

VVER OPERATIONAL EXPERIENCE – EFFECT OF PRECONDITIONING AND PRIMARY WATER CHEMISTRY ON RADIOACTIVITY BUILD-UP

M. ZMÍTKO¹, J. KYSELA¹, K. DUDJAKOVÁ¹,
M. MARTYKÁN², J. JANEŠÍK², V. HANUS², P. MARCINSKÝ³

¹NUCLEAR RESEARCH INSTITUTE REZ PLC, 250 68 HUSINEC-REZ, CZECH REPUBLIC, zmi@ujv.cz

²ČEZ-E TE, NPP TEMELÍN, 373 05 TEMELÍN, CZECH REPUBLIC

³SE-EMO, NPP MOCHOVCE, 935 39 MOCHOVCE, SLOVAKIA

ABSTRACT *The primary coolant technology approaches currently used in VVER units are reviewed and compared with those used in PWR units. Standard and modified water chemistries differing in boron-potassium control are discussed. Preparation of the VVER Primary Water Chemistry Guidelines in the Czech Republic is noted. Operational experience of some VVER units, operated in the Czech Republic and Slovakia, in the field of the primary water chemistry, and radioactivity transport and build-up are presented. In Mochovce and Temelín units, a surface preconditioning (passivation) procedure has been applied during hot functional tests. The main principles of the controlled primary water chemistry applied during the hot functional tests are reviewed and importance of the water chemistry, technological and other relevant parameters is stressed regarding to the quality of the passive layer formed on the primary system surfaces. The first operational experience obtained in the course of beginning of these units operation is presented mainly with respect to the corrosion products coolant and surface activities. Effect of the initial passivation performed during hot functional tests and the primary water chemistry on corrosion products radioactivity level and radiation situation is discussed.*

1. INTRODUCTION

VVER units differ significantly from Western designed PWRs and originate from a separate design and development history. Two major designs are in operation or under construction in Europe and Asia, the 6-loop design rated at 440 MWe and the 4-loop design rated 1000 MWe. At present more than 40 VVER-type units are operated in seven countries and number of units is under construction.

Materials inventories used in VVER units differ from that at PWRs. All surfaces of the primary circuit with the primary coolant are either made from or plated with stainless steel (austenitic, titanium stabilized stainless steel, equivalent to 321 SS, is used). Standard Russian fuel has Zr-1%Nb clad and Zr or SS spacer grids. The fuel assembly of VVER-440 units has Zr-2.5%Nb outer sheath. Components from Stellite hard facing alloys are not used at VVER stations. Some of these stations have antimony/graphite in the main coolant pump seals.

Also VVER primary coolant technology differs from that at PWRs: potassium is used as main alkalizing agent (small amount of sodium as an impurity and lithium growing during the cycle from nuclear reaction is present in the coolant) and hydrogen formed due to radiolytic processes is kept in specified range by ammonia dosing. Nevertheless, main objectives of the VVER primary coolant chemistry are the same as at PWRs: to assure primary system pressure boundary integrity, fuel cladding integrity and to minimize out-of-core radiation fields. The principles mentioned above were applied at development of the VVER Primary Water Chemistry Guidelines [1].

2. PRIMARY COOLANT TECHNOLOGY

As in PWRs, VVER's chemistry has to ensure alkaline reducing conditions in the primary system during the normal operation. Several modifications of VVER primary coolant chemistry which differ in the way how the boron-potassium coordination is controlled during the cycle (standard and modified chemistry) and in way how

hydrogen is produced and maintained in the coolant (ammonia, hydrazine and hydrogen chemistry) have been applied.

2.1. Standard Water Chemistry This water chemistry was developed in late 70s and was intended to be a constant pH regime, however, the pHs were calculated according to old Meek method which is now known to give an error in high-temperature pH_T determination. This type of boron/potassium control is still used at some VVER plants.

