Present status and recent improvements of water chemistry at Russian VVER plants

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Introduction

The current Russian nuclear program includes life extension of the oldest plants and construction of new plants in Russia and abroad. Water chemistry is an important contributor to reliable plant operation, safety barrier integrity, plant component lifetime, radiation safety, environmental impact. Primary and secondary water chemistry guidelines of Russian VVER plants have been modified to meet the new safety standards. Some changes in new water chemistry specifications are based on investigations and studies of recent abnormal events at VVER plants caused generalised corrosion problems, flow assisted corrosion, corrosion cracking, foreign material intrusion, equipment fouling, etc. Traditionally, the primary and secondary system water chemistry at VVER plants differ from water chemistry at Western designed PWRs due to different design and development history. Co-operation between Russian and Western organisations and specialists under some recent joint programs brought about useful findings from both VVER and PWR chemistry control programs, which may be successfully implemented in future projects and at PWR and VVER plants in operation.

At present 14 VVER units of different generation are in operation at 5 Russian NPPs. There are eight 4-loop pressurised water reactors VVER-1000 (1000 MWe) and six 6-loop pressurised water reactors VVER-440 (440 MWe).

Russian prototypes of VVER reactors are no longer in operation at Novovoronezh 1, 2 NPPs (VVER-210 and VVER-365).

The oldest VVER-440 units at Novovoronezh and Kola NPPs are expiring their original design operation life of 30 years in the near future. To address this issue lifetime extension programmes are being developed.

Recently Rostov unit 1 with new VVER-1000 (NSSS V-320 type) started commercial power operation. Kalinin unit 3 with a similar reactor is under construction.

Generally, water chemistry at East European VVER plants (about 40 VVER-440 and VVER-1000 units in Ukraine, Bulgaria, Slovakia, Czech Republic, Hungary, Finland and Armenia) is similar to water chemistry at Russian VVER plants. Due to similar design and structural materials some water chemistry improvements were introduced at East European plants after they has been successfully implemented at Russian plants and vice versa. Some water chemistry improvements will be implemented at modern VVER plants under construction in Ukraine, Slovakia, Czech Republic, Iran, China, India.

The objectives of water chemistry improvements at VVER plants

General objectives of water chemistry improvements at VVER plants are as follows:

- new NPP safety standards require implementation of action levels, diagnostic chemical control
- new radiation safety rules for NPPs require reduction of radiation dose limits for plant personnel and strict effluent limitations
- corrosion cracking and erosion-corrosion countermeasures include pH_T optimisation and limitation of chloride, fluorides, sulphate, nitrate and organic
- plant life extension of old-generation plants
- fuel cycle improvements require high fuel cladding reliability

In 2001 a new revisions of primary water chemistry guidelines were elaborated to be introduced at Russian VVER-440 and VVER-1000 plants. The updated primary water chemistry specifications include optimised boron-potassium mode and hydrogen concentration, implementation of action levels, diagnostic chemical control, water chemistry of some auxiliary systems, chemical quality control.

Present status of VVER primary water chemistry

Boron-potassium-ammonia primary water chemistry has been used at VVER plants since early 1970s. Boron-potassium mode is based on continuous coolant pH_T value during the entire fuel cycle has been successfully used at VVER plants to reduce radiation fields. At the beginning of 1990s VVER-440 and VVER-1000 boron-alkaline modes were modified to exclude an error in pH_T calculation according to the old Meek method. VVER fuel manufacturers increased the maximum permissible total alkali metal content (mainly potassium) in coolant up to 0.5 mM based on corrosion tests of Zr-1%Nb alloy and austenitic stainless steel. A high permissible limit of potassium content in coolant provided constant optimal pH_T value during fuel cycles. No corrosion problems of VVER primary components caused by water chemistry were revealed. Short-lived ^{42}K generation from potassium is a minor weakness of VVER primary chemistry. Moreover, ^{42}K can be used as an indicator of primary coolant small leakage into the SG secondary side.

Generally, ammonia dosing into coolant is used as a source of hydrogen owing to decomposition in core by radiolytic reaction: $\mathbf{2\ NH_3 \rightarrow N_2 + 3\ H_2}$

The presence of ammonia and potassium instead of lithium in VVER primary coolant compared to PWR may be used to explain AOA absence at VVER plant.

