Chemistry and Corrosion Issues in Supercritical Water Reactors

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Abstract. At the United Nations Millennium Summit, the President of the Russian Federation presented the initiative regarding energy supply for sustained development of mankind, radical solution of problems posed by proliferation of nuclear weapons, and global environmental improvement. Over the past years, Russia together with other countries of the world has seen nuclear renaissance. It is noteworthy that besides mass-scale construction of new nuclear plants some promising innovative projects are being developed by leading nuclear companies worldwide. Russia could significantly contribute to this process by sharing its huge experience and results of investigations. Russia has marked 45 year anniversary of commercial nuclear power industry. It was 45 years ago that a well known VVER reactor and a channel type reactor were put into operation at Novovoronezh NPP and at Beloyarsk NPP, respectively. Beloyarsk NPP's experience with channel type reactor operation could be of special interest for the development of new generation supercritical water reactors. It is because already 45 years ago superheated nuclear steam was successfully used at AMB-100 and AMB-200 channel-type boiling reactors. Water chemistry for supercritical water reactors is vital. Optimum selection of structural materials and chemistry controls are two important issues. Despite multiple studies chemistry for supercritical water reactors is not clearly determined. Unlike thermodynamics or thermo-hydraulics, chemistry cannot be based solely on theoretical calculations. It requires direct and precise testing results with due account of real water parameters. It's a very costly and time-consuming process. Fortunately, some accumulated experience with superheated nuclear stream could help nuclear professional determine approaches to optimum chemistry. The report highlights principles of and approaches to chemistry controls in new generation supercritical water reactors. The report provides recommendations on how to arrange water chemistry controls using the experience of supercritical water plants accumulated in the thermal industry, as well as the experience with operation of Beloyarsk channel-type boiling reactors using nuclear steam overheat up to 510-550ºC.

1. INTRODUCTION

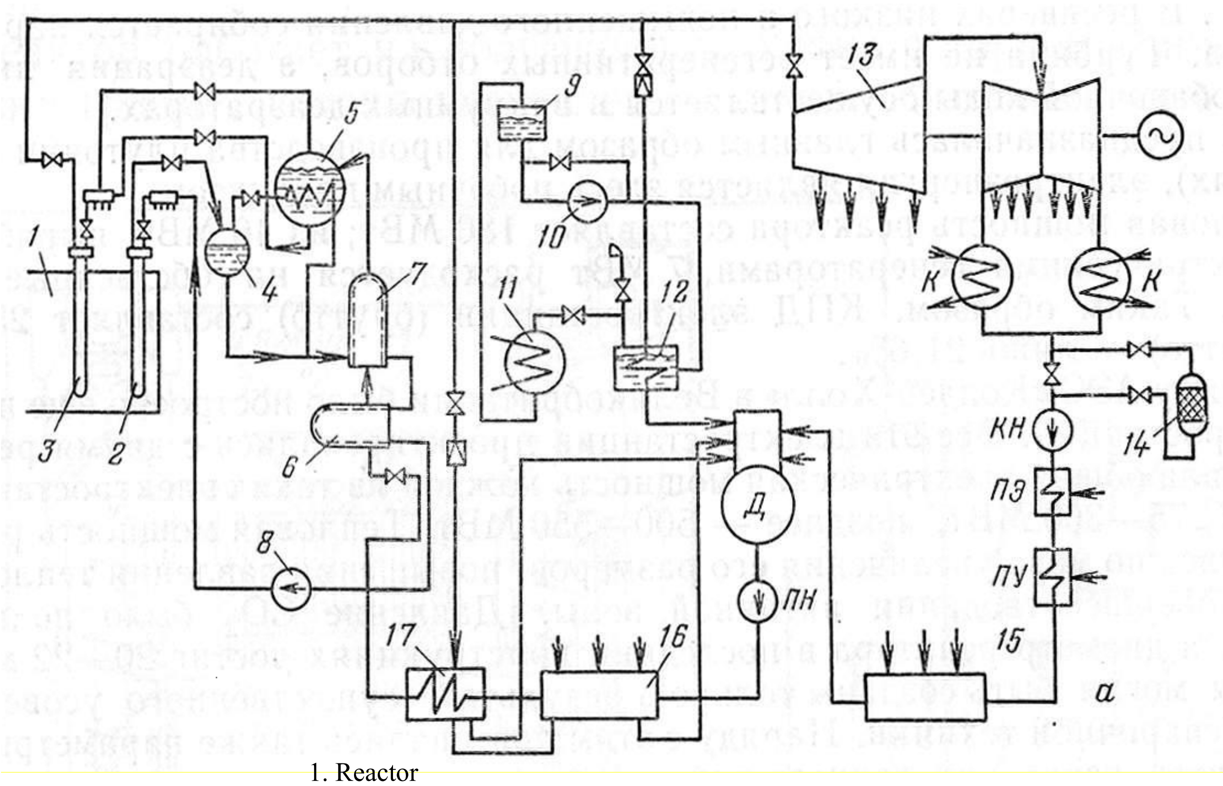
Selection of a future type of a nuclear power plant (NPPs) will need to take into consideration the following requirements:

- Safety
- Low cost (less than $1000/kWt-h)
- Acceptable environmental policy
- Cost-efficiency

To a certain extent new generation reactors, including sodium-cooled fast reactors, as well as supercritical water-cooled reactors (SCWR) meet the above requirements. Supercritical water-cooled reactors are included in the list of Generation IV reactors. Implementation of a one-through reactor cooling process, which does not require steam generators, allows to achieve higher thermal efficiency (up to 44-48%) as compared to top performing in this aspect existing NPPs (less that 33%). Supercritical water (with pressure above 22.12 MPa and temperature above 374.3 ºC) is a single flow fluid, which is very temperature dependent. Heat removal is performed under pseudo critical temperature, which is equal to maximum thermal capacity. At 25 MPs this temperature is 385 ºC.

2. CHARACTERISTICS OF BELOYARSK UNITS 1 AND 2

Beloyarsk NPP has accumulated unique experience of operating reactors with superheated nuclear steam. Figures 1 and 2 show principal diagrams of heat supply systems of Beloyarsk Units 1 and 2, which were connected to the grid in 1964 and 1967, respectively.



1. Reactor
2. Evaporation channel
3. Steam superheating channel
4. Steam drum
5. Evaporator
6 and 7. Economizer first and second stages, respectively
8. Circulating water pump
9. Emergency cooling tank
10. Condenser pump
11. Condenser
12. Operating condenser
13. Turbine generator
14. Condensate demineralizer
15. Low pressure heater
16. High pressure heater
17. Heat exchanger

Fig. 1. Principal diagram of Beloyarsk Unit 1 heat supply system.

At Beloyarsk Unit 1, water at 300ºC and 15.2 MPa flows into reactor channels, from where a steam-water mixture goes into a drum separator. Saturated steam at 10.8 MPa comes out of an evaporator into steam superheating reactor channels where it is heated up to 500-550 ºC. Superheated steam is then delivered to a 100 MWe turbine. Beloyarsk Unit 1 operation has shown that radiological protection could also be provided with a single-circuit system. The experience with Beloyarsk Unit 1 operation was used to develop a single-circuit Unit 2 with nuclear steam superheating and two 100 MWe turbines.

3. SUPPRESSION OF WATER RADIOLYSIS IN BELOYARSK UNIT 1 AND 2 REACTORS

Special studies were conducted to look into the effectiveness of reactor water radiolysis suppression using hydrogen during steam formation, as well as into the possibility of using hydrogen for reactor water radiolysis suppression in steam superheating reactor channels.

Steam and water samples were taken from a steam drum and at the discharge of reactor coolant pumps (RCP). For the purpose of the testing, samples were also taken at the inlet and outlet of superheating channels. To identify hydrogen concentration required for water and steam radiolysis suppression, feedwater treatment with ammonia was discontinued.

The ammonia had been used to maintain proper pH value and suppress water radiolysis caused by hydrogen during partial ammonia decomposition. During the period 16-18 June 1965, hydrogen concentration in saturated steam was 45-88 nml/kg. In circulating water concentration of hydrogen dissolved in water was in the 2.7-12.8 nml/kg range. Despite excessive hydrogen, oxygen concentration in gas phase was 2.3 ppm at the beginning of the test and then decreased to 0.1 ppm. Concentration of oxygen dissolved in concentrated water did not exceed 0.01-0.03 ppm at the RCP discharge.