2.2. Modified Water Chemistry In the beginning of 90s, instead of the „Standard Water Chemistry“ has been developed and introduced „Modified Water Chemistry“ which ensures the constant pH_T and stable physical-chemical conditions during the whole reactor cycle what should reduce radiation fields. The choice of the optimal pH_T was a result of the plant data analysis as well as of the mathematical modelling. For VVER-440 units the pH_{300} in range of 7.1-7.3 and 7.0-7.2 for VVER-1000 was chosen as an optimum. This type of water chemistry has been introduced at many plants (e.g. Dukovany and Temelín in the Czech Republic, Bohunice in Slovakia, and at Russian and Ukrainian plants). At the same time, utilities specify different maximum potassium level allowed (20 ppm at the Czech, Russian and Ukrainian units; 16.4 ppm at Bohunice). Boron/potassium co-ordination for the standard and modified chemistries of VVER-440 and VVER-1000 units are given in Fig.1 and Fig.2. Typical high-temperature pH course during the reactor cycle for the standard and modified chemistries are shown in Fig.3.

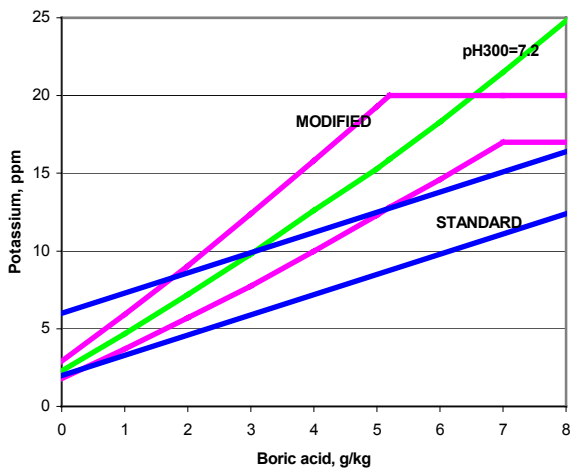


Fig. 1 Boron/potassium co-ordination for the standard and modified water chemistry of VVER-440 units

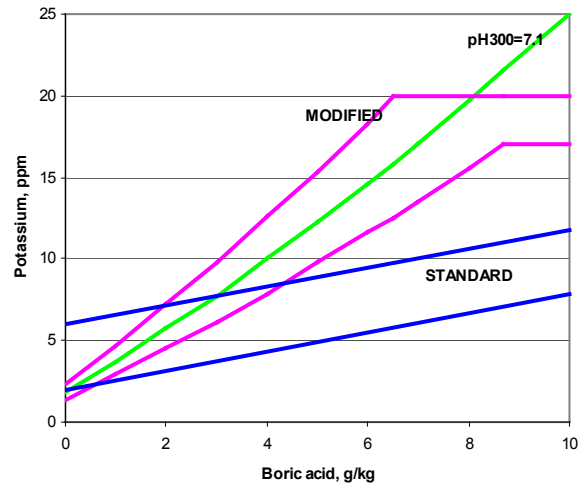


Fig. 2 Boron/potassium co-ordination for the standard and modified water chemistry of VVER-1000 units

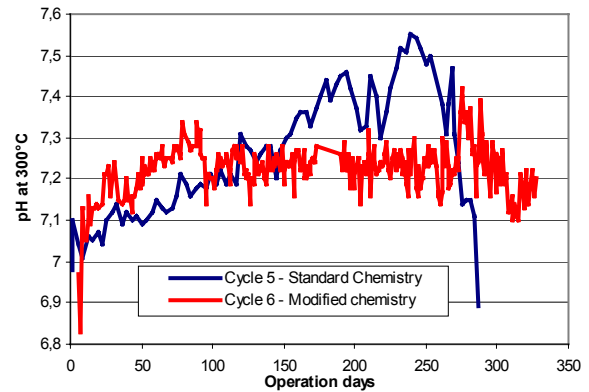


Fig. 3 Typical pH_{300} course of the standard and modified water chemistries during the reactor cycle (VVER-440 unit)

