



AMMONIA ROLE IN WWER PRIMARY CIRCUIT WATER CHEMISTRY OPTIMIZATION

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Abstract

Ammonia influence on iron crud's solubility at 300 °C and different relations of boric acid and alkaline cation sum are considered. Reduction of dose rate on WWER-440 steam generators at average ammonia concentration increasing is empirically explained. Practical recommendations on optimization of WWER primary circuit water chemistry are given.

1. Ammonia Role in WWER Primary Circuit

For WWER primary circuits of NPPs reducing boron-potassium regime, consisting in keeping boric acid concentration corresponding to fuel burn-up level, with the acid neutralizing by potassium hydroxide, is accepted [1-2]. Ammonia concentration is within limits providing reducing regime at the expense of hydrogen formation in result of ammonia decomposition at temperature > 200 °C under ionizing radiation conditions [1-3].

Because of lack of technical measuring aids, pH_T does not appear under standard control at domestic NPPs. pH of water solutions consisting of several components is a complex function of these components concentrations and dissociation constants thereof, depending on temperature. Therefore, it is difficult to judge about pH_{300} value of a solution of the same composition by pH_{25} value. In change of the component concentration relationship, first of all of $H_3BO_3/\Sigma(K, Na, Li)$, pH_T value changes and corrosion products (CP), iron, nickel, cobalt solubility in different section of the circuit changes accordingly. CP solubility in the core and steam generators tube plate determines direction and intensity of mass transfer of iron CP as well as of radionuclides. Optimum relationship $H_3BO_3/\Sigma(K, Na, Li)$ assessment in practice is not used and attending personnel can not predict current water chemistry deviation from optimum. Therefore, operating personal does not often connect these variations of relationship $H_3BO_3/\Sigma(K, Na, Li)$ during the campaign with radiation conditions change [4].

Empirically expressed appreciable ammonia concentration effect upon dose rate build-up on steam generators (Figure 1) is not theoretically explained yet [5]. Moreover, theoretically ammonia influence upon pH value and accordingly upon mass transfer processes at temperatures > 200 °C is considered negligible. It is known that with temperature rise ammonia dissociation constant values decrease sharply (for example, comparing with alkaline metal hydroxides) and as a result it is supposed that the most part of it is in the form of NH_4OH neutral molecules [3]. The aim of our work was to find out NH_3 role and importance of the primary circuit coolant with equipment interactions on the basis of $Fe_3O_4-H_2O-H_3BO_3-KOH-NH_3-H_2$ system calculational analysis.

As there is no agreed-upon code of constants of water dissociation boric acid, potassium hydroxide and ammonia in temperature range 25-300 °C, first of all it was necessary to check up pH_T

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calculation correctness. There are known experimental and calculated pH values for water solutions, containing NH_3 , LiOH and H_3BO_3 in different proportions [6-8]. We have calculated pH_T values for the same solutions by the model [9] using interconsistent constants of H_3BO_3 , LiOH , NH_3 dissociation.

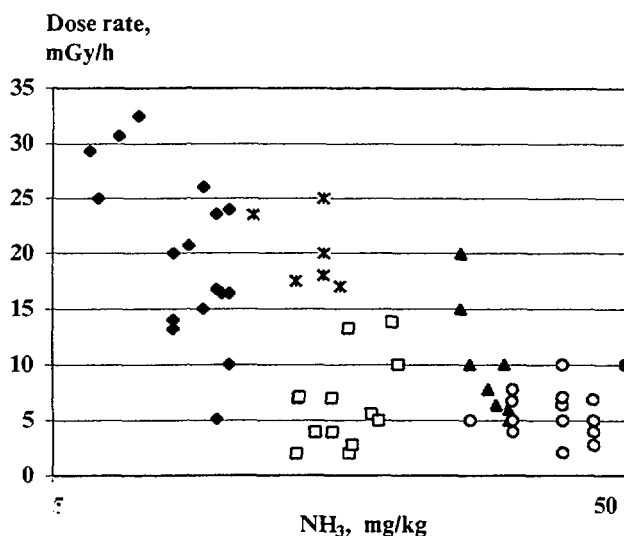


FIG. 1. Dose rate from WWER-440 steam generator collectors at different ammonia concentrations in 1 circuit water [5]

- ◆ Bohunice, unit 1,2
- Bohunice, units 3,4
- ▲ PAKS, unit 2 (standard regime)
- Kola NPP, unit 3
- × Greiph, unit 3
- PAKS unit 2 (with N_2H_4)

Absolute disagreement of experimental and calculational values of pH_T [6-8] and calculational pH_T values obtained does not exceed 0,3 (Figure 2). Advantage of calculations, we have performed, is absence of any systematical mistake as well, evidenced by discrepancy of pH_T values, we have obtained, and those of publications both in positive and negative regions (Fig. 2).