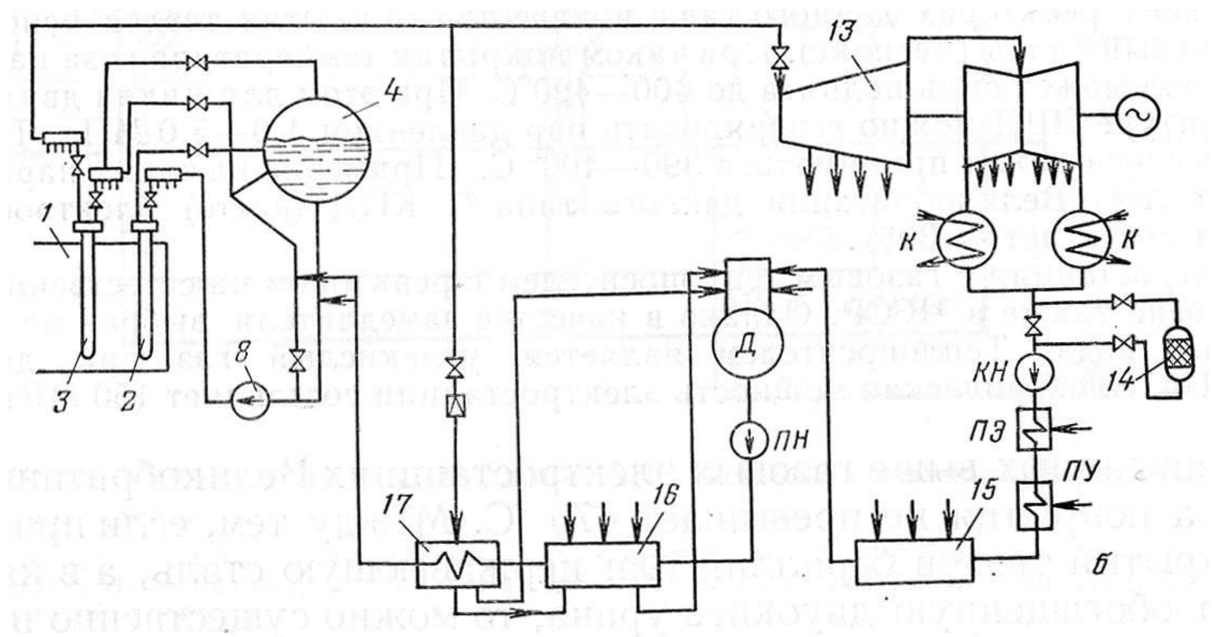


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Fig. 2. Principal diagram of Beloyarsk Unit 2 heat supply system.

The second stage included the studies of steam radiolysis in steam superheating reactor channels and possible steam suppression by means of increased hydrogen content. During testing conducted from 1-7 July 1965, hydrogen content in steam and circulating water made up 1.2-6.2 and 1.2-1.8 nml/kg, respectively. Oxygen content in steam did not exceed 0.15 ppm and was equal to 0.02 ppm while in circulating water. The testing results are indicative of effective water radiolysis suppression.
Additional testing was conducted at 60% rated reactor thermal power, with steam pressure at 8.5 and 6.5 MPa and steam temperature at 298 ˚C and 395˚C at the inlet and outlet of superheating channels, respectively.

With pressure at 12.5 MPa hydrogen content in superheating channels was 20-45 nml/l. At the same time, oxygen content in saturated steam and superheated steam at the superheating channel outlets was 0.01 ppm and approx. 0.1 ppm, respectively [1-6].

Testing showed that oxygen content decreases at superheating channel outlets to 0.03 ppm only if hydrogen content is above 45 nml/l. Steam-gas mixture in turbine ejectors consists of hydrogen (62-65%) and oxygen (8-10%) with hydrogen content in steam equal to 40-45 nml/kg. As a result, the need arises to add air to this mixture to make it explosion-proof, i.e. hydrogen content should be less than 2-3% [7].

