4} (%)
2.11	33,0	-0,11	12,8	-	-0,19	67,4
2.12	-	-	-	0,40	0,21	0,9
2.13	-	-	-	0,40	0,21	0,7
2.14	-	-	-	-	-	-
2.15	-	-	-	0,40	0,21	0,8

IV.3. Measurement of corrosion products at NPP Jaslovske Bohunice, 2007-2008

In 2007 – 2008, six samples for Mössbauer effect experiments collected from different parts of NPP Bohunice unit, were prepared by crushing to powder pieces (Table 5). These samples consist of corrosion products taken from the small coolant circuit of pumps (sample no. 3.1), deposits scraped from filters after filtration of SG - feed water during operation (sample no. 3.2), corrosion products taken from SG42 pipelines - low level (sample no. 3.3), mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42 (sample no. 3.4), deposit from filters after refiltering 340 l of feed water of SG S3-09 during passivation on 27. and 28. 5. 08 (sample no. 3.5) and finally deposit from filters after refiltering 367 l of feed water of SG S4-09 during passivation on 27. and 28. 5. 08 (sample no. 3.6). All samples were measured at room temperature in transmission geometry using a ^{57}Co(Rh) source. Calibration was performed with α-Fe. Hyperfine parameters of the spectra including spectral area (A_{rel}), isomer shift (*IS*), quadrupole splitting (*QS*), as well as hyperfine magnetic field (B_{hf}), were refined using the CONFIT fitting software [24], the accuracy values in their determination are of ±0.5 % for relative area A_{rel}, ±0.04 mm/s for Isomer Shift and Quadrupole splitting and ±0.5 T for hyperfine field, correspondingly. Hyperfine parameters for the identified components (hematite, magnetite, goethite, lepidocrocite, feroxyhyte) are taken from [25].

All measured spectra contain iron in magnetic and many times also in paramagnetic phases. Magnetic phases contains iron in nonstoichiometric magnetite $Fe_{3-x}M_xO_4$, where M_x represents impurities and vacancies which substitute iron in octahedral (B) sites. Another magnetic fraction is hematite α-Fe_2O_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 crystallized form with low degree (or without) substitution. Both the substitution and the presence of small superparamagnetic particles make the situation more complicated [26]. 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 an external magnetic field [27].

Mössbauer spectrum (Fig. 5) of sample no. 3.1 (corrosion products taken from small coolant circuit of pumps) consists of three magnetically split components, where the component with hyperfine field B_{hf} = 35.8 T was identified as goethite (α-FeOOH). Hyperfine parameters of the remaining two magnetically split components are assigned to A – sites and B – sites of magnetite (Fe_3O_4). One paramagnetic spectral component has appeared. According to water environment and pH [28], this component should be assigned to hydroxide (feroxyhyte δ-FeOOH).

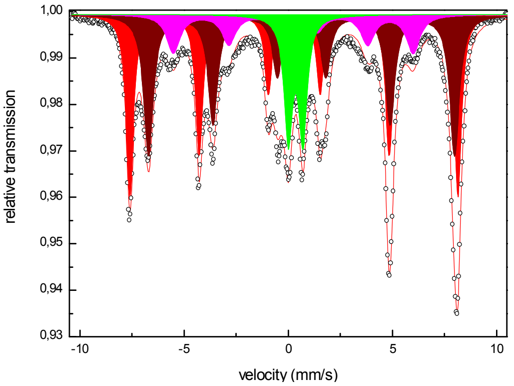

FIG. 5. Mössbauer spectrum of sample no. 3.1. A-site (red), B-site (dark red) magnetite, goethite (pink) and hydroxide (green) were identified.

Sample no. 3.2 (deposits scraped from filters after filtration of SG - feed water during operation) also consists of three magnetically split components, where two of them were assigned to magnetite (Fe_3O_4) as in previous spectra, and the remaining magnetically split component was identified as hematite (α-Fe_2O_3). Paramagnetic part of the spectra was formed by one doublet, which was hyperfine parameters assigned to hydroxide (lepidocrocite γ-FeOOH). The spectrum is shown in Fig. 6.