2.3. Ammonia Water Chemistry There are different approaches in VVERs how reduction conditions in the coolant are established. Normally, ammonia is dosed into the primary coolant with make-up water and due to its radiolytical decomposition hydrogen concentration is maintained in the reactor water. Except hydrogen also gaseous nitrogen is produced. It means that radiolytical production of hydrogen depends on reactor power what differs from PWR practice where gaseous hydrogen is dosed through volume control tank and is not affected by reactor operation. Typical ammonia concentration in the VVER primary coolant ranges in 10-15 ppm and resulting hydrogen concentration in 25-35 Nml/kg. Last years there is a trend to reduce hydrogen concentration down to 20 Nml/kg (Dukovany, Temelín units).

2.4. Hydrazine Water Chemistry Except ammonia hydrazine is also used to achieve hydrogen concentration in the primary coolant. In this case, hydrazine is continuously fed into the coolant where it is decomposed due to thermolytic and radiolytic processes to ammonia, hydrogen and nitrogen. Hydrazine water chemistry was developed with the aim to reduce radioactivity build-up on the primary surfaces. It was firstly demonstrated at Russian's Kola plant. At present, hydrazine water chemistry is used at Paks units in Hungary. Mechanism of hydrazine influence on corrosion products transport and radioactivity build-up is not yet fully understood.

Hydrazine water chemistry is accompanied by higher ammonia and hydrogen level compared to ammonia chemistry. Ammonia lies in range of 30-40 ppm, hydrogen fluctuates in range of 40-60 Nml/kg.

2.5. Hydrogen Water Chemistry Direct hydrogen gas dosing is considered as a new VVER coolant technology approach which should avoid ammonia usage in the primary coolant causing problems with liquid radioactive wastes, ion exchange resins operation and pH control. For this reason a special injection technology has been developed. There is an intention to implement hydrogen injection technology at Southukrainian NPP.

2.6. VVER Primary Water Chemistry Guidelines Taking into account obtained operational experience in VVER units as well as the best world practice the VVER Primary Water Chemistry Guidelines have been developed in the Czech Republic by Nuclear Research Institute Rez [1].

Table 1. VVER water chemistry specification for reactor power operation (control parameters)

Control parameter	Sampl. Frequency	Typical value	Action level		
			1	2	3
Chlorides, ppm	3xW	<0.05	-	>0.1	>1.0
Fluorides, ppm	3xW	<0.05	-	>0.1	>1.0
Sulphates, ppm	3xW	<0.05	-	>0.1 5	>1.0
Oxygen, ppb	OLM	<5	>5	>10	>100
Hydrogen, Nml/kg	OLM	20-40	<20; >40	<10; >50	<5
Total alkalinity as potassium, mmol/kg	3xW	Related to pH ₃₀₀	-	>0.5	-
pH at 300°C	calculation	7.1-7.3 ¹⁾ 7.0-7.2 ²⁾	<7.1; >7.3 <7.0; >7.2	<6.9; >7.5	-

¹⁾ for VVER-440 units

²⁾ for VVER-1000 units

The Guidelines formulate requirements for the primary water chemistry parameters (control and diagnostic parameters) and their monitoring, including appropriate action levels for start-up, nominal operation and shut-down (see Tables 1, 2).

Table 2. VVER water chemistry specification for reactor power operation (diagnostic parameters)

Diagnostic parameters	Sampling frequency	Typical value
pH at 25°C	1xD	5.7-10.2
Conductivity, µS/cm	1xD	25-125
Boric acid, g/kg	1xD	As required for reactivity control
Ammonia, ppm	1xD	>5
Suspended solids, ppm	1xW	<0.1
Silica (SiO ₂), ppm	1xW	<1.0

3. OPERATIONAL EXPERIENCE

Two units of VVER-440 at NPP Mochovce in Slovakia and two units of VVER-1000 at NPP Temelín in the Czech Republic were commissioned in past years. The hot functional tests (HFT) were conducted at controlled primary water chemistry with the aim to develop a protective passive film on the primary circuit surfaces. Special water chemistry guidelines were developed and implemented at this period. Also, some surveillance samples (corrosion coupons) were placed into the primary circuit and subsequently analyzed to obtain information about characteristics of the formed passive film.