This year a new revision of primary water chemistry guidelines was elaborated to be introduced at Russian WWER-440 and WWER-1000 plants. The updated primary water chemistry specifications include optimised boron-potassium mode (fig.1) and hydrogen level, implementation of action levels, diagnostic chemical control, water chemistry of fuel pool and other auxiliary systems, chemicals quality control.

Recent improvements of VVER primary water chemistry

Some of VVER plants (Novovoronezh, Kalinin, South-Ukraine) modified primary water chemistry during shutdown to reduce activity release reduction or/and improve the radiation situation near primary components before upcoming maintenance outages. Depending on contribution of corrosion products or/and iodine the above effects may be provided by H^+-cation exchanger or/and OH^--exchanger input to operation during shutdown.

Primary coolant high temperature filtration with flow-rate above 400 t/h has been experienced during 15 years at 15 operating WWER-1000 Units in Ukraine, Russia and Bulgaria.

Ammonia by hydrogen substitution for VVER primary coolant treatment is now being investigated at Kalinin and South-Ukraine NPPs with the TRACTEBEL support under TACIS program. The project is mainly aimed at reducing radwaste.

Since 1980 hydrazine-hydrate dosing has been applied instead of standard ammonia treatment at Kola 1-4 WWER-440 units to reduce accumulation of radioactive deposits of corrosion products on the inner surfaces of the primary circuit. Thanks to successful results hydrazine treatment was implemented at Rovno (Ukraine) and Paks (Hungary) VVER plants. Radiation exposure of personnel and radiation fields were reduced with minor costs thanks to hydrazine primary water chemistry introduction.

The results of recent experimental studies allowed to explain the hydrazine dosing influence on:

- corrosion rate of structural materials in primary system
- behaviour of radioactive corrosion products in primary system during steady-state and transient operation modes
- radiolytic generation of oxydising radiolytic products in core and its corrosion activity in primary system
- radiation situation during refuelling and maintenance outages

Corrosion tests of specimens exposed in steam and water phases in Kola plant pressurizers showed that hydrazine primary water chemistry allowed to reduce generalised corrosion wear of austenitic stainless steel as compared to standard ammonia chemistry. A lower value of corrosion rate for austenitic stainless steels can explain a lower dose rate and lower accumulation of radioactive corrosion products on primary components in case of hydrazine primary water chemistry as compared to standard ammonia primary water chemistry.

The main features & experimental study of radiation chemistry in VVER primary coolant

The most important type of localised corrosion of austenitic steel in primary systems is stress corrosion cracking (SCC). The impact of water chemistry on SCC is mainly determined by presence of both corrosion active anions (chlorides, sulphates, fluorides, etc.) and oxidant species (primarily dissolved oxygen).

Recent investigations of radiolytic processes in VVER conditions using the MORAVA-H2 program package showed that hydrazine treatment reduces concentration of active oxidant species (hydrogen peroxide, hydroperoxide-radical, etc.). Implementation of hydrazine primary water chemistry instead of standard ammonia primary water chemistry can therefore lead to reduction of oxidant induced localised corrosion of austenitic steel in primary system.

The oxygen concentration is lower because it is thermally bound to hydrazine. The hydrogen peroxide concentration is lower (without hydrazine its content is 1.5ppb) because of its accelerated decomposition in presence of hydrazine.

The investigations of the abnormal events related to simultaneously dissolved hydrogen and oxygen presence in VVER primary coolant during power operation revealed extremely high radiolytic activity of nitrates and their control necessity.

Present status & improvements of VVER secondary water chemistry

The absence of feed-water treatment in steam-water cycle of old-generation VVER plants from the start of operation till late 1970s led to significant corrosion of secondary components and piping made out of copper alloy and steel. Since late 1970s the water treatment by ammonia and/or hydrazine-hydrate has been used to prevent corrosion problems. Hydrazine-ammonia secondary water chemistry optimisation at VVER plants during subsequent 10-15 years failed to result in noticeable success. The fact is that carbon steel is mitigated at pH value above 9.5 while copper alloy corrosion is significantly intensified in presence of ammonia at pH value above 9.0.