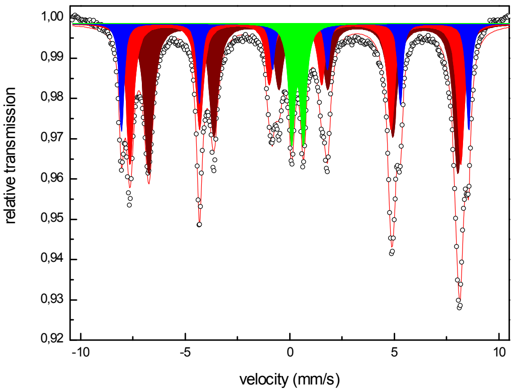

FIG. 6. Mössbauer spectrum of sample no.3. 2. A-site (red), B-site (dark red) magnetite, haematite (blue) and hydroxide (green) were identified.

The spectrum (Fig. 7) of sample no. 3.3 (corrosion products taken from SG42 pipelines - low level) consists only of two magnetically split components with hyperfine parameters assigned to A – sites and B – sites of nearly stoichiometric magnetite (Fe_3O_4) with a relative area ratio β = 1.85.

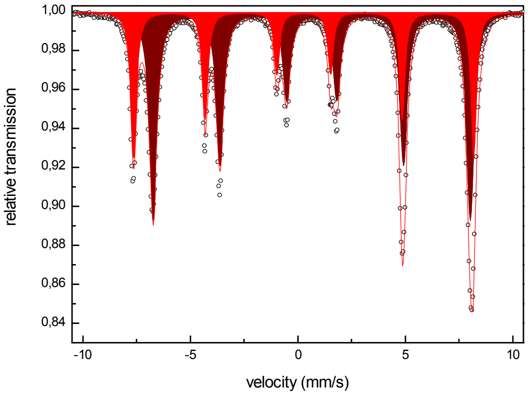

FIG. 7. Mössbauer spectrum of sample no. 3.3. A-site (red) and B-site (dark red) magnetite were identified.

Sample no. 3.4 (mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42) also consists of one magnetically split component which corresponds to hematite (α-Fe_2O_3) and two magnetically split components which were assigned to magnetite (Fe_3O_4) as in previous spectra, and the remaining paramagnetic component was identified as hydroxide. Spectrum of sample no. 3.4 is shown in Fig. 8.

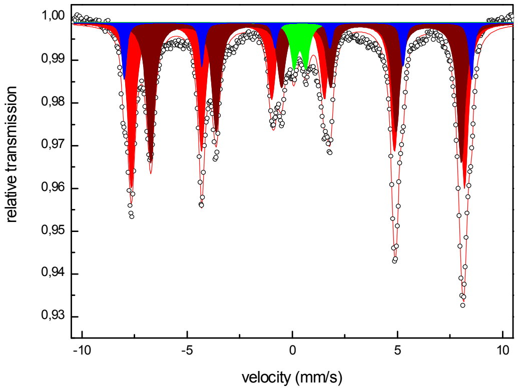

FIG.8. Mössbauer spectrum of sample no. 3.4. Haematite (blue), A-site (red), B-site (dark red) magnetite and hydroxide (green) were identified.

Both sample no. 3.5 (deposit from filters after refiltering 340 l of feed water of SG S3-09 during passivation on 27. and 28. 5. 08) and sample no. 3.6 (deposit from filters after refiltering 367 l of feed water of SG S4-09 during passivation on 27. and 28. 5. 08) consist of three magnetically split components, identified as hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) and the remaining paramagnetic component in both spectra was assigned to hydroxide (lepidocrocite γ-FeOOH). Spectra of samples no. 3.5 and 3.6 are shown in Figs. 9 and 10.

