

WATER-CHEMISTRY OPERATING CONDITION OF THE SECOND CIRCUIT POWER UNITS No 1–4 RIVNE NPP WITH ETHANOLAMINE'S CORRECTIVE TREATMENT

*P.N. Kuznetsov, A.U. Tichomirov
NNEGC "Energoatom", SS "Rivne NPP",
Varash, Ukraine*

E-mail: KuzPN@rnpp.atom.gov.ua, TihAU@rnpp.atom.gov.ua

The analysis of ethanolamine (ETA) operation results water-chemistry condition (WCC) of the second circuit power units No 1–4 Rivne NPP was provided. The control data in the experimental and industrial exploitation ETA WCC (2006–2016 years), assessment and evaluation of the steam generators operating condensate systems (FSD BOU) and clean steam generator blow down water (SVO-5) at maintaining the water-chemistry of ETA was systematized and summarising.

PACS: 82.20.-w, 82.80.-d

INTRODUCTION

Maintains of the purity of the heat exchange surface of the tubes of steam generators (SG) WWER is the main condition for the prevention of stress corrosion cracking of heat exchange tubes PG (steel Cr18Ni10Ti), the composition of deposits on heat exchange tubes SG consists mainly of iron and copper compounds-products of corrosion of equipment and pipelines condensatno-feed circuit, entering the feed water to PG. For suppressing corrosion and deposition of corrosion products is a key factor in the pH the aqueous medium formed on the metal surface by vapor condensation.

For domestic PWR NPP the hydrazine-ammoniac water-chemistry of the second circuit power unit (HA WCC) is a designed. When applying the HA WCC design of chemical solutions, because of the high distribution coefficient of ammonia, the aqueous phase steam-water mixture has a lower pH, and does not provide adequate protection of the metal, which leads to increased corrosion.

At present it is completed the transition of Ukrainian NPPs with the designed water-chemistry regimes on dosing morpholine or ethanolamine (ETA) regimes. ETA compared with morpholine has a smaller molecular weight and larger dissociation constant and to obtain the same pH, ETA requires less than morpholine.

In order to reduce erosion-corrosion deterioration of pipelines and the second circuit power equipment, heat exchangers reduce HA skid surfaces, in 2006 at unit number 3 Rivne NPP trial operation commenced ETA WCC, later in 2007, 2008, 2009, and similar work for units number 4, 1, 2 Rivne was provided. Now, all power units of Rivne work in commercial operation with ETA WCOC.

ETA WCOC OF THE POWER UNITS No 1–4 RIVNE NPP

Prior to dosing ETA at power units of Rivne NPP, in accordance with the [1], the hydrazine-ammonia mode was supported. When ETA WCC was introduced regulated range of feed water pH₂₅ SG values ranged from 8.8 to 9.2 units, in purge water SG from 8.0 to 9.2 units. The average iron concentration in the feed water in the management of ETA WCOC at the time of the transition units at Rivne NPP water-chemistry ETA was

at a level of 8 to 15 ppb. Dynamics of average values (for the number of power units 1–4 Rivne NPP) the mass concentrations of iron and copper in the feed water SG presented on Fig 1.

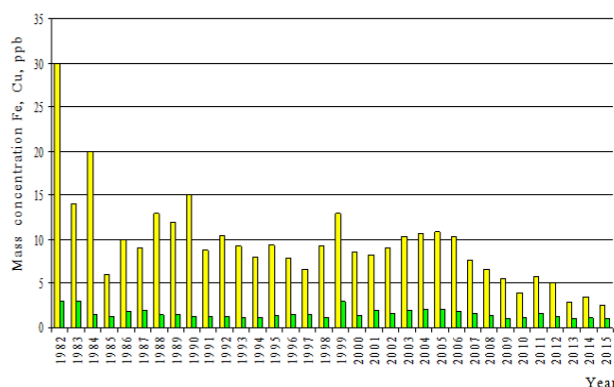


Fig. 1. Dynamics of changes in the content of the corrosion products in the feed water SG

The averaged values of nutrient and blow down water quality indicators of SG at power units 1–4 RNPP before transitions on this water-chemistry and dosing of ETA are shown in Tables 1, 2, and additional measurements the concentration of iron, copper and pH₂₅ in different stream of the second circuit. Figs. 2, 3 shows the operating pH₂₅ and mass concentration of iron flows of the second circuit its at the SG and ETA WCC.

