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**Recommended Reactor Coolant Water Chemistry Requirements for
WWER-1000 Units with ²³⁵U Higher Enriched Fuel**

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1. Introduction

The last decade worldwide experience of PWRs and WWERs confirms the trends for the improvement of the nuclear power industry electricity production through the implementation of high burn-up or high fuel duty, which are usually accompanied with the usage of UO₂ fuel with higher content of ²³⁵U – 4.0% – 4.5% (5.0%). By the realization of these approaches for economic performance improving in some PWRs in USA, France, Korea, etc. a series of fuel issues with safety significance have been experienced. The main of these unexpected fuel issues after M.S. Chatterton [1] are Incomplete control rod insertion (IRI) events, Axial Offset Anomaly – AOA (Crud Induced Power Shift -CIPS), high crud buildup and higher oxidation levels.

It was concluded that the onset of sub-cooled nucleate boiling (SNB) on the fuel cladding surfaces and the initial excess reactivity of the core are the primary and basic factors accompanying the implementation of uranium fuel with higher ²³⁵U content, aiming extended fuel cycles and higher burn-up of the fuel in Pressurized Water Reactors. As main consequences of the presence of these factors the modifications of chemical / electrochemical environments of nuclear fuel cladding- and reactor coolant system- surfaces are evaluated. [2] These conclusions are the reason for:

- The determination of the choices of the type of fuel cladding materials in respect with their enough corrosion resistance to the specific fuel cladding environment, created by the presence of SNB;
- The development and implementation of primary circuit water chemistry guidelines ensuring the necessary low corrosion rates of primary circuit materials and limitation of cladding deposition and out-of-core radioactivity buildup;
- Implementation of additional neutron absorbers which allow enough decrease of the initial concentration of H₃BO₃ in coolant, so that its neutralization will be possible with the permitted alkalizing agent concentrations.

2. WWER-1000 Reactors in Nuclear Power Plant Kozloduy – Bulgaria.

At Kozloduy NPP Bulgaria, WWER-1000 reactors (typeV 320), produced in former Soviet Union / Russia) are in operation since 1988 – plant Unit 5 and 1993 – plant Unit 6.

WWER-1000 reactors are also in operation in Russia, Ukraine, Czech Republic, People's Republic of China and Iran. All WWER-1000 reactors are Soviet Union or Russian production, excluding NPP Temelin WWER-1000 units which are Czech production.

A comparison of the main plant parameters of WWER-1000 reactors and Westinghouse-supplied PWRs can be found in Table 1 [3].

Table 1. Plant parameter comparison

Plant parameter		Westinghouse-supplied PWRs		WWER-1000
Thermal power	MW _{th}	2 775	3 411	3 000
Number of coolant loops	-	3	4	4
Number of fuel assemblies	-	157	193	163
Core equivalent diameter	m	3.04	3.37	3.17
Core volume	m ³	26.6	32.6	28.7
Core uranium loading (U)	Mg	67-72	82-88	80.9
Core power density	kW.L ⁻¹	105	105	105
Core specific power	kW.kg ⁻¹	38-41	38-41	37
Core temperature rise	°C	36	36	32.6

The specific features of WWER-1000 units in Bulgarian Nuclear Power Plant are:

- The steam generators with austenitic stainless steel 08Cr18N10T tubing;
- The steam generators are with horizontal straight tubing;
- The fuel elements cladding material is Zr-1%Nb (Zr1Nb) alloy - recent trade name E 110;
- As a main neutron absorber is applied dissolved in coolant boric acid (with natural ¹⁰B content);
- As a pH control agent in the reactor coolant, potassium hydroxide is introduced (the high temperature coolant values – pH_T = pH₃₀₀ are the main criteria determining the applied alkalizing reagent quantity necessary for the neutralization of boric acid in the coolant); The values of pH₃₀₀ are required to be in the range of pH₃₀₀ = 7,0 - 7,2 for the entire operation period; Practically, as it is shown in Figure 1 [4], the buildup of lithium (⁷Li), based on the neutron reaction: ¹⁰B (n, α) → ⁷Li (n, α), takes place during the entire period of the cycle and even makes up a significant part of the total alkalizing ion concentration in the coolant;
- The necessary for the suppressing of radiolysis process, quantity of hydrogen in the primary circuit, is generated by radiolysis of the specially injected NH₃ in the coolant.