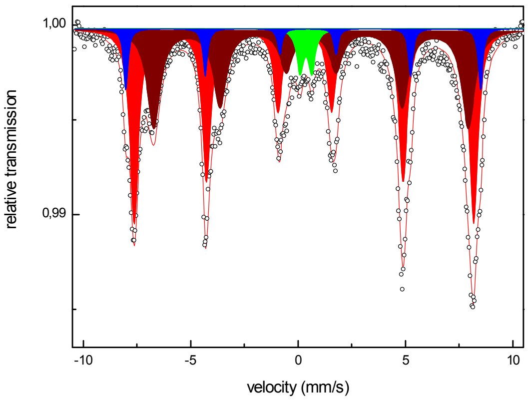

FIG. 9. Mössbauer spectrum of sample no.3.5. Haematite (blue), A-site (red), B-site (dark red) magnetite and hydroxide (green) were identified.

Based on the comparison of results from specimens 3.5 and 3.6, it can be concluded that longer passivation leads more to magnetite fraction (from 88% to 91%) in the corrosion products composition. As it was mentioned above, all hydroxides could be also small superparamagnetic particles.

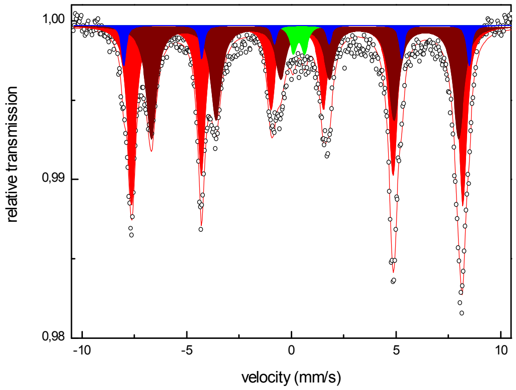

FIG. 10. Mössbauer spectrum of sample no. 3.6. Haematite (blue), A-site (red), B-site (dark red) magnetite and hydroxide (green) were identified.

The refined spectral parameters of individual components including spectral area (A_{rel}), isomer shift (*IS*), quadrupole splitting (*QS*), as well as hyperfine magnetic field (B_{hf}) are listed in Table 6 for room (300 K) temperature Mössbauer effect experiments. Hyperfine parameters for identified components (hematite, magnetite, goethite, lepidocrocite, feroxyhyte) are listed in [25].

Major fraction in all samples consists of magnetically ordered iron oxides, mainly magnetite (apart from samples no. 3.1 and 3.2, where also goethite and hematite 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 tetrahedral 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 an 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^{3+} 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 the octahedral B - sites. Fe^{2+} and Fe^{3+} are indistinguishable due to a 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^{3+} ions and eight Fe^{2+} and 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 stoichiometry. Assuming that the room temperature ratio of the recoil-free fractions fB/ fA for the B - and A - sites is 0.97 [29], the intensity ratio β for perfect stoichiometry should be 1.94. 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 the 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$_2$O$_3$ phase. It should be noted that in our samples the intensity ratio β is far from 1.94 (for perfect stoichiometry), it varies from 0.97 up to 1.85.

TABLE 6. Spectral parameters of individual components including spectral area (A_{rel}), isomer shift (IS), quadrupole splitting (QS), as well as hyperfine magnetic field (B_{hf}) for each sample with the corresponding components.