In general, development of a stable protective passive film on the RCS surfaces requires the water chemistry conditions as close as possible to those at normal operation, i.e. alkaline-reduction conditions in the case of VVER units. Only in such a way it is possible to avoid any transformations of the passive film and loss of its protective features at further operation of the unit. Except the controlled water chemistry, a stability of technological parameters (temperature, pressure) during HFT, utilization of a purification system and sufficient time period are another key factors affecting development of proper passive film.

3.1. Hot Functional Tests

3.1.1 Technological aspects

Commissioning of the VVER units consists of two major parts: flushing and cold hydrostatic testing, and HFT. The HFT are performed with stainless steel fuel assembly imitators in the core, at pressures and temperatures close to the nominal (260°C/12.3 MPa for VVER-440 units and 285°C/15.7 MPa for VVER-1000). There was no boric

acid added at any stage of the tests. In contrast to PWRs, there is no technology for gaseous hydrogen dosing into the primary coolant in VVERs. (At normal VVER unit operation hydrogen in the coolant is formed by radiolytical decomposition of ammonia). Surveillance corrosion coupons were placed in the reactor pressure vessel (RPV) for further analysis of the developed passive film.

3.1.2 Water chemistry specification

Water chemistry specification for the HFT stage of both VVER-440 and 1000 is given in Table 3.

Table 3. Water chemistry specification for period of HFT of VVER-440 and VVER-1000 units

Parameter	Limit	Note
pH @ 25°C	5.6-7.5	Before KOH dosing
pH @ 25°C	9-10.5	After KOH dosing
pH @ 300°C (calculated)	6.9-7.5	After KOH dosing
Cl ⁻ and F ⁻ , ppm	<0.1	
K ⁺ , ppm	2-5	After KOH dosing
O ₂ , ppm	<0,02	At >120°C
SiO ₂ , ppm	<0,2	
Suspended solids, ppm	<0,2	
H ₂ , Nml/kg	2-5	Expected level

Main principles of the water chemistry control are summarized as follows:

- Hydrazine is added into make-up water at temperature above 60°C to reduce dissolved oxygen in the coolant. Only stoichiometric amount of hydrazine is required to avoid its surplus in the coolant and ammonia formation. According to results of EPRI experiments focused on a study of various surface treatment technologies [2], the surface preconditioning at presence of ammonia and hydrazine results in formation of thick, porous, low-compact passive layer which has higher, in comparison with other preconditioning technologies, corrosion release and Co60 activity pick-up.
- Ammonia dosing is not recommended for the same reason as mentioned in the above paragraph.
- Coolant pH is adjusted by KOH dosing so that pH value related to 300°C lies in range of 6.9-7.5, i.e. potassium concentration should be in range of 2-5 ppm. KOH dosing is started at temperatures above 170°C to promote the Schikorr reaction (2) of transformation of iron hydroxide to magnetite

$$\text{Fe (s)} + 2 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2\text{(s)} + \text{H}_2 \quad (1)$$

$$3 \text{Fe(OH)}_2 \text{(s)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} + 2 \text{H}_2\text{O} + \text{H}_2 \quad (2)$$
- Reduction conditions in the coolant are adjusted by both very low concentration of dissolved oxygen and hydrogen produced by the corrosion reaction of structural material with the coolant. To keep a sufficient

hydrogen level in the coolant, thermal degasification that is normally utilized during the unit's operation should not be operated during HFT.