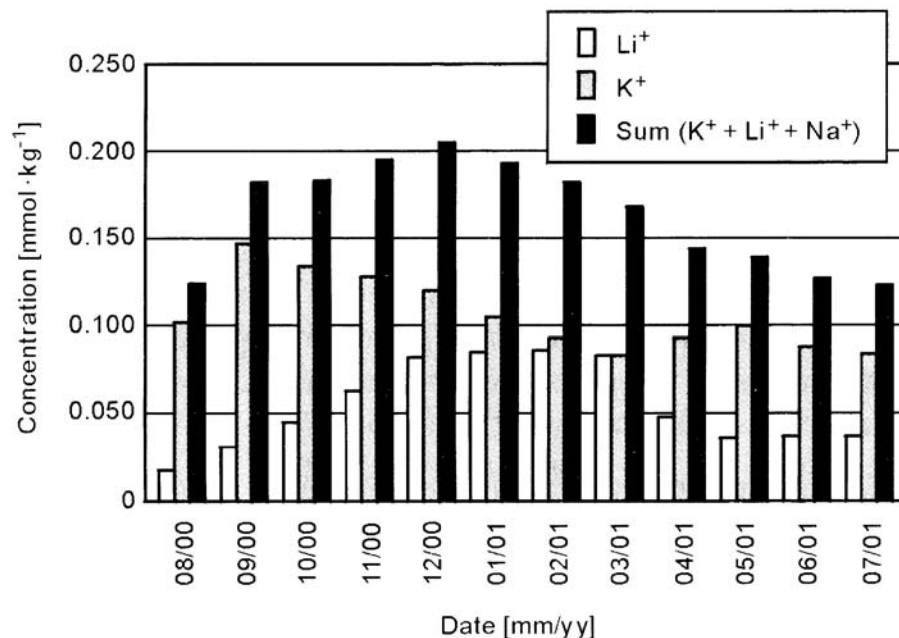


Fig. 1 Change in the coolant Li⁺, K⁺, and total alkalinizing ion concentrations (monthly average values) [4]

3. Use of ²³⁵U higher enriched fuel in the WWER-1000 reactors in the Nuclear Power Plant Kozloduy.

In accordance with worldwide trends for the improvement of the nuclear power industry electricity production through the implementation of more highly enriched ²³⁵U uranium fuel, the management of NPP Kozloduy decided to introduce more highly enriched (up to 4,3%) ²³⁵U fuel in plant Units 5 & 6 (WWER-1000). This process was carried out over the course of four 12-month fuel cycles, by the implementation of advanced fuel assemblies of the type TVSA [5], imported from Russia – JSC TVEL Co, which have uranium fuel with up to 4,3% ²³⁵U enrichment. A solid burnable absorber (Gd) is integrated into the TVSA fuel – uranium-gadolinium (U-Gd₂O₃) fuel – with 5% Gd₂O₃.

The full implementation of the TVSA fuel was realized step by step, in accordance with a coordinated program between Kozloduy NPP and JSC TVEL.

The 15-th fuel cycle of Unit 5, NPP Kozloduy, was the first fuel cycle after the finalization of the step-by-step introduction of ²³⁵U higher enriched fuel, realized through the implementation of TVSA advanced fuel assemblies. [6]

The operation practice of Unit 5, NPP Kozloduy over all four fuel cycles during which ²³⁵U higher enriched fuel was introduced step-by-step, was considered by us, taking into account M.Chatterton [1] assumption of the US PRWs practice which shows that “the higher duty cores (usually by implementation of more highly enriched ²³⁵U fuel) are always accompanied by increased boiling mainly on the feed fuel assemblies, and that the fuel cladding deposits tend to accumulate to the greatest extent in the higher sub-cooled nucleate boiling (SNB) regions of the core.”