Improvements of VVER secondary water chemistry

High alkaline water chemistry is appropriate both at new generation VVER plants designed without cycle components out of copper alloys (Temelin, Bushehr, Tianjin, Kudankulam) and at VVER plants where components made out of copper are substituted by those made out of titanium or stainless steel.

The lithium borate dosing into feed-water is experienced since mid 1990s at six VVER-1000 Units at Zaporozhe NPP (Ukraine).

In the beginning 1990s preliminary corrosion tests at Kozloduy NPP confirmed good compatibility of condenser tube copper alloy type CuNi5%Fe1% with morfoline chemistry in VVER secondary system.

Secondary water treatment by morfoline for Kalinin and South-Ukraine NPPs was elaborated with the TRACTEBEL support under TACIS programs. The projects are mainly aimed at reducing carbon steel erosion and generalised corrosion in steam-water cycles. Morfoline secondary water chemistry was successfully tested at South-Ukraine NPP.

Corrosion problems of steam generators at VVER plants

No steam generator at VVER-440 was replaced before the end of the design lifetime of 30 years operation. Maximum amount of plugged heat exchanger tubes in steam generators at the oldest operating Novovoronezh-3 VVER-440 plant does not exceed 5% (of 10% permissible level) after 28 years of operation including the first 10 years without feed-water chemical conditioning.

In 1999 for the first time in the VVER practice four steam generators were replaced at Balakovo 2 due to damaged heat exchanger tubes (about 10% of the total 11,000 tubes) mainly located in lower rows near "hot" headers.

In 1986-1991 some steam generators were replaced at VVER-1000 plants due to damaged outlet headers. The study of the causes has concluded that "cold" headers were damaged through stress corrosion cracking from secondary side in local zone. Corrosion originated from the narrow gap between header and heat exchanger tubes. Accumulation of corrosion active agents in the above gap significantly increased a cracking rate.

In mid 1990s two damaged the "cold" headers were repaired at two VVER-1000 plants using special welding technology.