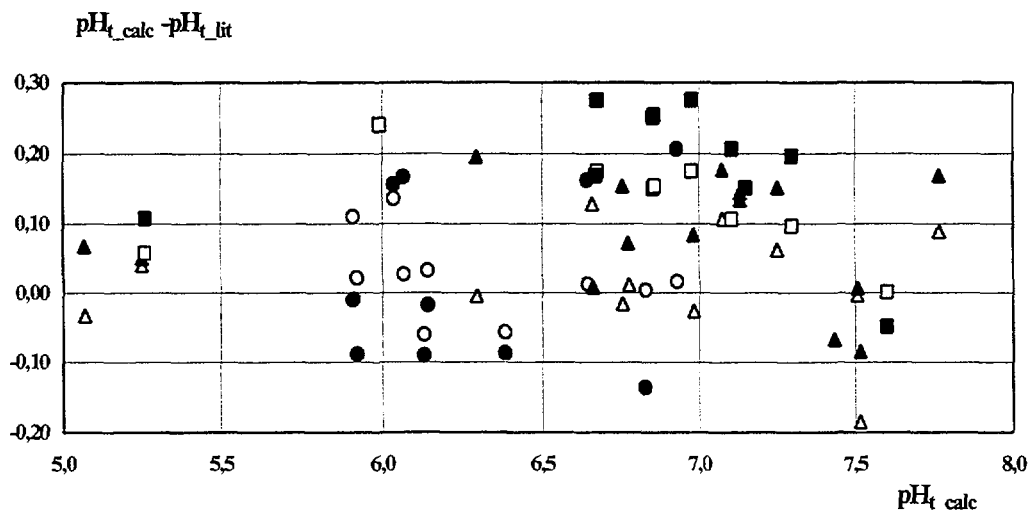


FIG. 2. Results of assessment of the calculational and experimental pH values coincidence

- calculation by [6]
- experiment by [6]
- △ calculation by [7]
- ▲ experiment by [7]
- calculation [8]
- experiment by [8]

2. Water Chemistry Optimization

It should be noted, that ammonia concentration effect upon pH_T values at temperatures $> 200\text{ }^\circ\text{C}$ depends on relations of boric acid and alkaline metal concentrations. Effect of ammonia concentration change upon pH_{300} value of solution with different relation $\text{H}_3\text{BO}_3/\Sigma(\text{K}, \text{Na}, \text{Li})$ is showing Fig. 3. Figure 3 shown that with alkaline metal content decrease ammonia concentration effect rises. The least effect of ammonia is at fine-fold potassium excess comparing with required ones according to OCT [1] (Fig. 3, curve 1). With the alkaline metals content decrease at constant boric acid concentration, effect of NH_3 upon pH_T value rises (Fig.3, curves 2,3,5). pH_T shift at ammonia content from 0,17 mg/kg to 53,8 mg/kg account for 0,2 unit pH_T for 0,1 mmol/kg K (Fig.3, curve 2), for 0,01 mmol/kg K - 0,9 unit pH_T (Fig.3, curve 3) and without potassium - 1,2 unit pH_T (Fig.3, curve 5). pH_{300} value change has effect upon magnetite solubility. Magnetite solubility dependence on pH_T at $300\text{ }^\circ\text{C}$ is shown in Figure 4. Magnetite solubility values in the temperature range $25\text{-}350\text{ }^\circ\text{C}$ in coordinated water chemistry at different ammonia concentration are shown in Table 1. From Figure 3, 4 and Table 1 it is evident that at optimal relation $\text{H}_3\text{BO}_3/\text{KOH}$ corresponding to the coordinated conditions [1], boric acid and ammonia concentrations variation has practically no effect upon magnetite solubility at working temperature of operation at rated power.