Table 1

The average values of SG feed water quality parameters at power units No 1–4 RNPP

pH, units	$\chi(\text{H}^+)$, $\mu\text{Sm/cm}$	ETA, ppm	N ₂ H ₄	NH ₃	Fe	Cu
			ppb			
8.8-9.2 (8.9-9.3)*	≤0.3	(0.4-1.5)	≥20 (≥10)*	–	≤15 (≤10)*	≤5 (≤3)*
Average values at HA WCC						
8.90	0.18	–	124	284	7.63	1.3
Average values at ETA WCC						
9.07	0.18	1.16	18	48	2.7	≤1
*Normalized values for ETA WCC [2]						

Table 2
The averaged values of SG parameters of quality of blowdown water at power units No 1–4 RNPP

Blowdown water SG					
pH, units	$\chi(H^+)$, $\mu\text{Sm/cm}$	Cl ⁻	SO ₄ ²⁻	Na ⁺	Li ⁺
		mg/dm ³			
8.5-9.2 (9.0-9.8)*	≤5.0	≤100	≤200	≤300	—
Average values at HA WCC					
8.84	1.78	48	69	40	34
Average values at ETA WCC					
9.43	1.24	37	72	35	—
*Normalized values for ETA WCC [2]					

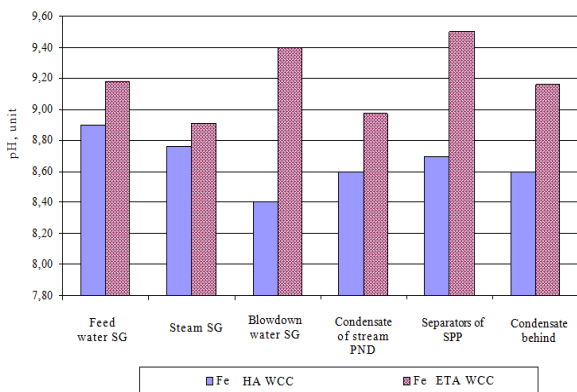


Fig. 2. pH value in the streams of the second circuit at HA and ETA WCC

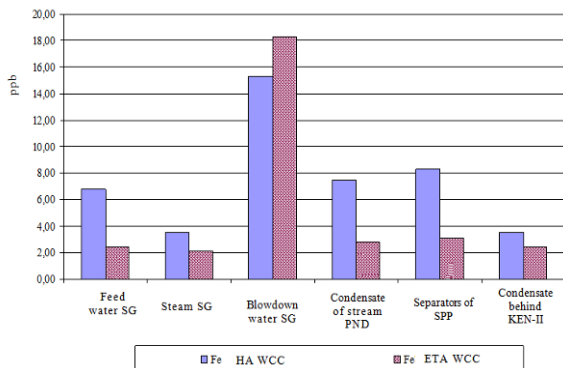


Fig. 3. The values of mass concentration of iron in the streams of second circuit at HA and ETA WCC

Transition of the power units No 1–4 in the Rivne NPP water-chemistry has allowed ETA to reduce the iron concentration in the feed water by increasing the pH of the two-phase media and alignment values pH_{25} in the steam streams and condensate-nutrient paths. In the conduct of HA WCC the main contribution to the nutrient pollution of water with corrosion products were added: condensate of the heating vapor PVD, PND and separatos SPP, at reducing of the pH_{25} values in these streams due to the high ratio of ammonia distribution.

ETA is an organic compound, by-products of thermal decomposition (degradation) which may be organic acids (formic acid, acetic acid, oxalic acid). A quantitative estimation of the generation of organic acids in the working medium flows in the management of water chemistry ETA WCC. Averaged results of

control are shown in Fig. 4, as seen in the formation of organic acids in the second flow path the working environment is not significant, the value does not affect the value of electrical conductivity of the sample passed through a cation exchange resin $\chi(H^+)$.