New VVER-1000 secondary water chemistry guidelines

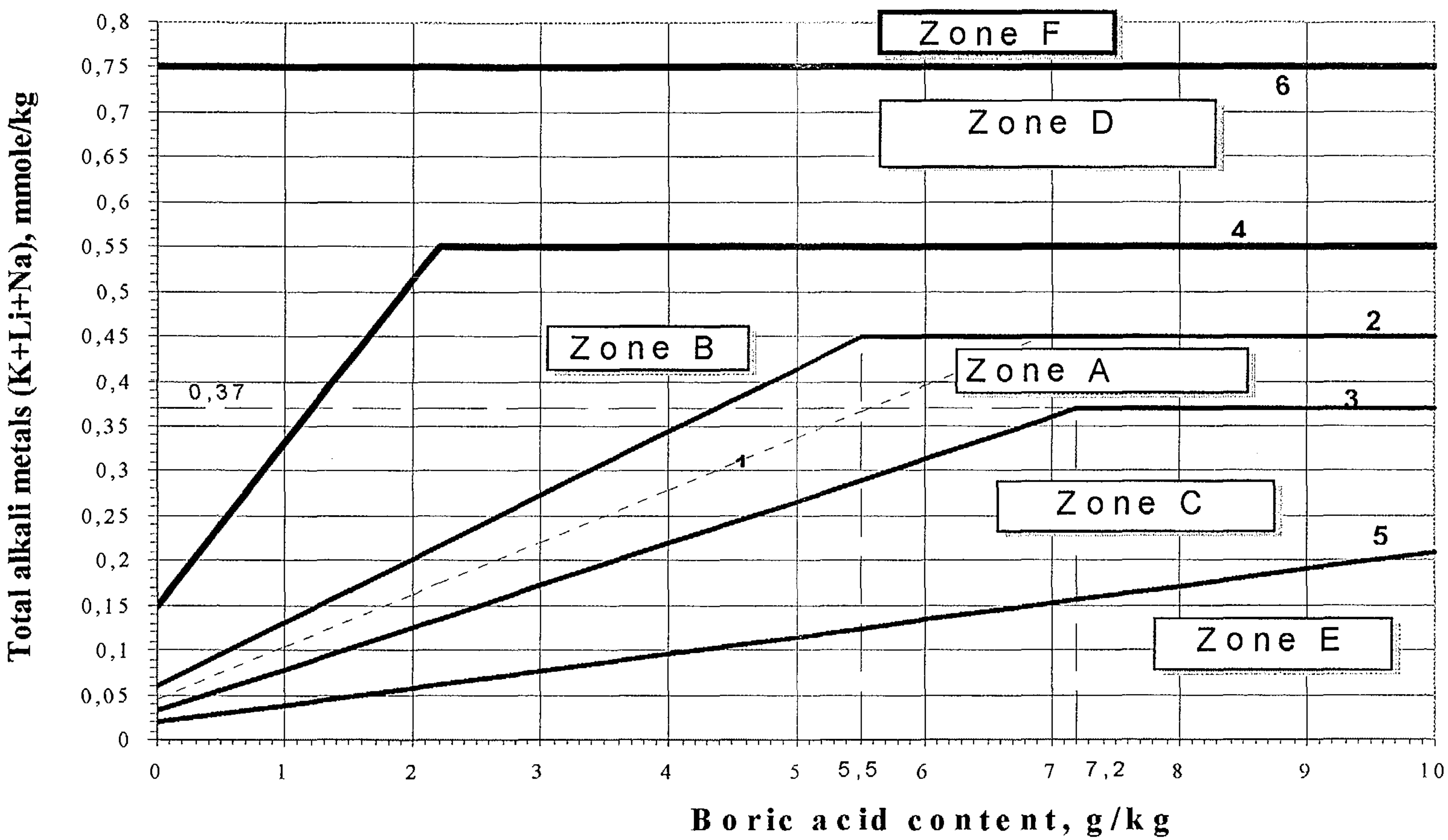
Since February 2000 new secondary water chemistry guidelines were introduced at Russian VVER-1000 plants. Present status of steam-water cycle chemistry at VVER plants is feed-water treatment by hydrazine/ammonia up to pH value of 8.8-9.2. Maximum permissible levels of iron and copper content in feed-water are 15 and 3ppb. In the early 1990s at VVER-100 plants the special partitions were implemented in water phase of steam generators near a "cold" headers to increase steam generator blow-down efficiency and provide representative chemical control of the blow-down water from maximum salt concentration zone. Thanks to the above upgrade the maximum salt concentration area was shifted from headers to the "cold" part related to a minimum heat transfer. The regular steam generator blow-down water chemical control covers cation conductivity, pH value, sodium, chloride and sulphate content. The lithium hydrate dosing into feed-water is prescribed by the updated version of the VVER-1000 secondary water chemistry guidelines to provide low alkaline conditions in SG bulk water in case of anomalous SG water acidification.

Main principles of steam generator water chemistry

The requirements for steam generator blow-down water quality in present VVER-1000 secondary water chemistry guidelines are based on molar ratio of evaporated water in any areas within steam generators. The limited values of steam generator blow-down water parameters took into account corrosion impact of water impurities on SG tubing and headers:

- corrosion cracking of tubing and collectors is prevented within pHt range 4.5-8.5
- maximum permissible deposits on tube surface 150 g/m2 or 25 μm provide concentration factor 10 for corrosion active impurities near the "hot" header (this area corresponds to the maximum heat transfer value of 250 kW/m2)
- maximum permissible chloride (0.1 ppm) was estimated based on tube cracking rate during steam generator lifetime in medium with 5ppb dissolved oxygen
- maximum permissible sulphate (0.3 ppm) was estimated based on their presence in cooling water and steam generator blowdown water compared to chloride
- maximum permissible sodium content (0.3ppm) corresponds to pH_T upper limit of 8.5 in case of concentration factor equal to 100 if chloride and sulphate content is within allowable ranges

According to calculations the appropriate steam generator water chemical control may be provided by on-line sodium and cation conductivity measurements.