Subsequently, K. Garbett et al [7], [8] explained that “The boiling in the core causes a change in the type, thickness, and composition of deposits (a change in composition from a standard nickel ferrite based crud, to one that is dominated by nickel oxide formation.)”

This established change in the deposits’ composition - the nickel oxide formation was the reason for our [9] opinion that the sub-cooled nucleate boiling (SNB) has a significant impact on the chemical environment of the Pressurized Water Reactor’s fuel cladding. After our conclusions [9] this effect is not a direct consequence of the boiling but is a result of local (at cladding surfaces) stripping out of dissolved in coolant hydrogen which favors local water radiolysis. By this water radiolysis process, the local oxidants: hydrogen peroxide (H_2O_2) together with some radiolytical water radicals are produced.

It was concluded that this change in cladding environment from reducing to oxidizing is in fact a consequence of the synergic impact of the boiling- and water radiolysis-processes on the Pressurized Water Reactor fuel cladding surfaces.[9]

By absence of SNB in WWER reactors, the liquid coolant radiolysis is practically full suppressed by the enough excess of diluted hydrogen in the coolant.

Our conclusion of the role of SNB for the physical-chemical environment change of the fuel cladding surfaces found a similar interpretation through computer calculations made by Arkhipov and Kabakchi [10]. After these authors “Still, thermal-hydraulic calculations of reactor plants with high power WWER show that volume boiling of coolant single jets is possible in the top part of reactor core under design power operating conditions. Result of formation of two-phase environment can be growth of concentration of oxidizers in the coolant due to both reduction of hydrogen concentration in a liquid phase as a result of an outlet of gases in steam bubbles, and thermoradiolytical processes in the steam phase”.

The above mentioned change in the fuel cladding environment characteristics creates a need for new criteria for corrosion resistance properties of fuel cladding materials in the presence of sub-cooled nucleate boiling. These materials should have high corrosion resistance due to this general change in the fuel cladding chemical environment.

The selection and implementation of such fuel cladding materials ensure a necessary precondition for both cladding material corrosion- and cladding autochthonic corrosion product deposition- prevention.

Long-years WWER operation practice indicates that the Russian alloy Zr1Nb (E 110) used as fuel cladding material has the necessary corrosion resistance under the real reactor operating conditions.

After the available information, only the French alloy M5 has shown the properties similar to the E 110 alloy. The data presented in Figure 2 [11] confirm this statement.