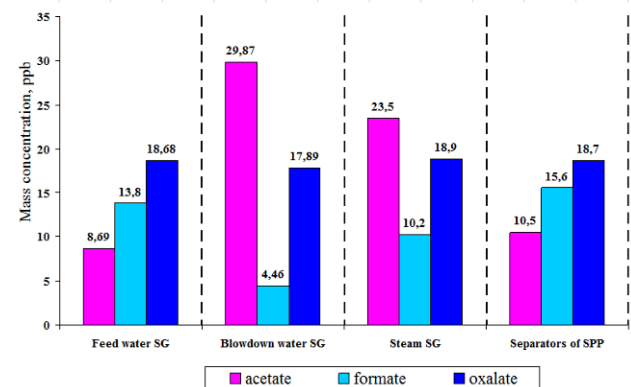


Fig. 4. The values of organic acid anions mass concentration in the streams of the second circuit at ETA WCC

The overall balance of the corrosion products in SG the conducted estimate of the accumulation of corrosion product deposits in the steam generator at the HA and ETA WCC. Tabl. 3 shows the calculated values of the accumulation of corrosion products in the SG for units 1–4 Rivne.

Table 3
Calculated values accumulation of corrosion products in SG for power units No 1–4 RNNP

PU, year	2005	2006	2007	2008	2009	2010
1	54	52	38	34	28	20
2	54	54	45	35	27	-72
3	190	125	-115	-184	-180	-170
4	331	163	103	36	-75	6.4
PU, year	2011	2012	2013	2014	2015	Total
1	29	26	-8	-31	-1	1548
2	-70	-44	-77	-48	-45	1335
3	-120	-171	-148	-155	-147	1215
4	5.2	-9	-2	-4	-16	538

When power unit HA WCC is operate the deposition rate of iron compounds in SG depends on the concentration of iron in the feed water and only slightly dependent on the concentration of iron in the blowdown water, the amount of precipitated iron is more than 60% of the amount of iron entering the SG when ETA WCC percentage of precipitation drops to 33%; iron output from purging increases from 1% at the HA ETA WCC to 7% of the amount of iron entering the SG [3]. ETA causes loosening and removing corrosion products previously deposited, as shown in Tabl. 3, after the transition to ETA WCC negative values of receipt of corrosion products within the SG volume are observed.

CONDITION OF THE POWER UNITS OF SG No 1–4 RIVNO NNP AT ETA WCC

Under the adoption of the ETA WCOC was a reduction of the specific values pollution heat exchange tubes (HET) of SG. For power units 1, 2 (PGV-213,

WWER-440) with 149 to 75 g/m² for the number of power units 3, 4 (PGV-1000M, the WWER-1000) with 90 to < 30 g/m². Reducing the specific contamination of internal surfaces of SG was due to “washout”, this effect, namely, loosening and removing them in the form of a fine slurry. While maintaining the water-chemistry of ETA, the results of the inspection PGV-1000M Rivne, on the bottom forming a cylindrical bottom – no sludge.

Condition of internal surfaces of SG power units No 1–4 at the Rivne NPP ETA WCC are shown in Figs. 5–8. Dynamics of changes in the average values of specific SG pollution TOT is shown in Figs. 9, 10. The chemical composition of SG deposits with ETA water-chemistry is shown in Tabl. 4.



Fig. 5. HET PGV-213 power unit No 1 Rivno NNP (start-up 1980). Chemical cleaning SG provided in 2003



Fig. 6. HET PGV-213 power unit No 1 Rivno NNP (start-up 1981), Chemical cleaning SG not provided



Fig. 7. HET PGV-1000M power unit No 3 Rivno NNP (start-up 1986), Chemical cleaning SG was provided periodically from 1998 to 2007



Fig. 8. HET PGV-1000M power unit No 4 Rivno NNP (start-up 2004). Chemical cleaning SG not provided

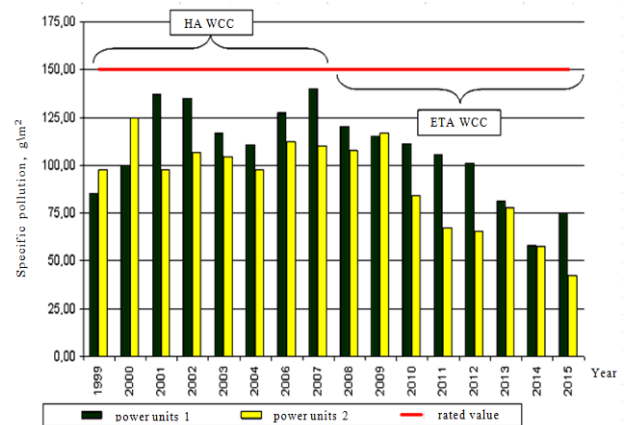


Fig. 9. Average values of specific pollution HET PGV-213 power unit No 1, 2 Rivno NNP

