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Chemistry and Corrosion Issues in Supercritical Water Reactors

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Introduction (1)

In 2000, at the United Nations Millennium Summit, the President of the RF 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.
Besides mass-scale construction of new nuclear plants some promising innovative projects are being developed by leading nuclear companies worldwide.
Russia could contribute to this process by sharing its huge experience with nuclear installations and results of comprehensive investigations.

Introduction (2)

Russia has marked 45th anniversary of commercial nuclear power industry.
45 years ago, VVER and channel power reactor were put into operation.
Beloyarsk NPP's experience with channel reactor operation could be of special interest for the development of SCWR.
Superheated steam was successfully used at AMB-100 and AMB-200 channel-type boiling reactors during 45 years.
Selection of structural materials and chemistry controls for SCWR are important issues.
Despite multiple studies chemistry for SCWR is not clearly determined.
Chemistry cannot be based solely on theoretical calculations.
Direct and precise testing with due account of real parameters is a very costly and time-consuming process.
Some accumulated experience with overheated nuclear steam could help nuclear professional to determine optimum chemistry.
Report highlights principles and approaches to chemistry controls in SCWRs.
Recommendations for SCWR are based on the experience of supercritical fossil faired power plants, as well as on the experience with operation of AMB reactors using nuclear superheated steam up to 510-550ºC.

SCWR development in Russia (1)

Gidropress develops some new Super WWER design with SCWR

6th International Conference
«Safety Insurance for VVER Nuclear Power Plants»
26 - 29 May 2009, Podolsk, OKB “GIDROPRESS"

18 papers at Section 6:
Innovative Reactors of 4th Generation, Cooled by Supercritical Water

International Workshop on
SUPERCRITICAL WATER AND STEAM IN NUCLEAR POWER ENGINEERING: PROBLEMS AND SOLUTIONS
22-23 October 2008, NIKIET, Moscow
(24 papers)

From nuclear superheated steam to SCWR

N.A.Dollezhal: Evolution of nuclear superheated steam

1948 – development of AM reactor (9,8 MPa, 290°C)

1954 – AM reactor commissioning

1958 – report at Geneva conference on AMB (12 MPa, 550°C)

1964 – AMB-100 reactor commissioning

1967 – AMB-200 reactor commissioning

1965 г. – preliminary design project of AMB-3 (24 MPa, 540°C)

Parameters	AMB 1&2	RBMK-S	AMB 3	SCWR
Power, MWt	100 & 200	1200	1000	850
Pressure, MPa	8,8	6,5	24	24
Temperature, °C	500	450	540	540

Ref.: A.A.Petrov, A.A.Romenkov, O.A.Yarmolenko “NIKIET Experience in the Development and Operation of Pressure-Tube Reactors with High and Supercritical Coolant Parameters”

A.A.Petrov, A.A.Romenkov, O.A.Yarmolenko "Potential of Beloyarsk NPP operational experience in area of nuclear superheated steam for both SCWR and new generation nuclear reactors with high coolant parameters"

(10-11.07.09, Scientific conference «45 years of Beloyarsk NPP»)