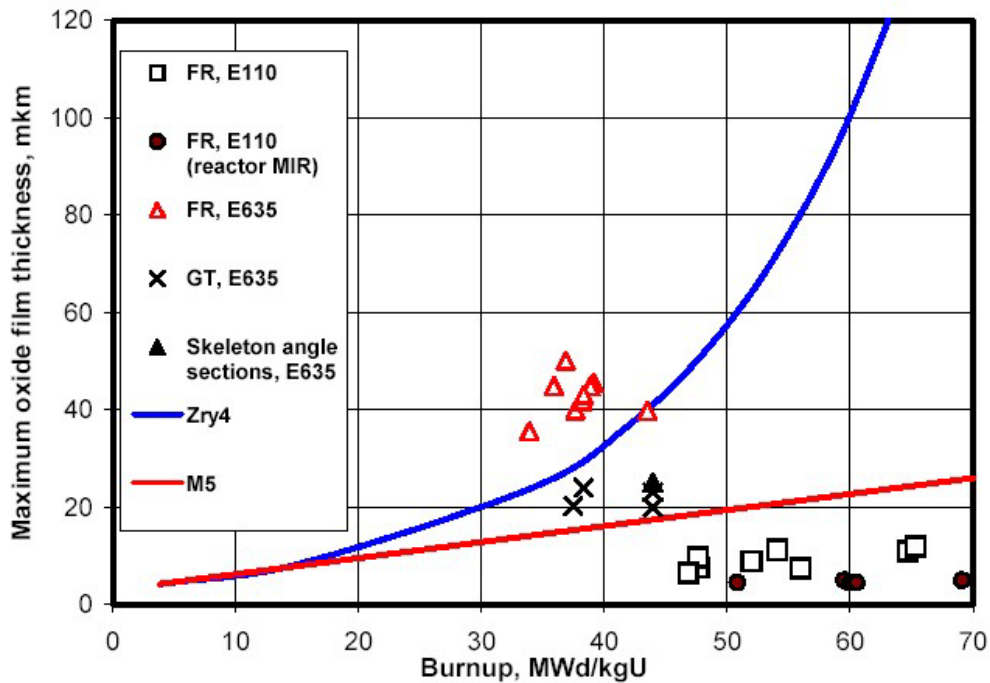


Fig.2 Maximal oxide film thickness as a function of fuel burnup [11]

As these figure's data indicate, the application of alloys E 110, or M5 ensures the significant reduction of cladding surface autochthonic corrosion product deposition (oxide thickness – 5-10 μ m). (Under these conditions the boron hideout and neutron flux depression will be restricted, and the Axial Offset Anomaly onset will be prevented.)

This conclusion shows how unrealistic the long supported opinion of core designers actually has been that AOA problems can be eliminated by primary circuit water chemistry changes without changes in the fuel cladding materials.

The sub-cooled nucleate boiling (SNB) depends on the core duty. Its effect (change in the cladding chemical environment) is determined by the degree of local water radiolysis (at cladding surfaces). The corrosion damages and autochthonic deposit formation under these conditions depend mainly on the cladding material properties and can not be influenced by the coolant water chemistry characteristics.

Correctness requires it to be noted that primary coolant water chemistry plays a significant role in the depression of ex-core corrosion processes because the increase in corrosion product concentration in the coolant will increase the risk of occurrence of crud deposits (not autochthonic) on the cladding surfaces.

Corrosion processes in the primary circuit, corrosion product transport and activated coolant corrosion product characteristics depend directly on the coolant water chemistry and out-of-core construction materials.

For the WWER-1000 reactors the supplier developed and recommended for implementation (years 2000-2001) water chemistry primary circuit guidelines which ensure the depression of ex-core material corrosion processes, so that the coolant corrosion product concentration and coolant activated corrosion products to be significant and enough limited. The significant requirement of this coolant water chemistry is the keeping of the relation between coolant boric acid concentration and coolant total

alkalizing agent concentration so that the coolant pH_{300} to be $pH_{300} = 7.0-7.2$ throughout the entire operation period. These requirements, expressed in compact form in Figure 3 require the high temperature coolant pH values: $pH_{(300)}=7.0$; $pH_{(300)}=7.1$; $pH_{(300)}=7.2$ (**Area A**, in Fig.3) to be kept, using the necessary coolant alkalizing agent concentrations, corresponding to the actual coolant boric acid concentrations.

The required relations between these parameters are expressed in compact form in Fig.3 and in Table 2, in which the reactor operation levels as functions of the limit's deviations are given.