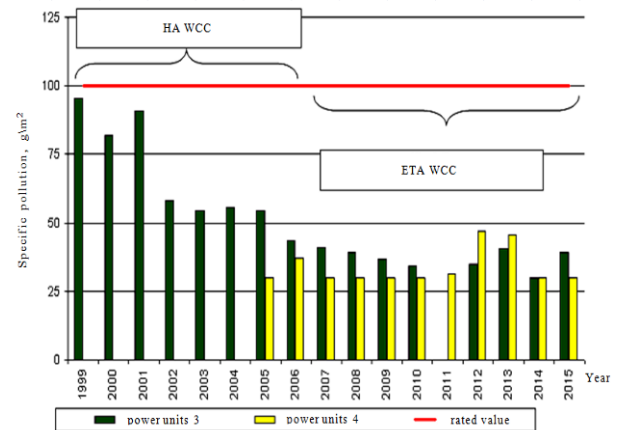


Fig. 10. Average values of specific pollution HET PGV-1000M power unit No 3, 4 Rivno NNP

Table 4

The chemical composition of the blank internal surfaces of the SG power units No 1–4 Rivno NNP at ETA WCC

Fe ₂ O ₃ , %	SiO ₂ , %	ΣCaO, MgO, %	CuO, %	ZnO, %	NiO, %	Cr ₂ O ₃ , %
80-90	1-5	1-10	0.2-6	0.2-2	0.1-1	0.001-0.1

After the introduction of the ETA WCC clear tendency to reduce and stabilize the indications for metal thinning and reducing the number of jamming

HET SG scheduled. That is connected with a decrease in erosion-corrosion wear of equipment and processes under sludge reduce corrosion. Dynamics of HET SG damping is shown in Fig. 11.

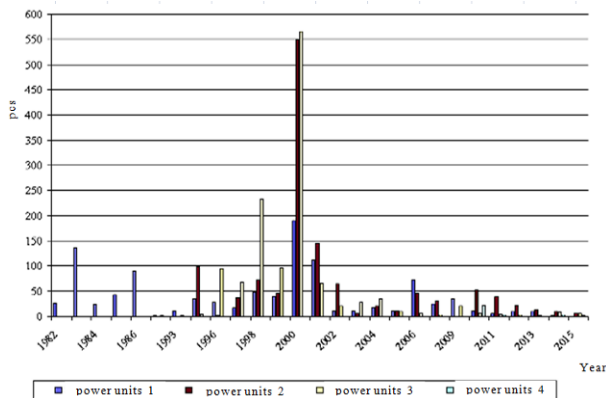


Fig. 11. Dynamics of HET SG damping on power units No 1–4 Rivno NNP

OPERATION OF ION-EXCHANGE FILTERS OF THE POWER UNITS No 1–4 AT ETA WCC RIVNO NNP

The influence of ETA on operation of the ion-exchange filters block desalting unit (FSD BOU) and CVO-5 power units 1–4 RNPP. To download the FSD BOU and ion exchangers filters blowdown water SG (SVO-5) on the Rivne NPP is used strong acid cationite Amberjet 1500 and 4400 N strongly basic anion exchanger Amberjet 4400 H.

When FSD BOU operates at ETA WCC coefficient of sodium purification ratios ranged from 1.0 to 3.0, and the average is 1.38. The saturation of the cationite in the FSD BOU ETA did not affect the values for sodium purification factors. Ratio sodium selectivity for the cationite for use ETA Amberjet 1500 N (containing 10...12% divinyl benzene) is 1.5, the coefficients of selectivity, monovalent cations are present in the condensate turbine are arranged in the following order: $NH_4 > Na > ETA$ [4].

According to the results of control within 1.5...2 months cationite work in the H-form FSD BOU, electrical conductivity values $\chi(H)$ for the treated condensate FSD values were less than 0.1 $\mu Sm/cm$, and gradually increased to 0.154 $\mu Sm/cm$. After moving to the ETA form the value of this indicator has stabilized at a level of 0.15...0.2 $\mu Sm/cm$, to "breakthrough" of sodium ions. When administered HA WCC FSD BOU work only in the H-OH form.