Sample	Components	Area [%]	Isomer shift [mm/s]	Quadrupole shift/splitting [mm/s]	Hyperfine field [T]
Sample no. 3.1 Small coolant circuit of pumps 17. 10. 2007	magnetite A-site	36.3	0.28	0.00	48.90
	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. 3.2. Deposites scraped from filters after filtration of SG - feed water during operation	hematite	15.8	0.38	-0.23	51.56
	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. 3.3. SG42 pipelines - low level	magnetite A-site	34.6	0.28	0.00	49.14
	magnetite B-site	65.4	0.65	0.00	45.83
Sample no. 3.4. Mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42	hematite	9.2	0.38	-0.22	51.29
	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. 3.5. Deposit from filters after refiltering 340 l of feed water of SG S3-09 during pasivation 27. and 28. 5. 08	hematite	8.3	0.36	-0.22	51.33
	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. 3.6. Deposit from filters after refiltering 367 l of feed water of SG S4-09 during pasivation 27. and 28. 5. 08	hematite	6.4	0.38	-0.25	51.26
	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	-

IV.4. Measurements of corrosion products from thermal loop in Nuclear Research Institute Řež, Czech Republic, 2010

Corrosion layers taken from testing pipelines of thermal loop in Nuclear Research Institute Řež (Czech Republic) were analyzed using Mössbauer spectroscopy. Thermal loop is used for chemical regimes evaluation of steam-water cycles and simulates the local environment of primary circuits of VVERs.

Corrosion layers from cut pieces of pipelines were scraped and powdered (Fig. 11.), then measured at room temperature in transmission geometry using a ^{57}Co(Rh) source. Calibration was performed with α-Fe. Hyperfine parameters of the spectra including spectral area (A_{rel}), isomer shift (IS), quadrupole splitting (QS), as well as hyperfine magnetic field (B_{hf}), were refined using the CONFIT fitting software [24], the accuracy values in their determination are of ±0.5 % for relative area A_{rel}, ±0.04 mm/s for isomer shift and Quadrupole splitting and ±0.5 T for hyperfine field, correspondingly.

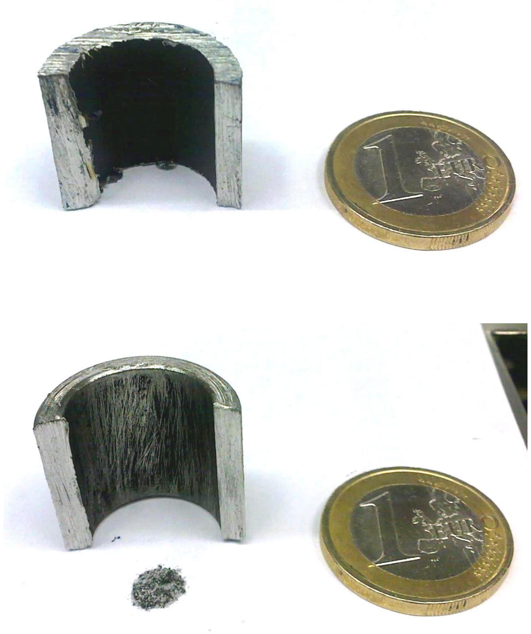

FIG. 11. Cut piece of pipeline (up), with scraped corrosion layer (bottom).

Measured spectra of scraped layers mostly consist of one singlet and magnetically split components with significant hyperfine field distribution. Singlet represents the austenitic fraction of base steel material of pipelines, magnetically split components with hyperfine field distribution were identified as martensitic fraction of base steel material. In some spectra, a small fraction of two magnetically ordered components has appeared. According to their spectral parameters, these components were assigned to magnetite A - and B - sites (Fig. 12).

From corrosion point of view, no other than magnetite component was revealed, which indicates a suitable local environment in the thermal loop of the research reactor in Řež.

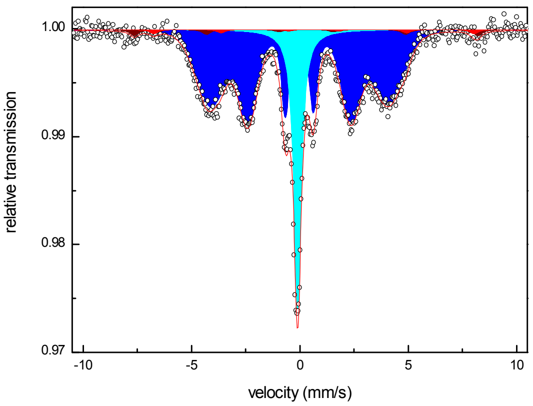

FIG. 12. MS spectrum of scraped corrosion layer. Austenitic fraction (light blue) and martensitic fraction (blue) came from base steel material, a small amount of magnetite (red, dark red) can also be seen.