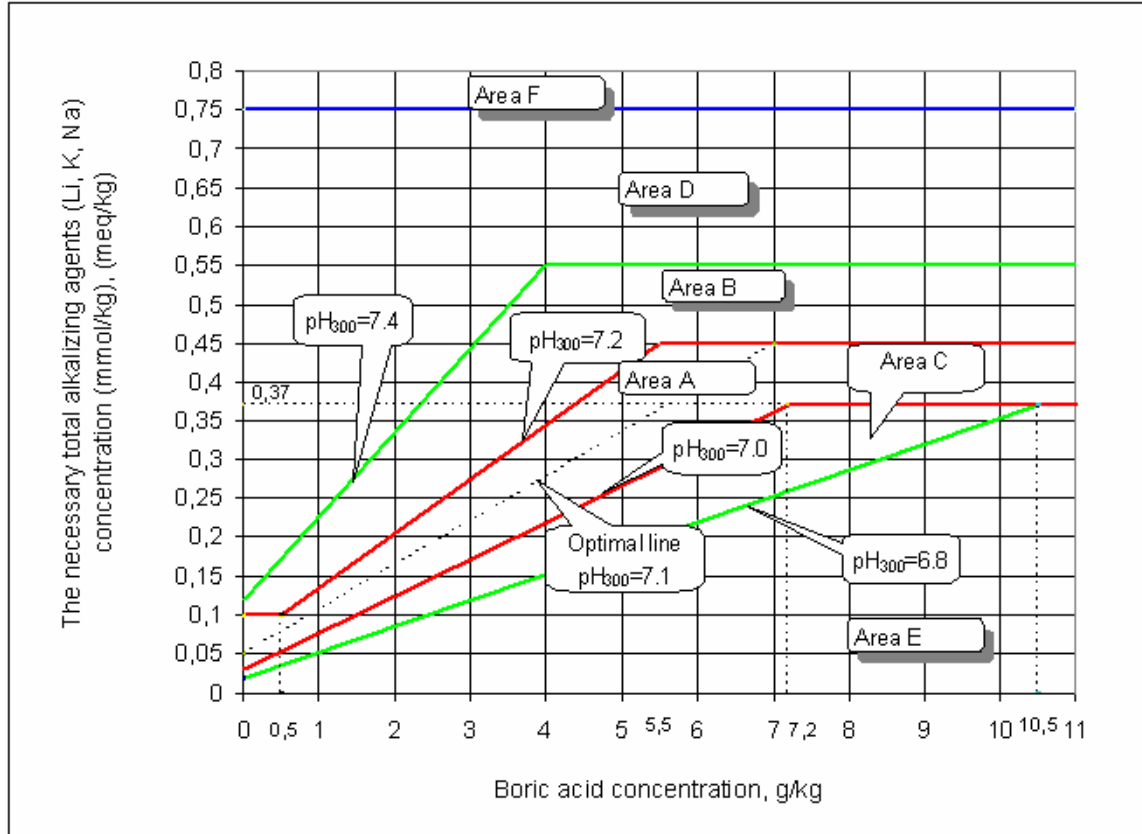


Fig.3 Kozloduy NPP Coolant Water Chemistry Requirements

Table 2. Required (bulk) Coolant pH_{300} as Results of Coolant Boric Acid Concentrations and Total Coolant Alkalizing Agent Concentrations / Operation Levels

Chemical Parameters	Limit	Limits Deviations		
		1 level (7 days)	2 level (24 hours →MCPL)	3 level (cold condition)
Total coolant alkalizing agents (K, Li, Na) concentration, mmol/kg as $f(H_3BO_3)$	Area A $pH_{(300)}= 7.0\div 7.2$	Area B $pH_{(300)}= 7.2\div 7.4$ Area C $pH_{(300)}= 6.8\div 7.0$	Area D $pH_{(300)} > 7.4$ Area E $pH_{(300)} < 6.8$	Area F

4. Coolant water chemistry & radiochemistry plant data during the power operation period of Unit 5, 15th fuel cycle.

The main water chemistry plant data for the full operation periods of the previous three fuel cycles (12-th, 13-th, 14-th), by which step-by-step implementation of TVSA fuel assemblies in Unit 5 of NPP Kozloduy was realized, showed undoubtedly that, practically, the water chemistry guideline requirements were kept - The coolant pH₃₀₀ values are always in the frame of Area A. Under these conditions the collected coolant radiochemistry plant data showed that it had been ensured fully acceptable low level of the nuclide activities in coolant. This indicates that the corrosion rates of out-of-core materials were enough limited and as a consequence, the activity buildup in primary circuit (a result of re-deposition of activated corrosion products on out-of-core surfaces) was restricted. (Only one exception was observed during the second part of 13-th fuel cycle (beginning of February 2007), when the coolant pH₃₀₀ values were decreased below 7.0, near to 6.8. As an answer of these pH value changes (with duration about 4-5 days), the specific activities of all nuclides in coolant increased up to 2 order higher.)