WWER-1000 boron-alkaline (K+Li+Na) mode: Dashed line 1 is optimized dependence
Zone A – target range, Zones B and C – action level 1, Zones D and E - action level 2, Zone F - action level 3

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Primary coolant chemical control data of Russian VVER-440 plants

(average value / variation ranges)

NPP ↓	pH_{25oC}	H_3BO_3	K+Li+Na	NH_3	H_2	O_2	Fe	Cu	pH_{300oC}
Limit →	5.9-10.3	0-10g/kg	0.02-0.5mM	>5ppm	2.7-5.4ppm	5ppb	ppb	20ppb	
Kola-1/V-230	8.0/6.5-9.7	1.5/0.01-7.1	0.12/0.02-0.32	12/6-17	3.9/2.7-5.4	8/5-10	60/22-120	<2.5	7.08/6.94-7.21
Kola-2/V-230	7.7/6.9-9.2	2.5/0.01-5.8	0.18/0.07-0.29	10/6-15	3.4/2.7-4.5	7/5-10	48/9-130	<2.5	7.09/6.92-7.43
Kola-3/V-213	8.3/7.6-9.1	1.8/0.5-2.9	0.18/0.07-0.35	32/9-58	3.9/3.0-5.0	5	50/30-100	<2.5	7.20/7.16-7.29
Kola-4/V-213	8.1/7.0-9.2	2.9/0.2-6.80	0.25/0.08-0.46	31/13-54	3.5/2.7-5.0	5	55/10-90	<2.5	7.18/7.04-7.26
NV-3/V-179	8.0/7.4-9.8	2.1/<0.1-3.8	0.17/0.04-0.22	6.0/5-8	3.0/2.7-3.6	<5	24/20-31	-	7.11/6.97-7.38
NV-4/V-179	8.0/7.2-9.7	2.7/<0.1-5.6	0.19/0.05-0.24	5.8/5-8	3.2/2.7-4.1	<5	27/19-54	-	7.08/6.90-7.32

*** - Chloride and fluoride contents does not exceed 0.05ppm**

Primary coolant chemical control data of Russian VVER-1000 plants

(average value / variation ranges)

NPP ↓	pH_{25oC}	H_3BO_3	K+Li+Na	NH_3	H_2	O_2	Fe	Cu	pH_{300oC}
Limit →	5.9-10.3	0-10g/kg	0.02-0.5mM	>5ppm	2.7-5.4ppm	5ppb	ppb	20ppb	
NV-5 (V-187)	7.5 6.8-8.3	2.4 0.2-5.9	0.18 0.06-0.27	4.7 4-7	3.8 2.7-4.4	<5	<20	<2.5	7.09 6.88-7.19
Balakovo-1 (V-320)	8.1 7.3-9.1	2.4 0.08-8.4	0.22 0.07-0.43	22 20-24	3.3 2.9-3.5	<5	18 14-26	4 3-6	7.17 6.97-7.36
Balakovo-2 (V-320)	7.7 7.4-8.9	4.0 0.006-6.2	0.28 0.09-0.34	23 19-26	3.2 2.9-3.5	<5	21 15-28	5 4-6	7.11 6.98-7.35
Balakovo-3 (V-320)	7.7 7.5-8.1	4.0 2.3-6.1	0.33 0.27-0.39	21 19-23	3.0 2.9-3.3	<5	21 10-29	5 3-7	7.16 6.97-7.29
Balakovo-4 (V-320)	7.7 7.4-8.0	3.1 1.0-5.2	0.28 0.17-0.36	23 20-26	3.0 2.7-3.1	<5	20 13-32	5 3-7	7.19 7.01-7.29
Kalinin-1 (V-338)	7.7 7.3-8.3	2.5 0.27-4.2	0.22 0.08-0.32	15 10-18	2.8 2.7-2.9	<5	5	<2.5	7.17 7.12-7.25
Kalinin-1 (V-338)	7.8 7.5-8.6	2.2 0.23-4.7	0.20 0.07-0.35	16 12-22	2.8 2.5-3.5	<5	5	<2.5	7.17 7.11-7.23