Table 2 data illustrate shut-down situation and show necessity of ammonia concentration increase in shut-down according to normative documents [1,2]. Relations of alkaline metals and boric acid for coordinated and updated [2] regimes, as well as corresponding pH_{300} changes at different ammonia concentrations are shown in Figure 5 and Figure 6. At the updated regime concentrations of alkaline metals are higher and average value of pH_T for a campaign is shifted into the alkaline region and therefore an average corrosion product content is higher (Fig.2 and 6). Besides, Figure 6 shows that for a long time of the camping in the updated regime ammonia concentration variations have no effect upon pH_T value. Consequence of aforesaid is a dose expense increase being observed at maintaining of 1 circuit water chemistry according to the updated regime, comparing with the coordinated one (Figure 7).

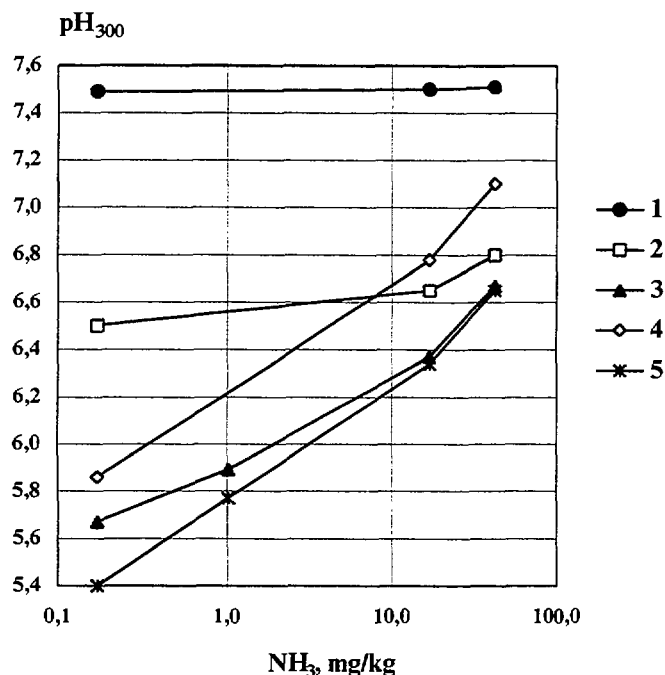


FIG. 3. Ammonia concentration effect upon pH_{300} at different relations of H_3BO_3 and K

- 1 - H_3BO_3 - 6,18 t/kg, K - 1 mmol/kg
- 2 - H_3BO_3 - 6,18 t/kg, K - 0,1 mmol/kg
- 3 - H_3BO_3 - 6,18 t/kg, K - 0,01 mmol/kg
- 4 - H_3BO_3 - 0 t/kg, K - 0 mmol/kg
- 5 - H_3BO_3 - 6,18 t/kg, K - 0 mmol/kg

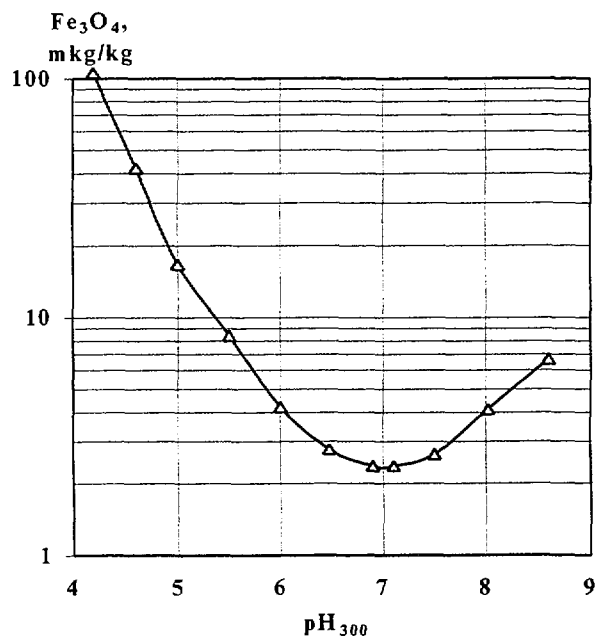


FIG. 4. Magnetite solubility dependence upon pH_T at the following relations of concentrations
 H_3BO_3 - 6,18-61,8 g/kg
 K - 100-1000 mmol/kg
 H_2 - 0,2 mg/kg