If it can be seen from the presented in Fig.4 data for the entire operation period of the 15-th fuel cycle (100% TVSA) of Unit 5, the coolant water chemistry plant data values are always in the frame of Area A. This very important fact should be evaluated as a confirmation that the requirement, coolant water chemistry plant data to be kept in the frame of Area A, is fully realizable by 100% TVSA fuel assemblies in the reactor core.

In the same time the obtained results allow a general evaluation to be made about the role, as a second solid neutron absorber, of the gadolinia (Gd₂O₃) which ensures great enough decrease in the initial coolant H₃BO₃ concentration by fuel cycles operated with higher enriched ²³⁵U fuel, so that boric acid can be neutralized with total alkalizing agent concentrations below 0, 45 mmol.kg⁻¹. (This value is lower than the permitted maximal total coolant alkalizing agent concentration - 0, 50 mmol.kg⁻¹).

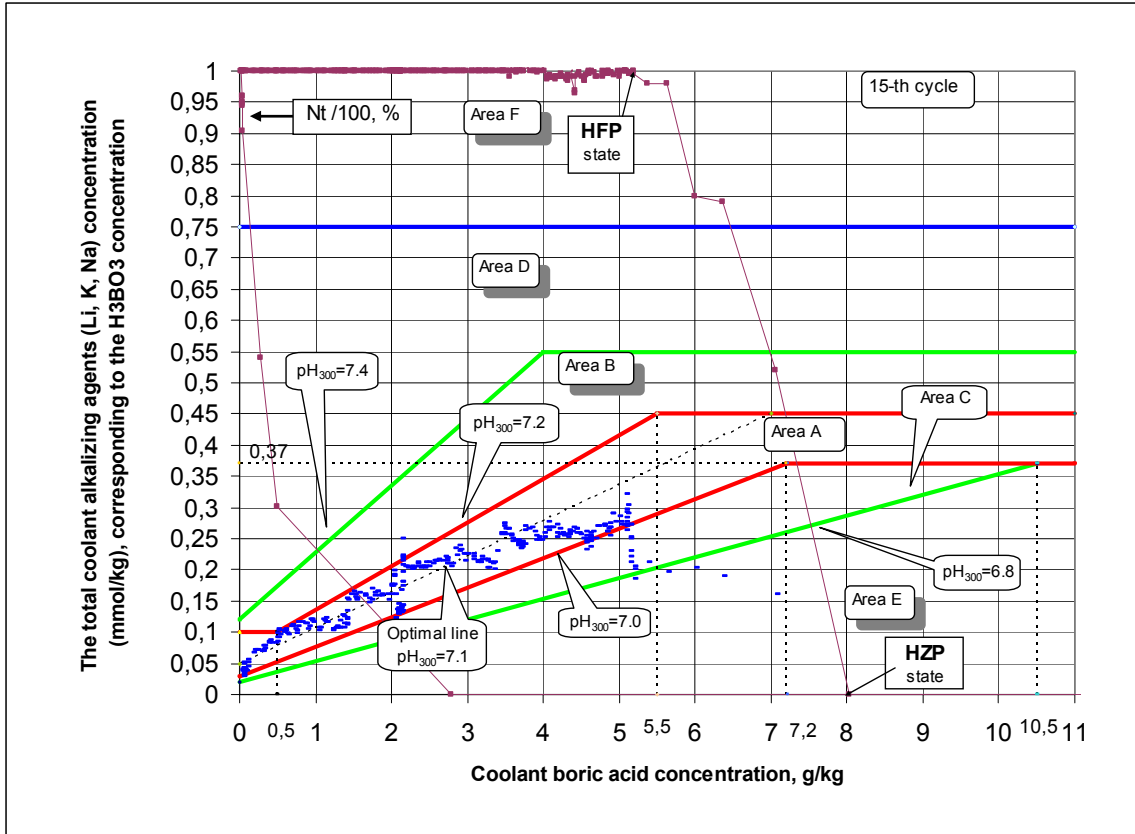


Fig.4 Coolant Water Chemistry Plant Data for the entire 15-th Fuel Cycle of Unit 5 [12]
HZP – Hot Zero Power State **BOC** – Beginning of Cycle
HFP – Hot Full Power State **EOC** – End of Cycle