- Purification system(s), based on the ion exchange resins technology in VVER-440 units, and on the ion exchange resins and high-temperature mechanical filtration technologies in VVER-1000 units, should be continuously in operation at maximum flow rate in order to remove corrosion products circulated in the primary coolant.

3.2. Operation Experience during HFT The hot functional tests with the controlled passivation stage have been applied at NPP Mochovce, units 1 & 2 (EMO-1 and EMO-2), and at NPP Temelín, units 1 & 2 (ETE-1 and ETE-2). The main technological parameters, including operational mode of the purification system(s), and water chemistry parameters during the HFT are summarized in Table 4.

Table 4. Technological and water chemistry parameters during HFT at various units

Parameter	EMO-1	EMO-2	ETE-1	ETE-2
Duration at temp., hrs	140	260	320	240
Temp., °C	255-265	258-265	280-285	275-295
Pressure, MPa	12.2-12.3	12.2-12.3	15.5-15.7	15.5-15.7
Purification systems	Ion exchange resins; flow rate 25-38 m ³ /h		High-temp. mechanical filtration 240-280 m ³ /h; ion exchange resins 15-25 m ³ /h	
Purification system operation	Not continual 46 hrs	Whole HFT	Whole HFT	Whole HFT
pH at 25°C	9.5-10.5	9.5-10	9-10.9	9.3-10.2
K ⁺ , ppm	6.0±3.5	3.6±1.4	4.6±4.6	4.1±1.8
H ₂ , Nml/kg	3.2±2.3	2.0±1.1	12.2±5.1	5.6±2.3
O ₂ , ppb	<10	3-9	1-2	2-4
NH ₃ , ppm	0.2-2	0.5-4	0.05-0.4	<0.1
SiO ₂ , ppm	<0.02	n.a.	0.05-1	0.1-2

It was noted that dissolved hydrogen concentration strongly depends on amount of potassium. The higher the potassium dosed the higher the hydrogen concentration. Also, the coolant temperature effect was noticed from the comparison between the Mochovce and Temelín units: more hydrogen was produced in Temelín due to higher temperature and higher intensity (rate) of the corrosion reaction.

There was also evidence that concentrations of corrosion products in the coolant are lower in the case of Temelín units. This fact can be explained by a presence of high-temperature filtration of the coolant at VVER-1000 units. The highest concentration of corrosion products and

impurities was observed in Mochovce-1 unit that is probably related to the limited utilization of purification system. The results also indicate that concentration of soluble iron is very close to the solubility limit of magnetite and nickel-ferrite at given conditions (1-5 ppb).

3.3. Passivation Layer Investigation Surveillance corrosion coupons placed in the RPV during HFT were used to determine the quality of the passive film formed on the primary surfaces. SEM/EDX and XRD techniques were employed to study morphology, chemical and phase composition. It was identified that corrosion layers in Temelín units consist of two spinels with different lattice parameters. Elemental composition of corrosion layer corresponds to formulas from $(\text{Ni}_{0.05}\text{Fe}_{0.8}\text{Cr}_{0.15})_3\text{O}_4$ to $(\text{Ni}_{0.1}\text{Fe}_{0.6}\text{Cr}_{0.3})_3\text{O}_4$. In all cases, the coupons were covered by a layer of loose crud that was formed by small, well-developed crystals of 1-2 μm size (see Figure 4). Thickness of this crud layer differed from case to case and lay typically in range of 1-3 μm . Well-developed passive film was observed only on coupons from Temelín units. In Mochovce the passive film thickness was below a resolution limit of SEM (0.1 μm). A typical view of passive film is shown in Figure 5. It can be seen that the passive film has a rather uniform and compact structure with typical thickness of $0.6 \pm 0.1 \mu\text{m}$.