Beloyarsk Unit 2's uranium-graphite boiling reactor operated per a one-circuit thermal configuration: steam generated in the reactor vessel was admitted directly into the turbine, while steam condensate served as the major feedwater component. Water chemistry was supposed to provide minimum deposition on fuel surface and minimum corrosion rate in structural materials, while different structural materials were used, including austenitic steel 08X18H10T, pearlitic steel and copper alloy [1-5].

The major difficulty in providing water chemistry control in the said reactor was related to the need for reliable coolant radiolysis suppression. Gaseous molecular products such as hydrogen and oxygen resulting from water coolant radiolysis are admitted with steam into the turbine and then into high pressure heater with extracted steam, causing accelerated corrosion in the steam-water cycle piping [5].

The studies into water radiolysis kinetics, decomposition of ammonia, and nitrite and nitrate formation in the coolant were conducted at Beloyarsk Unit 2. Additionally, ways of suppressing water radiolysis and removing radiolytic oxygen were studied. Testing was conducted with reactor operating within a wide reactor power range of 45 to130 MWt. [5].

Beloyarsk Unit 2 implemented hydrazine-ammonia feedwater treatment. This kind of chemical treatment has a number of weaknesses. Under the impact of radiation in the core ammonia is decomposed into nitrogen and hydrogen producing nitrites and nitrates. The amount of nitrates increases in proportion to reactor power and with reactor at 130 MWt nitrate concentration reaches 1.24 ppm [5].

4. BELOYARSK UNIT 1 AND UNIT 2 WATER CHEMISTRY

Different structural materials were used in heat removal systems at Beloyarsk Units 1 and 2. In Unit 2, corrosion-resistant steel account for 22% of surfaces (reactor channels and piping, separators in steam drums) and pearlitic steel, cupronickel for 78%. Radiolysis in Unit 1's evaporator channels was suppressed by means of ammonia injection. However, this could not be performed at Unit 2 due to increased corrosion of condenser and low pressure heater with tubes made from copper alloy. Hydrazine was, therefore, initially used for oxygen scavenging, while neutral water chemistry was introduced in 1972. This allowed to reduce crud deposition on the fuel. Specified limits and actual coolant parameters of water and steam at Beloyarsk Unit 2 at operating conditions are shown in Tables 2 and 3, respectively. According to the comparative data from Tables 2, reactor coolant rated values under normal operating conditions were within specified water chemistry norms

5. WATER CHEMISTRY EXPERIENCE IN SUPERCRITICAL THERMAL POWER STATIONS

Experience with water chemistry performance improvement at supercritical thermal power plants has shown that use of alkalizing agents has significantly complicated water chemistry controls and at the same time has failed to preclude deposition growth on heat-strained boiler tubing. Power Engineering Research Institute (ENIN) developed and introduced neutral-oxygen water chemistry in 1970s. The said chemistry has proved to be much more efficient in terms of corrosion and deposition reduction and environmental benefits than earlier applied hydrazine-ammonia chemistry. Major advantages of neutral-oxygen water chemistry in thermal power plants are as follows:

- reduced deposition on boiler surfaces
- increased boiler operation intervals between chemical cleaning
- increased reliability of boiler tubing operation
- lower flow accelerated corrosion (FAC) in inlet sections of high pressure heaters

- increased duration of filtration cycles of mixed bed condensate polisher system
- reduced demand in chemicals
- reduced volume of water waste

Table. 1. Beloyarsk Unit 2 water and steam specified and measured (in brackets) chemical parameters

Chemical parameters	Feedwater	Reactor coolant	Reactor blowdown water	Saturated/ superheated steam	Turbine condensate
Total hardness (µg-eq./kg)	3 (<3)	15 (<3)	- (3-6)	-	3 (3)
Alkalinity (µg-eq./kg)	_	_	50	_	_
Sodium (ppb)	-	-	-	-	10
Silica (ppb	30	-	1000(100-300)	20 (5-15)	-
Chlorides (ppb)	- (25)	30[a] (25)	- (25)	-	-
Iron (ppb)	- (20-60)	60(20-60)	- (30-60)	- (20-30)	-
Copper (ppb)	5	-	- (7-30)	- (0.4/-)	5 (0.8)
Corrosion products (ppb)	-	-	500	-	5
Dissolved oxygen (ppb)	10 (10-15)	- (30)	- (30)	-(5000-6000)	30 (40-50)
pH value at 25 ºC	- (9.2-9.5)	8.0 (8-9)	- (9.0-9.5)	- (9.0-9.5)	- (9.0-9.5)
Ammonia (ppm)	(1-2.5)	(0.6-1.4)	(0.6-1.4)	(0.8-2)	(1-2)
Activity (Ci/kg)	-	-	(10)	(-/0.1)	-

[a] Increase in reactor water chloride up to 150 ppb was allowed within 20 hrs.