V. Conclusions

Material degradation and corrosion are serious risks for long-term and reliable operation of NPP. The paper summarizes results of long-term measurements (1984-2008) of corrosion products phase composition using Mössbauer spectroscopy.

The first period (mostly results achieved in the 80-ies) was important for proper Mössbauer technique improving [5]. The benefit from this period came via experience collection, optimization of measurement conditions and evaluation programs improvement. Unfortunately, the specimens were not well defined, and having in mind also different levels of techniques and evaluation procedures, it would be not serious to compare results from this period to results obtained from measurements after 1998.

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 proved 5 years in operation at SG35 seems to be the optimal solution of this problem. Nevertheless, periodical inspection of the feed water tubes corrosion (after 10, 15 and 20 years) was recommended.

Based on the results of visual inspection performed on April 19, 2002 at SG16 (NPP V1), it was confirmed, that the steam generator was in well condition also after 23 years of operation. Specimens taken from the internal body surface of PG16 confirmed that hematite concentration increases in the vertical direction (from the bottom part to the top one).

Results from 2008 confirm good operational experiences and suitable chemical regimes (reduction environment), which results mostly from the creation of magnetite (on the level of 70% or higher) and small portions of hematite, ghoetite or hydroxides.

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

Differences in hematite and magnetite contents in corrosion layers taken from hot and cold collectors at SG11 in 2004 have shown that there is a significant lower presence of magnetite in case of hot collector. This fact can be devoted from 2 parallel factors: (i) difference in temperature (about 298°C – HC) and (about 223°C - CC) and mostly due to (ii) higher dynamics of secondary water flowing in the neighbourhood of hot collector, which high probably remove the corrosion layer from the collector surface.

With the aim to summarize our results in the form suitable for daily use in the operational conditions, a "corrosion map" was created (see Fig. 13). Corrosion products phase composition (limited to magnetite and hematite only) is presented in the form of circular diagrams.

Basically, the corrosion of new feed water pipelines system (from austenitic steel) in combination to operation regimes (as at SG35 since 1998) goes to magnetite. In specimens taken from positions 5 to 14 (see Fig. 13 – right corner), the hematite presence is mostly on the internal surface of SG body (constructed from "carbon steel" according to GOST 20K). Its concentration increases towards the top of the body and is much significant in the same part of SG where flowing water via erosion removes the corrosion layer better than from the dry part of the internal surface or the upper part of the pipeline.

The long-term study of phase composition of corrosion products at VVER reactors is one of the preconditions 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. Based on the achieved results, the following points could be established as an outlook for the next period:

1. In collaboration with NPP-Bohunice experts for operation as well as for chemical regimes, several new additional samples from not studied places should be extracted and measured by Mössbauer spectroscopy with the aim to complete the existing "corrosion map".
2. Optimization of chemical regimes (having in mind the measured phase composition of measured corrosion specimens from the past) could be discussed and perhaps improved.
3. Optimization and re-evaluation of chemical solutions used in cleaning and/or decommissioning processes during NPP operation can be considered.

In connection to planned NPP Mochovce 3, 4, commissioning announced officially for 2013, it is recommended that all feed water pipelines and water distribution systems in steam generators should be immediately replaced before putting in operation by new ones constructed from austenitic steels. The Bohunice design with feed water distribution boxes is highly recommended.