- **Chloride and fluoride contents does not exceed 0.05 ppm**

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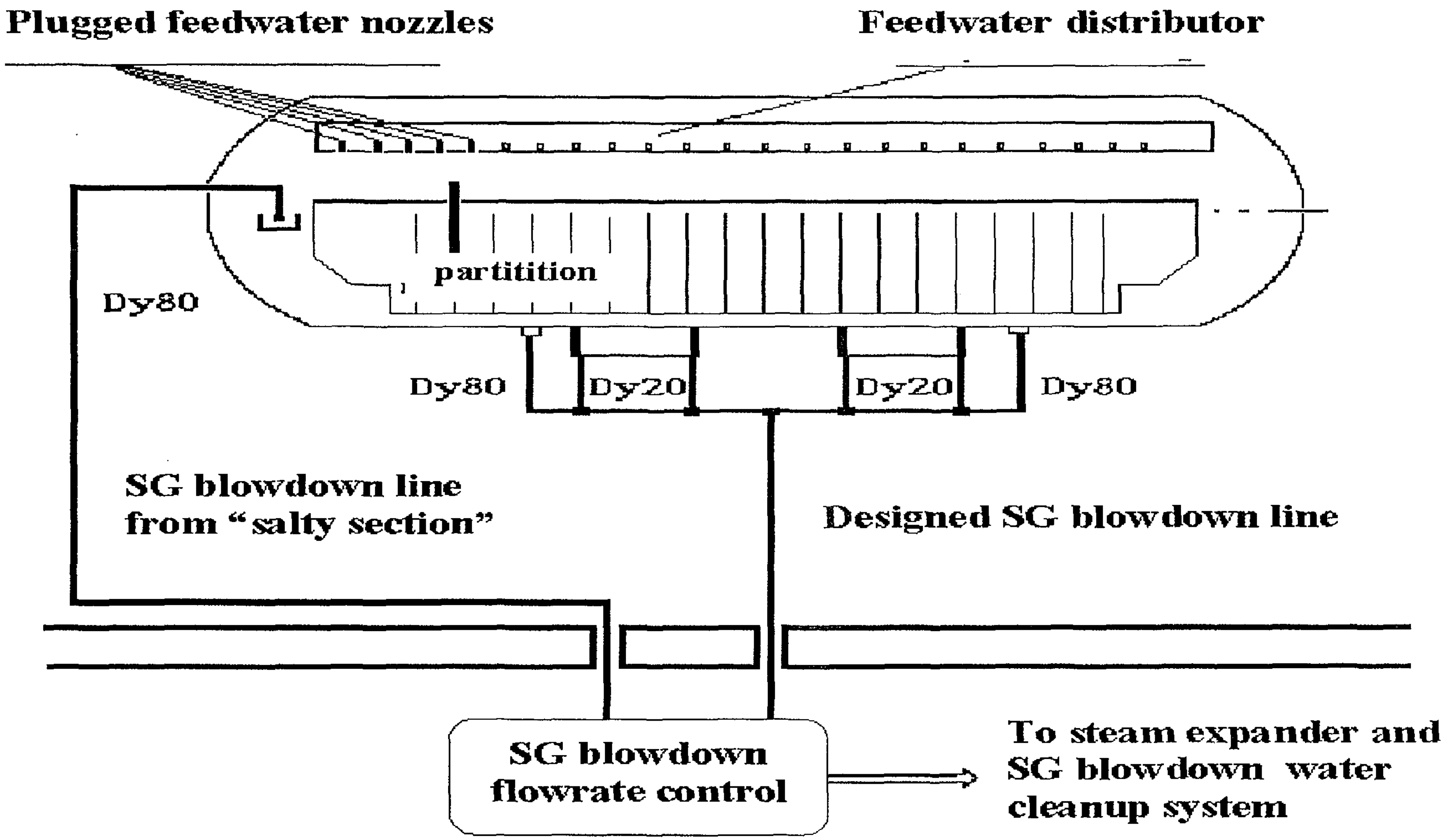