Selection of structural materials and component lifetime

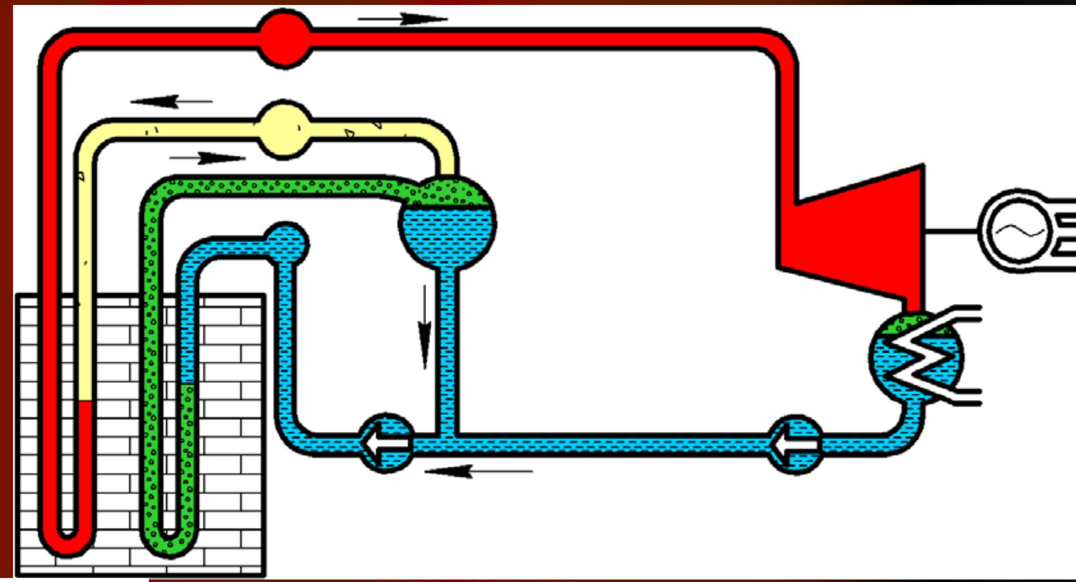
Operational experience of AMB and RBMK channel reactors is the basis for addressing problems:

- **Successful long-term operation of superheated steam channels is wide experimental experience for tube type fuel elements**
- **Experimental channel testing in superheated steam confirmed fuel rod reliable operation up to 17 MWt·day/kg**

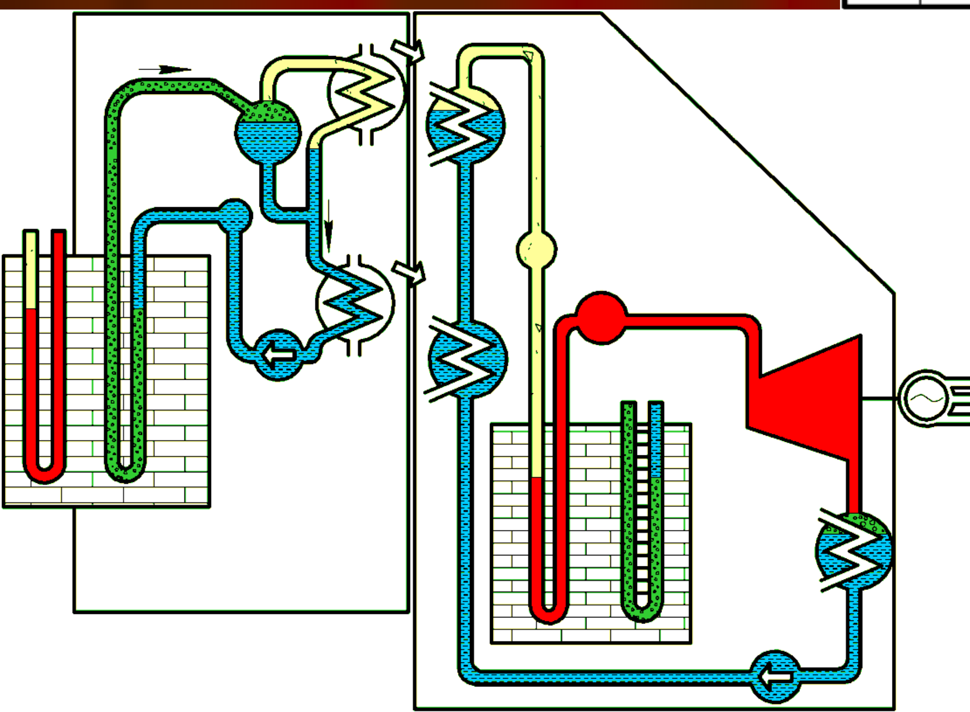
Beloyarsk NPP experience with nuclear superheated steam should be looked into for data on in-core structural material testing under superheated steam up to 700°C under SCWR conditions

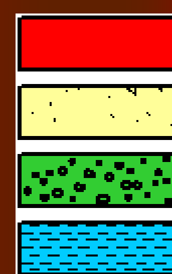
Principal Diagram of Beloyarsk Unit 1 & 2 Heat Supply System

Beloyarsk NPP has accumulated unique experience of operating reactors with superheated nuclear steam. Beloyarsk Units 1 and 2 were connected to the grid in 1964 and 1967, respectively.