The data presented in Figure 5 allow the conclusion to be made that the coolant activated corrosion product characteristics during the entire operation period of the 15-th fuel cycle, Unit 5, are practically the same as the observed coolant activated corrosion product characteristics during the corresponding period of the previous fuel cycles of the Unit5. This comparison shows that by 100% TVSA fuel assemblies in the reactor core of Unit 5 (15-th fuel cycle), the corrosion processes in primary circuit remained on the same low level, i.e. under these conditions, an increase in coolant corrosion aggressiveness can not be indicated.

The excellent radiochemistry coolant plant data (low level of coolant activity), obtained during the entire operation period of the 15-th fuel cycle of the Unit 5 are a good confirmation of the effectiveness of the coolant water chemistry, developed and applied in WWER-1000 Units in NPP Kozloduy, the main characteristic of which is the maintaining of coolant pH₃₀₀ values in the range of 7.0 – 7.2 (Area A).

NPP Kozloduy, Unit 5, 15th cycle

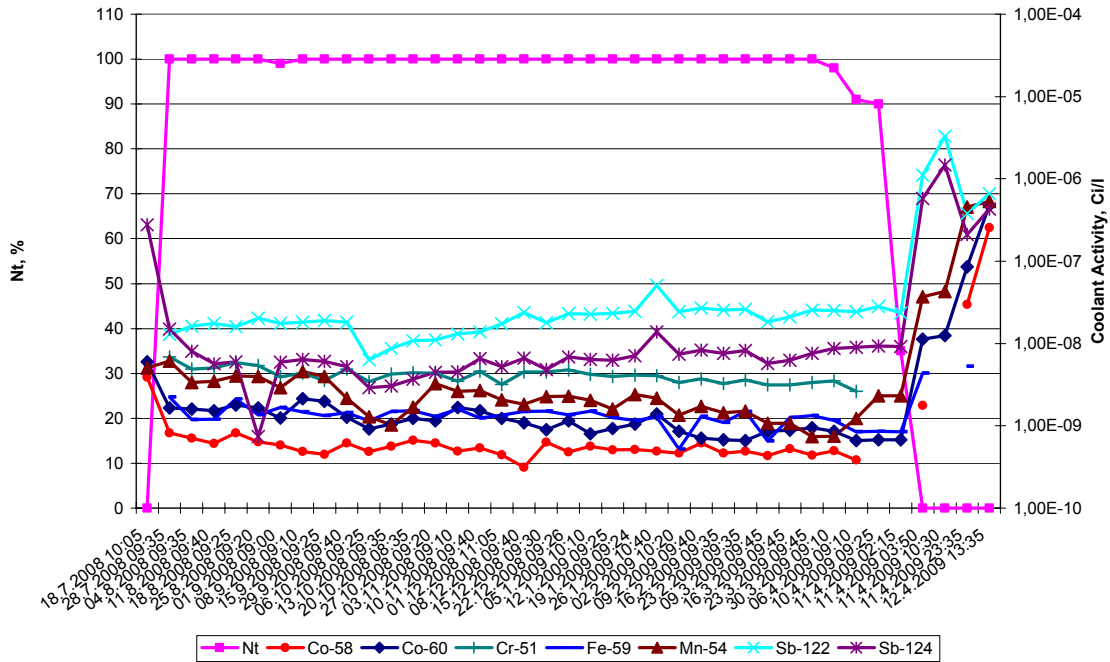


Fig.5 Coolant activated corrosion products for the entire operation period of the 15th fuel cycle, Unit 5, Kozloduy NPP [12]

Figure 5 data show also the presence of the antimony isotopes and mainly ¹²²Sb in the coolant during the entire operation and shutdown period. These relatively exotic observations require an explanation [13]:

The short half-life period (2,7 days) of ¹²²Sb is the reason for conclusion that ¹²²Sb enters in coolant permanently as a consequence of continuously generation and following dissolution of this antimony isotope in reactor coolant.