Steam generator blow-down system upgrade at VVER-1000 plants

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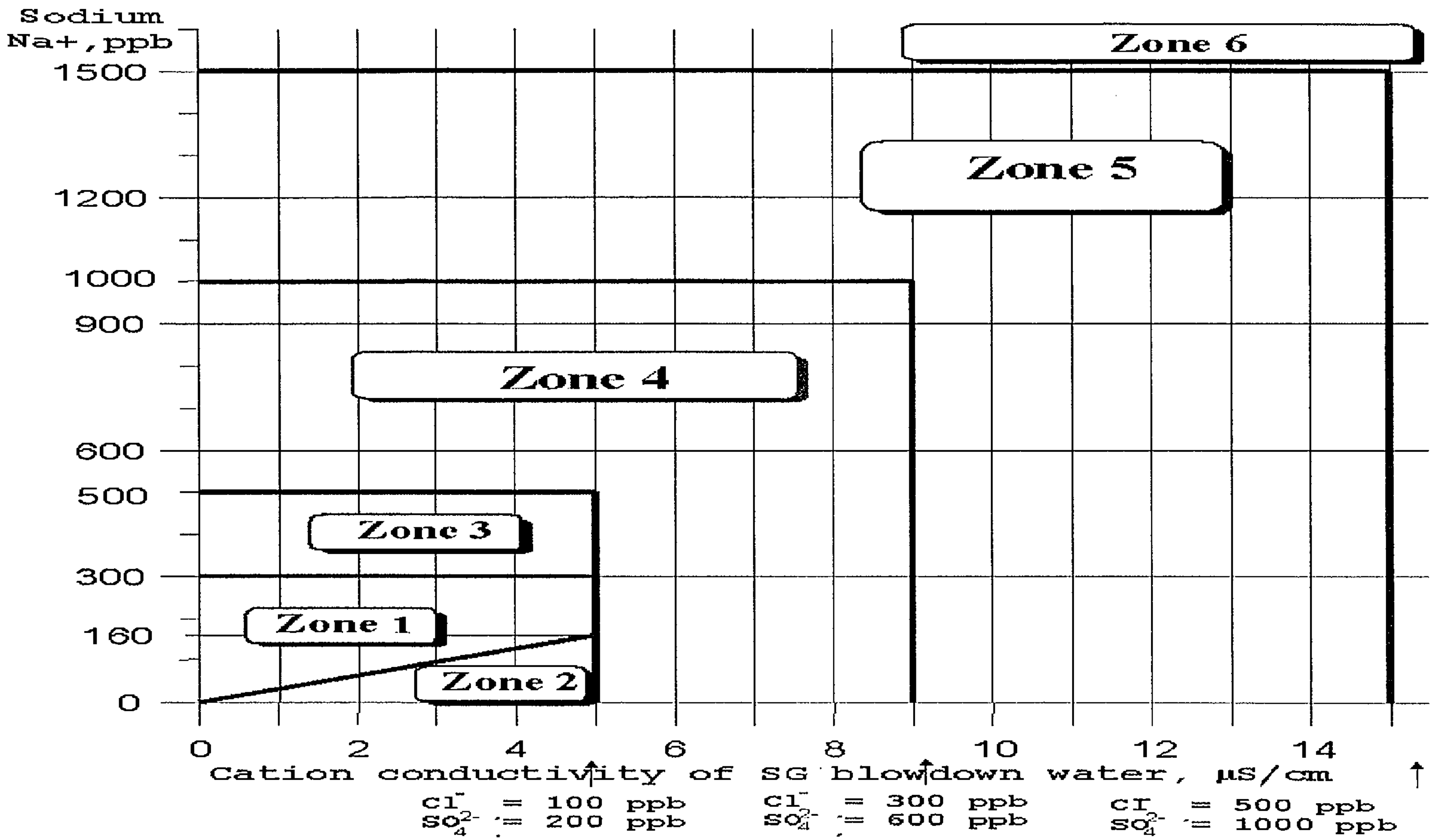

Steam generator blow-down water specifications for VVER-1000 plants /2000`Rev.

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Steam generator blow-down water (SG)/*feed-water* (FW) chemical control data of Russian VVER-440s (average values / variation ranges)