Under insertion of ETA WCC the ion load increases on the cation exchanger (CF) treatment plant blowdown water SG CVO-5. The filters CF SVO-5 at the HA and ETA WCC are the same and range from 45.000 to

65.000 m^3 . As a result of operation of CF SVO-5 at ETA WCC on the possibility of operating cationite SVO-5 in the form of ethanolamine was decision.

SUMMARY

The introduction of the ETA WCC at power units 1–4 RNPP leads to iron content in the feed water to SG decreased from 8...15 to 2.0...3.5 ppb. According to the mathematical balance calculations of revenue of corrosion products within the scope of SG at ETA, there are negative revenues of corrosion products (~ 150 kg) due to washout effect of ethanolamine. Reduction in feed water of the corrosion products concentrations SG units 1–4 indicates a decrease in erosion-corrosion wear of the second circuit equipment

After the change to ETA water chemistry values of specific contamination of heat exchange surfaces SG power units 1–4 RNPP reduced and maintained at a low level. Reduced specific pollution and maintaining it at a low level processes under sludge reduced corrosion and degradation of HET SG, which confirms the results of control and sludge dynamics of HET SG.

Maintaining of ETA WCC eliminated the periodic chemical cleaning of SG, chemical washing SG on RNPP not held since 2007.

Implementation and maintenance of water chemistry from the correctional treatment ethanolamine second circuit at the power units 1–4 RNPP possible to reduce erosion-corrosion wear of the second circuit equipment, reduce the flow of corrosion products from the feed water SG, reduce and maintain a minimum level of specific pollution of SG heat exchange surface.

REFERENCES

1. GND 95.1.06.02.002-04 "Water chemistry of the second circuit of NPP with VVER reactors. Technical requirements for the quality of the working environment. Correction treatment with hydrazine hydrate, morpholine, lithium hydroxide", 2004.
2. SOU NEC 1.028:2013 "Water chemistry secondary circuit of nuclear power plants with VVER. Technical requirements for a working environment second circuit", 2007.
3. Report "According to the study and assess the impact of ethanolamine water chemistry-2 on corrosion-erosion wear of equipment operating in single-phase and two-phase medium", 15.05.2007.
4. Report "Optimizing the performance of filter media in filters BOU, SVO-5 in terms of water chemistry of the second circuit with dosing etanoamina". SC "Ecologie", 17.11.2009.

Article received 27.12.2016

ВОДНО-ХИМИЧЕСКИЙ РЕЖИМ ВТОРОГО КОНТУРА ЭНЕРГБЛОКОВ №1–4 РОВЕНСКОЙ АЭС С КОРРЕКЦИОННОЙ ОБРАБОТКОЙ ЭТАНОЛАМИНОМ

П.Н. Кузнецов, А.Ю. Тихомиров

Проведен анализ результатов эксплуатации этаноламинового (ЭТА) водно-химического режима (ВХР) второго контура на энергоблоках №1–4 Ровенской АЭС, систематизированы и обобщены данные контроля при опытной и промышленной эксплуатации ЭТА ВХР (2006–2016 гг.), даны оценки состояния парогенераторов, эксплуатации систем конденсатоочистки (ФСД БОУ) и очистки продувочной воды парогенераторов (СВО-5) при поддержании ЭТА ВХР.

ВОДНО-ХІМІЧНИЙ РЕЖИМ ДРУГОГО КОНТУРА ЕНЕРГБЛОКІВ №1–4 РІВНЕНСЬКОЇ АЕС З КОРЕКЦІЙНОЇ ОБРОБКОЮ ЕТАНОЛАМІНОМ

П.М. Кузнецов, А.Ю. Тихомиров

Проведено аналіз результатів експлуатації етаноламінового (ЕТА) водно-хімічного режиму (ВХР) другого контура на енергоблоках №1–4 Рівненської АЕС, систематизовані та узагальнені дані контролю при дослідній та промисловій експлуатації ЕТА ВХР (2006–2016 рр.), дано оцінки стану парогенераторів, експлуатації систем конденсатоочищення (ФЗД БЗУ) і очищення продувочної води парогенераторів (СВО-5) при підтриманні ЕТА ВХР.