3.4. Radiation Situation After the HFT power operation of the units started. Up to now, several reactor cycles have been completed at both EMO and ETE units. During the cycles a standard monitoring of water chemistry parameters was performed, as well as monitoring of corrosion products concentrations and radioactivities in the primary coolant. Also, *in-situ* γ -spectrometry measurement was performed on the primary piping during the units shut-down.

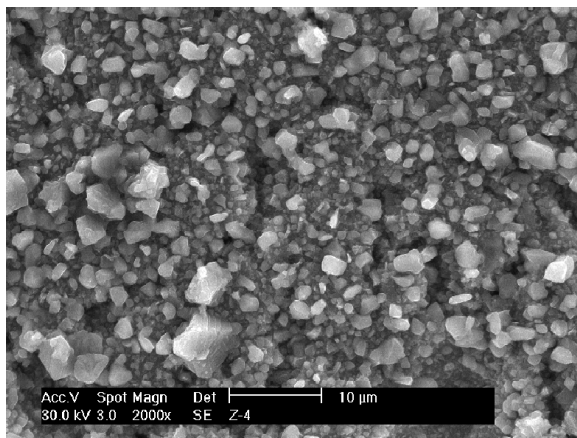


Fig. 4. A typical view of corrosion layer covering an outer surface of the surveillance corrosion coupons

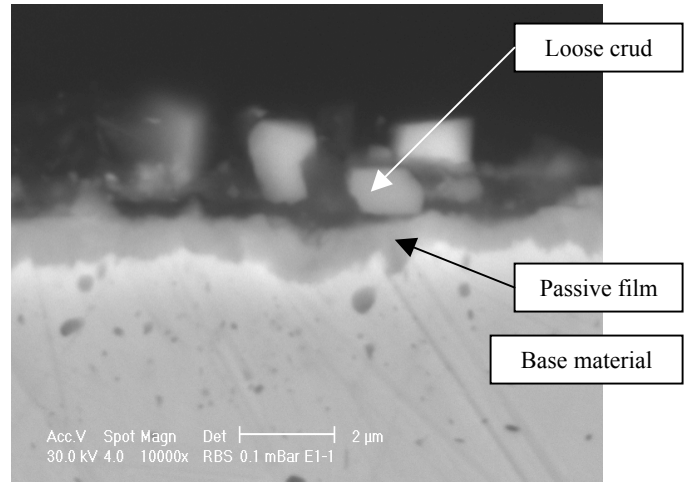


Fig. 5. A typical view of cross section of corrosion layers formed on surveillance coupons from ETE-1 and ETE-2 units. Passive film is apparent below the layer of loose crud

Results of the *in-situ* γ -spectrometry measurements on the hot and cold primary piping of EMO-1, EMO-2, ETE-1 and ETE-2 units are presented in Figure 6. Comparison of radioactivity of Mn54 in the primary coolant of Mochovce and Temelín units is shown in Figure 7. It can be seen that higher level of corrosion product radionuclides is attributed to EMO-1 unit. Both the surface and coolant activities differ significantly in the case of Mn54 and Co58. These radionuclides produced from Fe by nuclear reaction of $\text{Fe}54(n,p)\text{Mn}54$ and from Ni by reaction of $\text{Ni}58(n,p)\text{Co}58$ provide direct information about the efficiency of the passive film on the inner surfaces.

It is believed that radiation situation observed in these units is closely connected with the passivation stage performed during the hot functional tests. The way how the units were operated during the reactor cycles was rather similar and can not be a reason for the different radiation situation. Passivation in the case of EMO-1 lasted relatively shortly and due to technical problems the purification system was in operation only for a limited time. This is assumed to be as a main reason for the worse radiation situation at EMO-1 unit. Corrosion products released massively into the coolant during passivation stage had not been removed and during the subsequent operation of the reactor they were activated and redistributed around the primary circuit.