NPP		pH$_{25oC}$	X_H	Cl	Na	N_2H_4	O_2	Fe	Cu
Limit	SG	8.0-9.2	<6 μS/cm	<150 ppb	<300 ppb				
	FW	*8.8-9.2*	*<0.5 μS/cm*		*<5 ppb*	*>5ppb*	*<10ppb*	*<15 ppb*	*<3ppb*
Kola-1 (V-230)	SG	8.4/7.0-9.2	2.2/0.7-6.0	24/3-126	55/10-250				
	FW	*9.1/8.8-9.2*	*0.56/0.26-1.2*		*3/1-5*	*47/5-265*	*9/5-10*	*14/7-40*	*2.5*
Kola-2 (V-230)	SG	8.3/6.4-9.3	2.3/0.8-6.0	34/6-113	95/10-490				
	FW	*9.2/8.9-9.5*	*0.49/0.25-1.1*		*4/1-4*	*39/5-385*	*9/5-30*	*12/9-31*	*2.6/2-4*
Kola-3 (V-213)	SG	8.4/7.0-9.8	1.8/0.9-6.0	17/1-68	20/10-220				
	FW	*9.2/8.8-9.5*	*0.34/0.11-1.0*		*3/1-5*	*19/5-328*	*9/4-10*	*13/6-33*	*2.6/2-3*
Kola-4 (V-213)	SG	8.5/6.9-9.6	1.6/0.9-5.0	17/2-83	15/10-200				
	FW	*9.1/8.6-9.6*	*0.32/0.14-0.78*		*3/1-5*	*15/5-194*	*9/5-20*	*12/5-40*	*2.6/2-3*
NV-3 (V-179)	SG	8.3/8.0-8.4	1.8/1.4-2.2	<150	20/16-21				
	FW	*9.2/9.1-9.2*	*0.26/0.20-0.50*		*1.0*	*41/25-88*	*7/4-10*	*10/7-13*	*2.6/2-3*
NV-4 (V-179)	SG	8.4/8.1-8.9	2.1/1.0-2.0	<150	33/18-67				
	FW	*9.2/9.1-9.2*	*0.26/0.20-0.38*		*1.1/1.0-1.1*	*31/20-44*	*7/3-10*	*9/7-13*	*2.6/2-3*

- **Russian VVER-440 plants are not equipped CPS;**
- **Oil content in feed-water does not exceeds 0.05 ppm**

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Steam generator blow-down water (SG)/feed-water (FW) chemical control data of Russian WWER-1000s
(average values / variation ranges)

NPP↓		pH_{25oC}	X_H	Cl	Na	SO_4^{2+}	N_2H_4	O_2	Fe	Cu
Limit→	SG	8.0-9.2	<6 μS/cm	<150	<300 ppb	<300 ppb				
	FW	*8.8-9.2*	*<0.3 μS/cm*	ppb	*<5 ppb*		*>5ppb*	*<10ppb*	*<15ppb*	*<3ppl*
NV-5	SG	8.6/8.5-8.7	2.5/2.1-4.0	74/	112/30-221	166/80-240				
(V-187)	*FW*	8.6/8.5-8.9	0.14/0.1-0.2	16-124	1.1/1.0-1.5		70/40-90	10/10-15	12/10-15	2.5
Balakovo1	SG	8.5/8.2-8.9	3.2/2.2-3.3	<50	50/28-103	176/104-283	110/			
(V-320)	*FW*	8.9/8.8-9.0	0.18/0.15-0.24		1.1/1.1-1.5		68-148	5	10/7-12	<3
Balakovo2	SG	8.6/8.3-8.8	3.3/2.5-3.8	<50	105/50-231	176/104-283	106/			
(V-320)	*FW*	8.9/8.8-9.1	0.17/0.15-0.21		1.2/1.1-1.3		60-238	5	7.6/4-9	<3
Balakovo3	SG	8.4/8.0-8.9	2.2/1.5-3.2	<50	75/41-148	165/68-269				
(V-320)	*FW*	8.9/8.8-9.0	0.16/0.15-0.18		1.2/1.1-1.2		72/42-122	5	8.9/5-12	<3
Balakovo4	SG	8.7/8.5-8.9	3.1/2.1-4.5	<50	70/30-127	171/113-251	114/			
(V-320)	*FW*	8.9/8.8-9.0	0.17/0.14-0.23		1.2/1.2-1.3		65-131	5	11/9-12	<3
Kalinin-1	SG	8.6/8.3-9.0	2.3/1.8-2.8	56/50-83	61/39-102	126/87-144				
(V-338)	*FW*	8.9/8.8-9.0	0.20/0.13-0.30		1.2/0.8-1.7		47/16-83	10	7.2/5-11	2.6/2-
Kalinin-2	SG	8.7/8.1-9.0	2.7/2.3-3.3	60/50-80	93/46-143	166/64-207				
(V-338)	*FW*	8.9/8.8-9.0	0.20/0.15-0.25		1.4/1.0-1.7		52/47-57	10/10-14	5.6/5-7	2.6/2-

* - Oil content in feed-water does not exceeds 0.05 ppm

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