TABLE 1. MAGNETITE SOLUBILITY (mkg Fe/kg) IN THE SYSTEM $Fe_3O_4-H_2O-H_2-H_3BO_3-KOH-NH_3$ at H_2 CONCENTRATION 2 mg/kg

K, mmol/kg	H_3BO_3 g/kg	NH_3 , mg/kg				T, °C
		53,8	5,4	0,5	0,0	
0,22	6,18	11900	68200	82000	83900	25
0,02	0,62	136	5290	13600	14900	
0	0	0,4	1,0	1,6	1,7	
0,22	6,18	92	1130	3340	3830	100
0,02	0,62	9,2	57	226	326	
0	0,00	1,1	2,1	2,8	2,9	
0,22	6,18	18	75	153	175	150
0,02	0,62	4,5	12	20	23	
0	0	1,8	2,7	3,1	3,1	
0,22	6,18	7,7	14	17	18	200
0,02	0,62	3,7	5,4	6,1	6,2	
0	0	2,7	3,3	3,4	3,4	
0,22	6,18	5,1	5,8	5,9	5,9	250
0,02	0,62	3,8	4,2	4,3	4,3	
0	0	3,5	3,8	3,8	3,8	
0,22	6,18	5,1	4,7	4,7	4,7	300
0,02	0,62	4,8	4,5	4,5	4,5	
0	0	4,8	4,5	4,5	4,5	
0,22	6,18	5,5	4,0	3,7	3,7	350
0,02	0,62	5,5	4,0	3,7	3,7	
0	0	5,5	4,0	3,7	3,7	

TABLE 2. MAGNETITE SOLUBILITY VALUES UNDER SHUT-DOWN CONDITIONS

H ₃ BO ₃ , g/kg	K, mmol/kg	NH ₃ , mg/kg	pH _T	C _{Fe} , mkg/kg	T, °C
0,5	0,07	53,8	7,2	4,8	300
		5,4	7,1	4,5	
0,5	0,07	53,8	7,2	3,6	200
		5,4	6,9	5,2	
0,5	0,07	53,8	7,9	9,2	100
		5,4	7,4	54	
0,5	0,07	53,8	8,9	136	25
		5,4	7,9	5060	
8	0,07	53,8	7,2	12420	25
		5,4	6,2	74840	

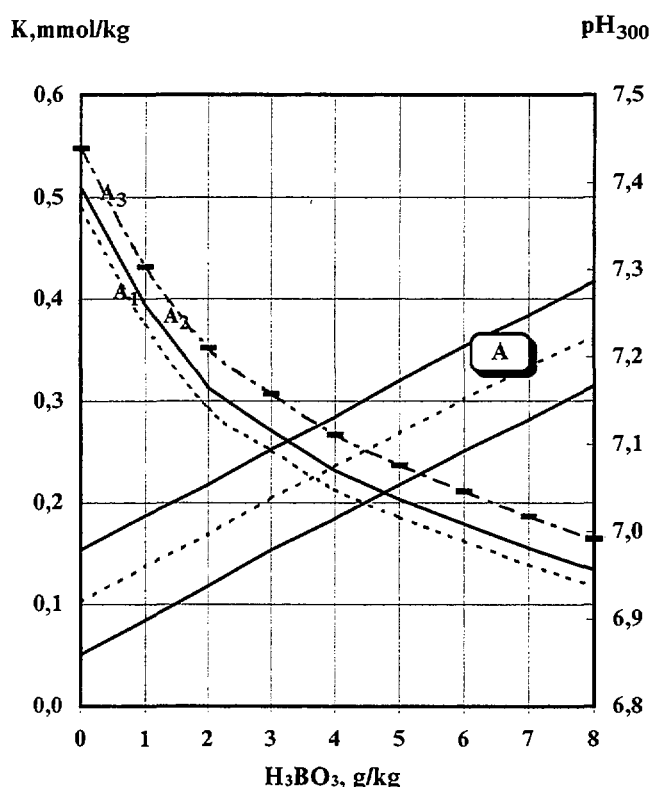


FIG. 5. Coordinated standard water chemistry by [1] and pH_{300} we have calculated for WWER-440