Major conditions for successful implementation of neutral-oxygen water chemistry
- deep condensate demineralization to conductivity value below 0.15 µS/cm
- copper alloy exclusion in heat exchangers and thorough preliminary cleanup from copper containing deposits
- preventing intrusion of both potentially acidic organic contaminants incl. resin fines from condensate polishing system
- preventing cooling water in-leakage in turbine condenser
- implementing chemical treatment monitoring system
- Potential issues in the case of neutral-oxygen water chemistry implementation
- increased oxidation in steam superheating surface
- corrosion cracking of austenitic tubes of steam reheater in the presence of chlorides
- erosion-corrosion in turbines
- corrosion of high pressure heater steam cooler coil

Conditions for minimizing the above adverse phenomena:

- removing gases from heat exchangers and continuous deaerator operation
- oxygen injection into the suction side of second condensate pump and booster pump

6. WATER CHEMISTRY OF WATER GRAPHITE SUPERCRITICAL REACTOR

While designing a once-through water cooled graphite moderated reactor (WGSR) with supercritical parameters (24.5 MPa, 540 ºC), selection of reactor materials is critical in view of long design life of this type of reactors (60 years). It appears expedient to completely exclude copper containing alloys and use a titanium condenser to ensure reliable condenser tightness. Additionally, it is necessary to preclude deposition on fuel and turbine by minimizing intrusion of corrosion products and silica into coolant. Composition of deposits in the narrow once-through section of the turbine is dependent on coolant chemistry (see Figure 3). Priority is given to high pure water achieved through chemical treatment system. Neutral water chemistry with demineralization of the entire turbine condenser flow by a condensate polisher seems to be the proper option.