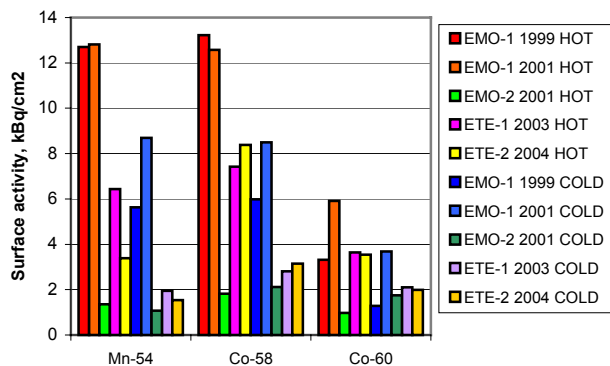


Fig. 6. Surface activities of selected radionuclides measured on the hot and cold primary piping of Mochovce and Temelin units

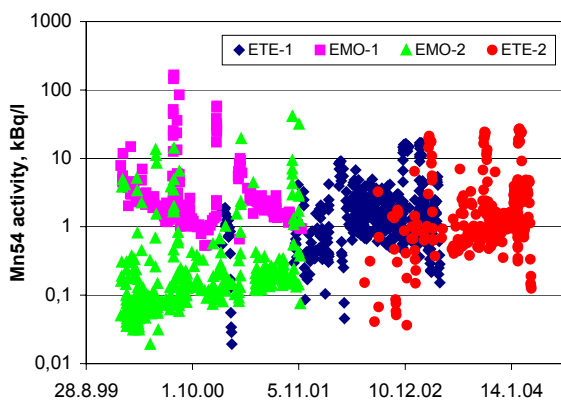


Fig. 7. Radioactivity of Mn54 in the primary coolant of Mochovce and Temelin units

4. CONCLUSIONS

VVER units are operated in mixed boron-potassium-ammonia water chemistry. Several modifications of the water chemistry, differing in boron-potassium coordination and in the way how hydrogen concentration is produced and maintain in the coolant, are used. From the operational experience point of view VVER units do not show any significant problems connected with the primary coolant chemistry.

The obtained operational experience demonstrated that the controlled water chemistry is a suitable method to form a protective passive film on the primary circuit surfaces during the hot functional tests. Quality of the passive film depends on duration of the passivation stage in the frame of the hot functional tests, on the stability of technological (temperature and pressure) and water chemistry parameters, and on proper utilization of the primary coolant purification system.

The elemental and phase composition of the corrosion and passive film formed on the inner surfaces corresponds with current understanding of stainless steel corrosion mechanisms at elevated temperatures [3,4]. The corrosion film formed on inner surfaces has the spinel structure and elemental composition corresponds to formulas from $(\text{Ni}_{0.05}\text{Fe}_{0.8}\text{Cr}_{0.15})_3\text{O}_4$ to $(\text{Ni}_{0.1}\text{Fe}_{0.6}\text{Cr}_{0.3})_3\text{O}_4$. The protective passive film developed is enriched in chromium in comparison with the base material. On the other hand, the loose crud circulated in the coolant and deposited on the surfaces contains much less chromium relative to iron.

It is believed that radiation situation observed in Mochovce and Temelin units is closely connected with the way how the passivation stage had been performed during the hot functional tests. The main reason for the worse radiation situation observed at Mochovce-1 unit was shorter passivation stage and limited utilization of the primary coolant purification system. Thus, corrosion products released during passivation had not been removed and were activated and redistributed around the primary circuit during the subsequent reactor operation.

REFERENCES

- [1] M. Zmítko, K. Splíchal, VVER-440 and VVER-1000 primary water chemistry guidelines, NRI report Z 872, November 2002.
- [2] H. Ocken, Surface treatment to reduce radiation fields; Test loop studies and plant demonstrations, EPRI report NP-5209-SR, April 1988.
- [3] J. Robertson, *Corr. Sci.*, **29**, 11/12, p.1275, 1989.
- [4] D. H. Lister et al., *Corr. Sci.*, **27**, p.113, 1987.