- A1 - NH₃=0 mg/kg
- A2 - NH₃=15 mg/kg
- - - - A3 - NH₃=50 mg/kg

At power adjustment using boric acid (for example, under emergency power decrease) immediately after injection thereof pH_T values decrease and corresponding magnetite solubility increase takes place. Then, somewhat delayed injection of potassium hydroxide solution is performed for acid neutralization. As a result, magnetite solubility change wave-like in time occurs and hence

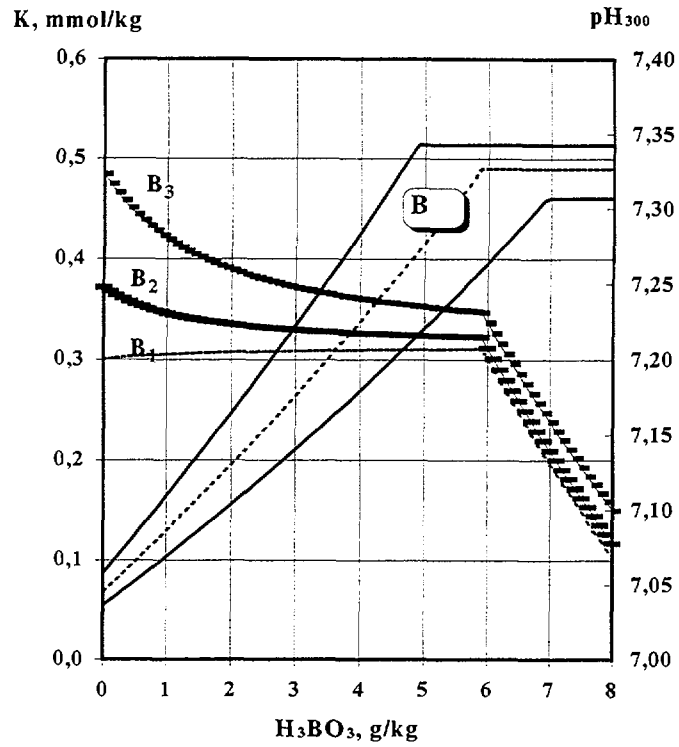


Fig. 6. Coordinated updated water chemistry by [2] and pH₃₀₀ we have calculated for WWER-440

- B1 - 0 mg/kg NH₃
- B2 - 15 mg/kg NH₃
- B3 - 50 mg/kg NH₃

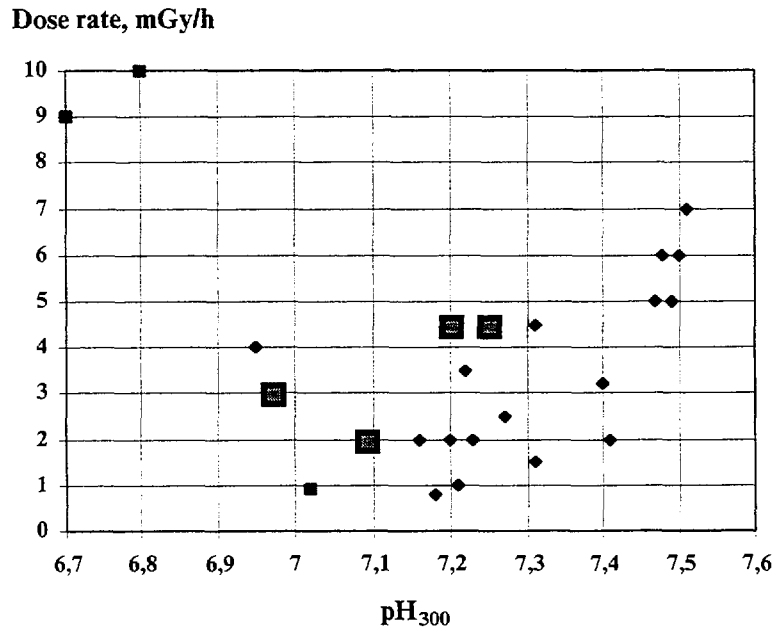


FIG. 7. Dose rate from WWER-440 steam generator collectors at different pH₃₀₀ values [10-12]

- ◆ SG [10] ■ SG [12] ■ SG [11]

mass transfer increases. In case of the updated regime these variations are more considerable because of higher allowable concentrations of alkaline metals. Discrepancies of current pH_T values and optimum one in the cases considered and in normal operation are caused by the procedure of the 1 circuit water chemistry control accepted at present. It does not provide stable reproduction of the relation $\text{H}_3\text{BO}_3/\Sigma(\text{K}, \text{Na}, \text{Li})$ being normalized in coolant because of delayed alkali solution injection and lack of operative automated control over the coolant composition. As a result of pH value deviation into acidic or alkaline regions from pH_T value, corresponding to minimum CP solubility, product corrosion content and ^{59}Fe activity increase [4].