Unit 2 – AMB-200





Superheated steam
Saturated steam
Steam-water mixture
Water phase

Unit 1 – AMB-100

Suppression of Water Radiolysis in AMB-100 and AMB-200

Special studies were conducted to look into the effectiveness of reactor water radiolysis suppression using hydrogen during steam formation and 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 RCP discharge. 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.

Ammonia had been used to maintain proper pH value and suppress water radiolysis caused by hydrogen during partial ammonia decomposition.

On 16-18 June 1965, hydrogen content in saturated steam was 45-88 nml/kg. Dissolved hydrogen in circulating water was within 2.7-12.8 nml/kg range. Despite excessive hydrogen, oxygen concentration in a gas phase was 2.3 ppm at the beginning of the test and then decreased to 0.1 ppm. Concentration of dissolved oxygen in water did not exceed 0.01-0.03 ppm at the RCP discharge.

AMB-100 and AMB-200 Water Chemistry Optimization

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), while pearlitic steel and cupronickel account for 78% of surfaces of secondary components.

Radiolysis in AMB-100's evaporator channels was suppressed by means of ammonia injection.

This technique could not be used at AMB-200 due to increased corrosion in condensers and low pressure heaters having copper alloy tubes.

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.

Reactor coolant rated values under normal operating conditions were within specified water chemistry norms

AMB-200 specified and measured (in brackets) water and steam parameters

Parameters	Feedwater	Reactor cooliant	Reactor blowdown water	Saturated/ superheated steam	Turbine condensate
Total hardness, µg-eq./kg	3 (<3)	15 (<3)	- (3-6)	-	3 (3)
Alkalinity (without ammonia), µg-eq./kg	_	_	50	_	_
Sodium, ppb	-	-	-	-	10
Silica, ppb	30	-	1000 (100-300)	20 (5-15)	-
Chloride, ppb	- (25)	30* (25)	- (25)	-	-
Iron, ppb	- (20-60)	60 (20-60)	- (30-60)	- (20-30)	-
Copper, ppb	5	-	- (7-30)	- (0.4/-)	5 (0.8)
Total corrosion products, ppb	-	-	500	-	5
Dissolved oxygen, ppb	10 (10-15)	- (30)	- (30)	- (5000-6000)	30 (40-50)
pH value	- (9.2-9.5)	8.0 (8.0-9.0)	- (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/l	-	-	(10)	(-/0.1)	-

* Increase in reactor water chlorides up to 150 ppb was allowed in abnormal situations within 20 hrs

Component replacement and fuel crud reduction

1% Cr carbon steel 12Х1МФ type,

Cupronickel Cu-Ni5%-Fe1% and brass

Austenitic steel Cr18%Ni10%Ti type

Replacement and isolation of LPHs #1...5 started in 1974 allowed to reduce both final feedwater copper from 6.7 to 1.5 ppb and fuel deposition growth from 0.4 to <0.2 mm per 1000 hr

EROSION-CORROSION ISSUES / RELIABILITY OF CORE COMPONENTS

In 1974, thick copper (75-80%) deposits in the upper section of the core with low coolant pH=6.6

Copper deposits in evaporator channels increased up to 0.6 mm over 3-4 years with pH=8.5

Flushing deposits from evaporating channels by phosphofic acid with some additives

Corrosion testing at experimental loops

AMB loop-steam-water cycle

Bench on HPH-6 and HPH-9 bypass sections

EROSION TESTING OF STRUCTURAL MATERIAL SPECIMEN IN FEEDWATER SYSTEM

In 1975-1976, corrosion testing of carbon steel 20 type specimens was conducted in feedwater system bypass sections to optimize chemistry to suppress FAC

FAC rate ~1 μm/hr at AMB-100 with hydrazine-ammonia feedwater treatment

Feedwater system section	FAC rate, μm/hr	
	Neutral chemistry	Oxidizing chemistry
Upstream of HPH-6	8-10	0,16-0,68
Downstream of HPH-9	9-16	0,02-0,1

Stabilizer presence in commercial hydrogen peroxide resulted in low pH of saturated and superheated steam, thereby aggravating FAC in low pressure turbines and regenerative heat exchangers on the heater drain side. Hydrogen peroxide was substituted by dissolved oxygen injection.