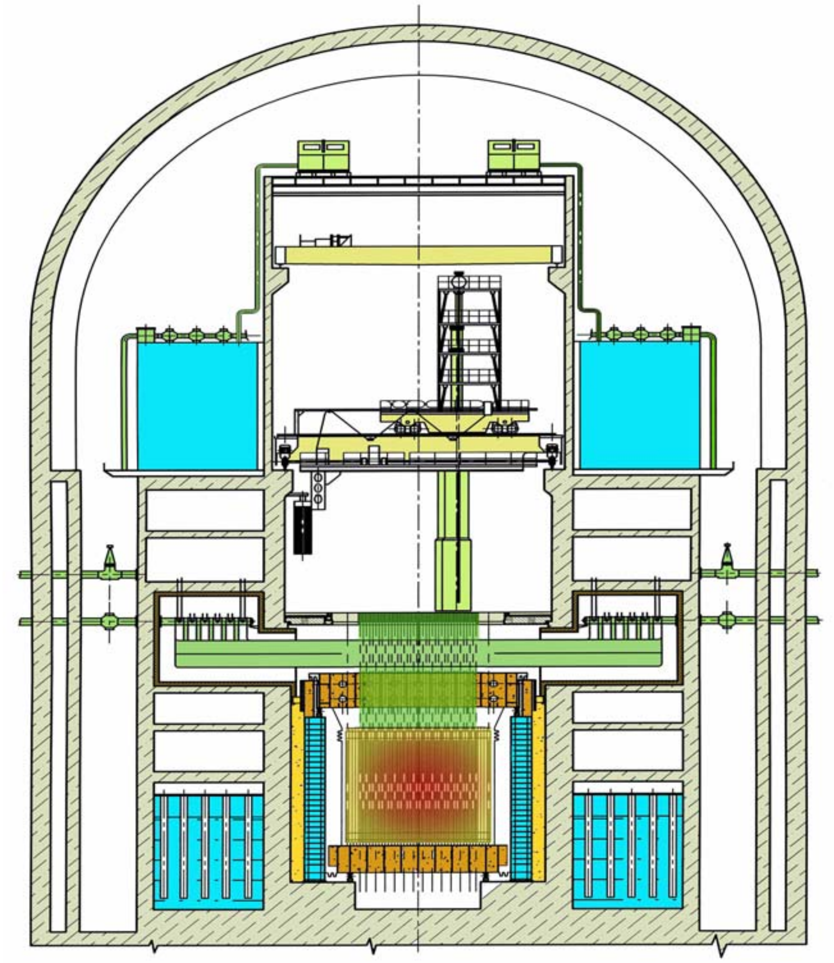

Fig. 3. Supercritical water-cooled graphite-moderated reactor

Neutral water chemistry with oxygen injection into condensate up to 200 ppb will allow to reduce transport of corrosion products. Water coolant radiolysis suppression by gaseous hydrogen injection into the intake of a feedwater pump has a number of challenges. At the early design stage, the following requirements to feedwater are proposed:

- conductivity < 0.1 µS/cm
- chlorides, sodium, copper < 2 ppb
- silica, dissolved oxygen < 20 ppb
- pH value 6.8-7.1 at 25ºC
- iron < 5 ppb
- oil < 100 ppb

Hydrogen injection is maintained allowing reduction in oxygen concentration by means of recombination.

The following challenges need to be addressed at the further design stages:
- selection of structural materials
- selection of water chemistry
- selection of coolant purification techniques
- minimization of radioactive corrosion products transport of from the reactor with a steam flow to balance-of-plant equipment

Water chemistry will be finally selected after the supercritical reactor design configuration is approved. Irrespective of water chemistry, effective purification from corrosion products should be developed.

Adsorbent like titanium-based Thermoxide™ that can operate at up to 350ºC could be used as a filter material at high temperature. These adsorbents could be periodically cleaned from accumulated corrosion products (Table 3).

Table 2. Characteristics of thermoxide adsorbents

Parameters	Thermoxide 3A	GDT-M
Physical condition	Glass-like spherical granules	Grains of irregular shape
Size of granules, mm	0.4-1.8	0.4-2.0
Bulk density of granules, kg/dm^3	1.05	1.85-1.95
Mechanical strength of granules, MPa	12-18	49-48
Static ion exchange capacity	2.6-2.8[a]	-
Capacity of corrosion products, kg/m^3	-	30-40

[a] for alkaline metals, with pH=7.0

High temperature coolant purification upstream of the reactor and condensate demineralizer are aimed to provide proper coolant quality.

Other advanced techniques including microfiltration should be considered besides high temperature filtration to allow highly effective purification of liquid and gaseous high temperature and aggressive media.

7. CONCLUSIONS

Chemistry peculiarities and corrosion protection issues in supercrtical water reactors were considered with due account of the experience of superheated steam reactors (Beloyarsk NNP) and fossil-fueled plants, which are similar to SCWCR plants in terms of coolant parameters. Different chemistry options were compared and neutral water chemistry was found to be the most suitable for SCWCR type of reactors. Some modifications are possible, as structural materials are not finalized.

Extremely pure coolant should be used at SCWCR plants. To address this challenge it seems expedient to use the entire experience accumulated in power engineering. Full flow condensate demineralization and pre-reactor mechanical cleanup of feedwater by means of high temperature filters are recommended to meet the above requirements. Optimized filter material should be selected to allow high temperature coolant filtration.

A condenser with titanium tubing is recommended to minimize cooling water in-leakage into condensate.

Reactor coolant radiolysis could be suppressed by means of injection of hydrogen, ammonia or hydrazine.

Microinjections of depleted zinc into the primary coolant may be effective to minimize corrosion processes and reduce cobalt radionuclide accumulation.

Different structural materials were bench tested directly in the coolant system of Beloyarsk NPP. Thorough studies of corrosion products behavior were conducted directly in the coolant system of Beloyarsk NPP using sophisticated techniques. This allowed studies of the impact of coolant quality on corrosion and corrosion products transport. In 1976, Beloyarsk 2 was the first in Russia to implement chemical monitoring system with state-of-the-art on-line chemical analyzers.

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