Taking into account that in most cases of adjustment under emergency protection, pH_T shift into acidic region is observed because of inopportune injection of potassium hydroxide solution, ammonia begins to play role of an alkalinizing agent, its importance in pH_T adjustment being increased with temperature decrease. Thus, data shown in Figure 1 can be interpreted as an effect of boric acid neutralization by ammonia, corresponding to the primary circuit water chemistry change towards conditions providing minimum magnetite solubility favoring thereby dose expenses decrease.

From Fig. 3 and Tables 1 and 2 it follows that ammonia concentration increase action is more effective at the campaign end and especially under shut-down and temperature reduction. At temperature below 200 °C (i.e. under the reactor shut-down and start-up conditions) pH_T is determined by ammonia concentration in WWER primary circuit water.

Data on activity build-up in steam generators of different loops are indirect confirmation of the proposal made - activity in different loops can differ 2-10 times, which is indicative of effect of high active water passing time via this loop under the reactor start-up and shut-down [4].

Radioactive corrosion products deposition build-up relation at two different regimes may be described by the following expression:

$$K_{\text{eff}} = C_1 \cdot D_1 \cdot \tau_1 / (C_2 \cdot D_2 \cdot \tau_2), \quad (1)$$

where

$C_{1,2}$ - magnetite solubility in regimes 1 and 2 respectively;

$D_{1,2}$ - diffusion factor in corresponding regime;

$\tau_{1,2}$ - operation duration in corresponding regime.

Operation at rated power is taken as a regime 1 and shut-down conditions - as a regime 2, corresponding values of solubility, diffusion factors and operation duration are given in Table 3.

TABLE 3. CALCULATION PARAMETERS BY EQUATION (1)

No regime	Temperature, °C	C_i , mol/kg	D_i , sm^2/s	τ_i , h
1	300	$10^{-7,3}$	$4 \cdot 10^{-4}$	$\sim 7 \cdot 10^3$
2	100-150	$10^{-3,5} - 10^{-4,5}$	$\sim 1,5 \cdot 10^{-4}$	10-20

Calculations for conditions, shown in Table 3, give values $K_{\text{eff}} \approx 0,5-2$, which confirmed validity of proposal of a great role of start-up and shut-down periods in redistribution and formation of radioactive depositions in the primary circuit.

Hence practical recommendations on primary circuit water chemistry conditioning naturally follow. The relation $\text{H}_3\text{BO}_3/\text{KOH}$ maintaining according to OCT [1] provides minimum mass transfer processes at all operation regimes. as the main reason of water chemistry quality deviation from optimum is separate injection of boric acid and potassium hydroxide solutions, it is expedient to adjust water chemistry by a solution containing mixture of boric acid (up to 43 g/kg) and potassium hydroxide (1-2 mmol/kg) [13]. Souring in neutron poisons injection is ruled out in case the emergency protection comes into operation at the reactor shut-down and start-up.

For water conditions variation moderating it expedient to maintain ammonia concentration closer to the upper allowable limit. A degree of approximation should be chosen for each unit individually. This is connected with hydrogen formation efficiency, quantity of hydrogen returned from vents, leakage volume, processes of make-up water preparation, LWR decontamination, processing and storing.

To decrease corrosion load upon the primary circuit equipment as well as radioactive curds build-up. It is expedient to use boric acid enriched in ^{10}B as a neutron poison rather than that containing a natural mixture of boron isotopes. In accordance with enrichment in ^{10}B , decrease of boric acid and potassium hydroxide quantity, being injected, is possible. From aforesaid it is evident, that maintaining of optimum water chemistry is simplified and possibility of disturbance thereof is decreased, besides, ammonia content as well as WWER primary circuit waste volume being processed can be decreased too.

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