Acknowledgement

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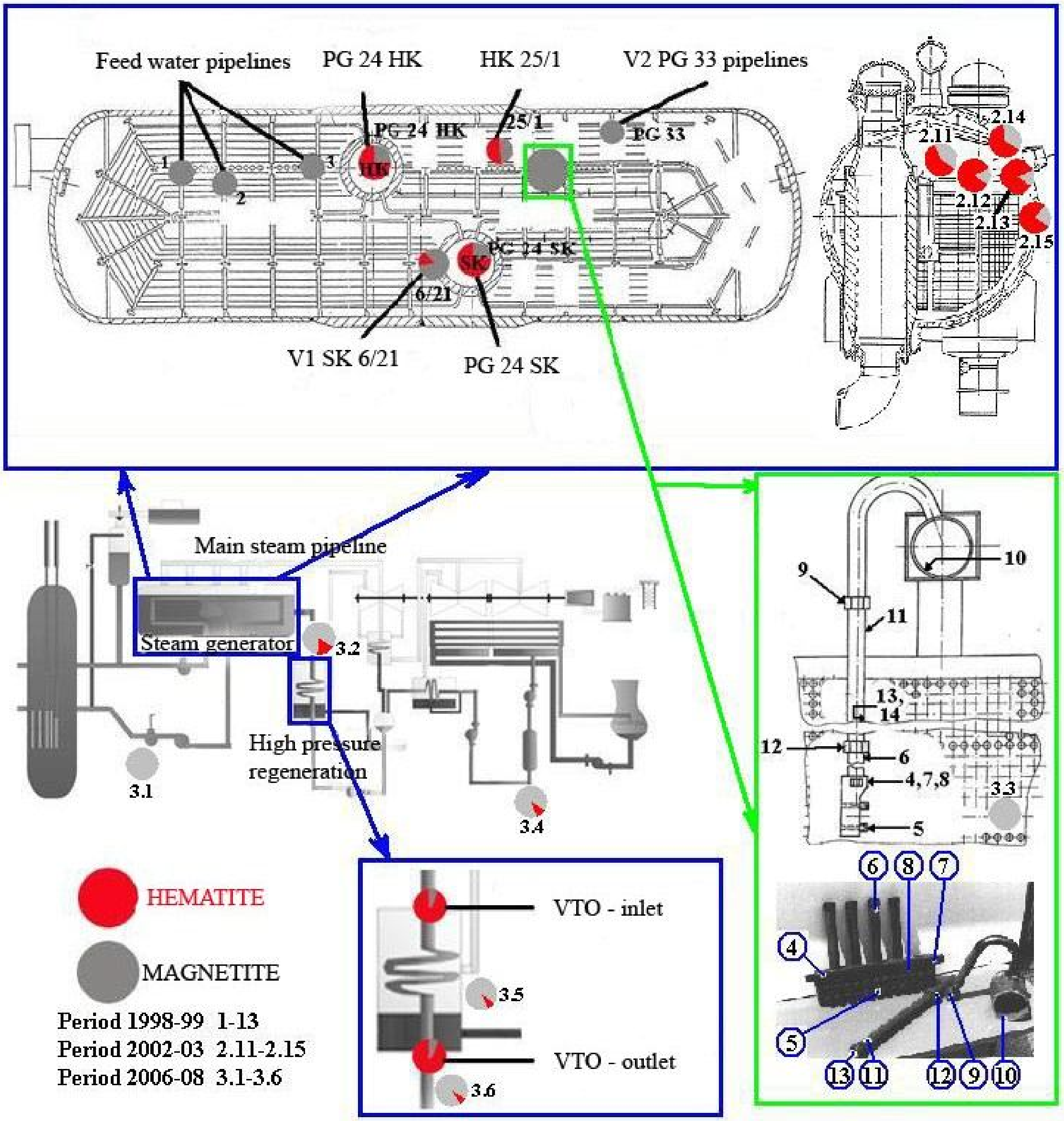

FIG. 13. "Corrosion map" of NPP V-2 Bohunice (Slovakia) performed according to results from period 1998-2008.

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