The chemical properties of antimony, which are different from the properties of transition elements, determine the presence of local oxidizing conditions at the cladding surfaces as the necessary factor for the oxidizing of the inactive precursor - ¹²¹Sb. As a result of activation by the neutron- and gamma- flux in the reactor core, ¹²²Sb originates after reactions:



The permanent ingress of ¹²²Sb in reactor coolant of WWER-1000 Units in NPP Kozloduy Bulgaria, observed by high duty reactor core, realized by the implementation of uranium-gadolinium (U-Gd₂O₃) fuel with up to 4,3% ²³⁵U enrichment, after our opinion [13], can be used as an indirect indication of the presence of SNB at the fuel cladding surfaces and for the local production of oxidants as a result of synergetic effect of SNB and water radiolysis processes. This possibility is important, taking into account that by the routine coolant control, the presence of oxidants is not indicated. This also

means that the local hydrogen in water phase at the cladding surfaces is not in sufficient concentration to mitigate the water radiolysis.

5. Evaluation of the approaches and results by the conversion of the WWER-1000 Units at NPP Kozloduy to the uranium fuel with 4.3% ²³⁵U.

The obtained water chemistry and radiochemistry plant data of WWER-1000 Units at NPP Kozloduy confirm that one realistic approach to problem-free implementation of highly enriched ²³⁵U (up to 4,3%) fuel has been found.

The realization of this approach in the WWER-1000 Units at NPP Kozloduy was practically carried out through:

- The implementation of Russian fuel assemblies TVSA which:
 - have as fuel cladding material E-110 alloy (Zr1Nb) with sufficient high corrosion resistance in the presence of SNB;
 - use burnable absorber (Gd) integrated in the uranium-gadolinium (U-Gd₂O₃) fuel (fuel rod with 5.0% Gd₂O₃).
- The development and implementation of water chemistry primary circuit guidelines, which require a relation between boric acid concentration and total alkalizing agent concentrations so that coolant pH₃₀₀ to be pH₃₀₀ = 7.0 – 7.2 throughout the entire operation period.

The applied coolant water chemistry ensures the necessary minimization of the corrosion processes of the primary circuit materials, including the steam generators tubing, manufactured of 08Cr18N10T stainless steel.

The realization of the above mentioned approaches practically has ensured the avoidance of the creation of the conditions necessary for AOA and IRI onset.

6. Recommended reactor coolant water chemistry requirements for WWER-1000 Units with ²³⁵U higher enriched fuel

The application experience of the introduction of highly enriched ²³⁵U (up to 4.3%) fuel in WWER-1000 Units in NPP Kozloduy allows the keeping of the water chemistry primary circuit guidelines which ensure coolant pH₃₀₀ = 7.0 – 7.2 throughout the entire operation period.

The realization of this coolant water chemistry is possible by the usage of second solid burnable neutron absorber - Gd₂O₃ which ensures a great enough decrease in the initial coolant H₃BO₃ concentration in fuel cycles operated with ²³⁵U enriched fuel, so that the coolant acid concentration can be neutralized with total alkalizing agent below 0.45mmol.kg⁻¹.

The applying of this coolant water chemistry ensures the necessary minimization of the corrosion processes of the primary circuit materials, including the steam generators tubing, manufactured of 08Cr18N10T stainless steel and as a consequence: Crud deposition on the fuel cladding surfaces will be maximal limited or avoided.

As a basic condition for the problem-free implementation of highly enriched ²³⁵U (up to 4.3% - 4.5%) fuel is the application of fuel cladding materials with enough corrosion resistance to the specific fuel cladding environment created by the presence of SNB – such alloys as French M5 and Russian E 110 (Zr1Nb).

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