Crud studies on AMB cycle components

Primary system surfaces incl. ~8,300 m^2 AS + stellite ~2 m^2

Secondary system incl. ~6,200 m^2 AS + 3,000 m^2 CS + 5,000 m^2 cupronickel + 2,000 m^2 brass + 4 m^2 stellite overlays

Total crud accumulation in the primary system outside of core ~80 kg (water section ~66%, steam-water section ~19%, steam section ~15%) are consistent with corrosion rate of ~1.2 mg/(m^2×hr)

Total crud accumulation in the secondary system ~770 kg

Crud thickness was ~2 mg/cm^2 in water section, ~0,6 mg/cm^2 in steam-water section, ~0,5 mg/cm^2 in steam section.

Primary system crud - Co-60, Co-58, Mn-54, Cr-51.

Secondary system - Co-60, Co-58, Mn-54, Cr-51, Sb-124

Reference

Radioactive Deposits in Technological Equipment Surfaces of Beloyarsk NPP. Atomic Energy. Vol.24. Iss.3. March 1968. P.219-222.

Studies of Long Lived Activity in AMB Coolant

Sampling of coolant from steam drum blowdown and steam

Steam drum blowdown:

Co-60 (filter ~97%, CatEx~2-7%, AnEx~1-3%),

Mn-54 (filter ~30-50%, CatEx ~50-70%, AnEx <3%),

Cr-51, Co-58 and Sb-124 (over 90% in insoluble form)

Drum steam: Co-60 and Mn-54

Dispersion analysis detected max activity of insolubles 3-10 µm (75% Co-60 and Cr-51, 63% Mn-54, 73% Co-58)

Sampling secondary coolant:

1) condensate of superheated steam, 2) steam condensate downstream of turbine, 3) evaporator blowdown,

4) condensate of evaporator saturated steam

Max superheated steam activity

Primarily activity in the form of insoluble particles >1 µm in size

Reference

Studies of Long Lived Activity in Beloyarsk NPP Coolant. Atomic Energy. Vol.24. Iss.3. March 1968. P.222-226

WATER CHEMISTRY EXPERIENCE IN SUPERCRITICAL THERMAL POWER STATIONS

Use of alkalizing agents has complicated water chemistry controls and has failed to preclude deposition growth on heat-strained boiler tubing.

Moscow State Power Engineering Research Institute (ENIN) developed neutral-oxygen water chemistry (NOWC), which has proved to be more efficient in terms of corrosion and deposition reduction, environmental benefits than earlier applied hydrazine-ammonia chemistry.

Major advantages of NOWC in thermal power plants:

-Reduced deposition on radiation surfaces of heat

-Increased boiler interflushing intervals

-Increased reliability of boiler tubing system operation

-Lower FAC in inlet sections of HPH

-Increased duration of filter cycles of MBD in condensate polishers

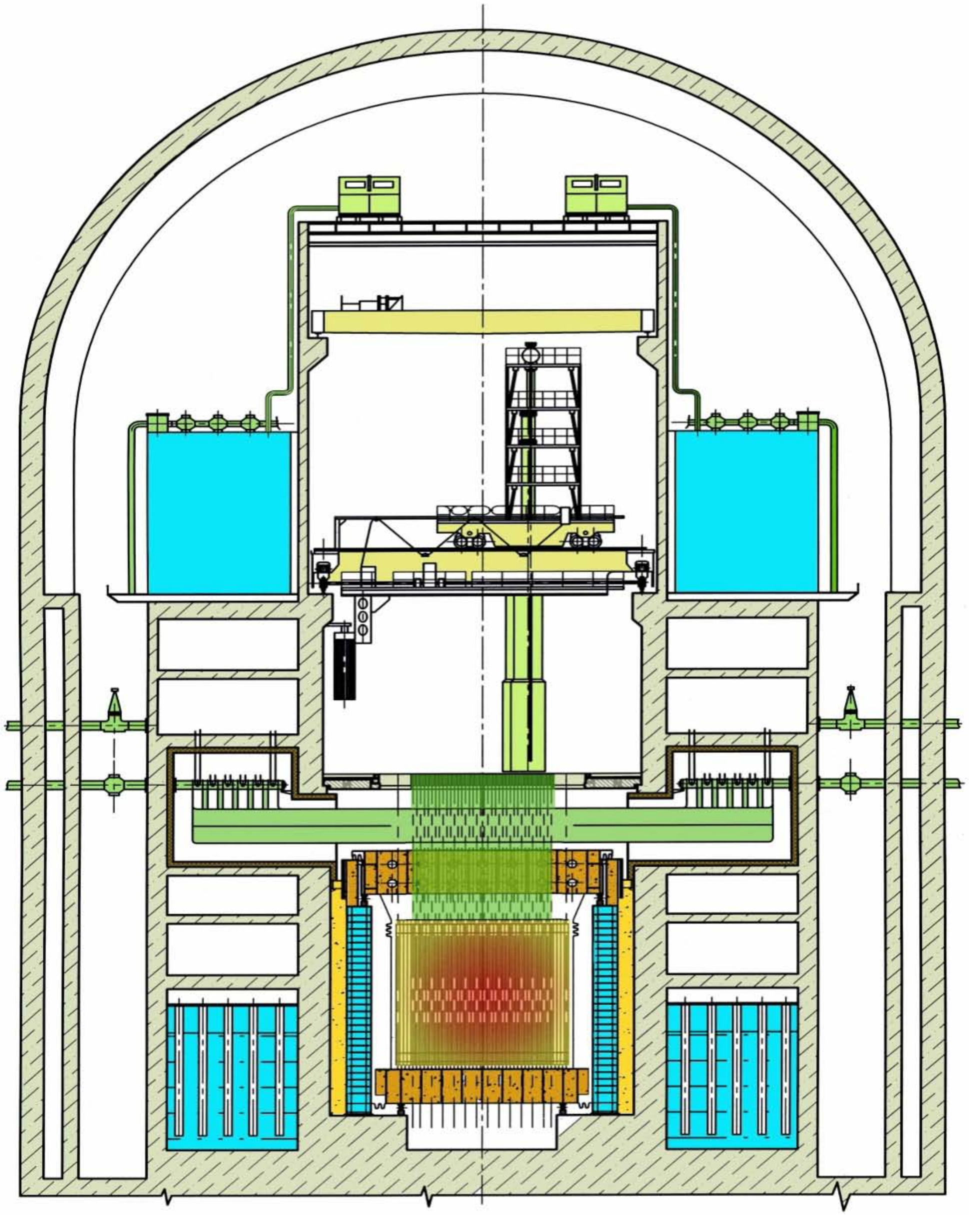
-Reduced demand in chemicals

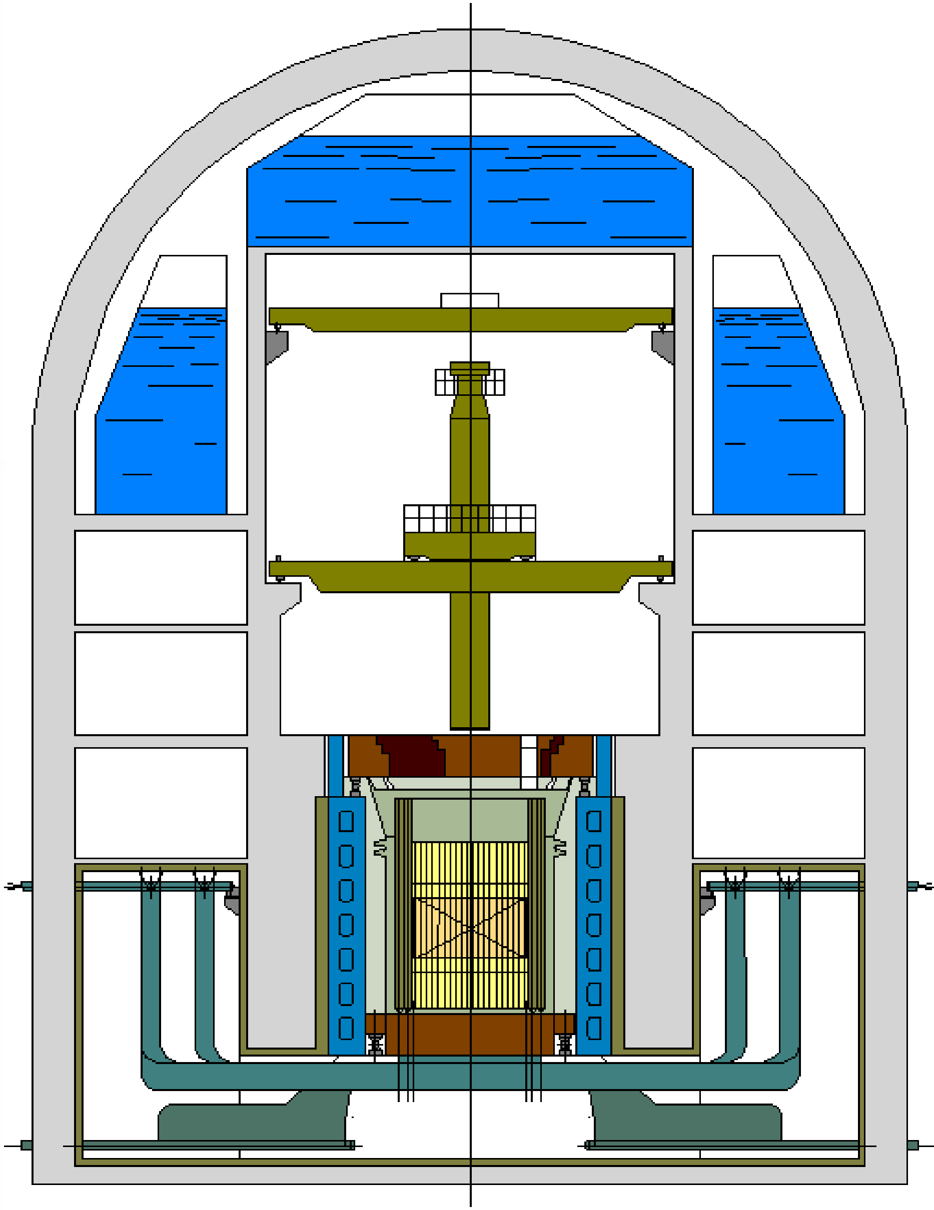
-Reduced volume of waste water

MAJOR CONDITIONS FOR SUCCESSFUL IMPLEMENTATION OF NEUTRAL-OXYGEN WATER CHEMISTRY IN SUPERCRITICAL THERMAL POWER STATIONS:

- Deep condensate demineralization to conductivity <0.15 µS/cm
- Avoiding the use of copper-containing alloys
- Preventing intrusion of organic contaminants and resin fines
- Preventing cooling water in-leakage in turbine condenser
- Implementation of chemical treatment monitoring system

Cross sections of supercritical water-cooled graphite-moderated reactor VGERS-850 (left) and fast channel power reactor BKER-300 (right)





INNOVATIVE CHANNEL SUPERCRITICAL REACTORS (1)

In 2006 NIKIET developed a concept of supercritical water cooled (25 MPa and 550°C) and graphite-moderated reactor VGERS.
VGERS facility is a pressure-tube once-through uranium-graphite reactor of generation IV designed for electricity and heat production.
Specific features of the pressure-tube structure permit designing a series of power units with electric power ranging from 850 MW to 1700 MW.
Development of VGERS is based on successful operation of fossil fuel units at supercritical pressure. The materials applicability to the fuel cladding and channels was verified during the tests of experimental channels at Beloyarsk NPP, which were conducted under temperature conditions including steam superheating. The experience in construction and operation of reactor with steam superheating available in Russia, R&D and working through the concepts of the pressure-tube reactors with the coolant supercritical parameters suggest that development of pressure-tube power reactor with a graphite moderator is the most practicable.
Economic effect of VGERS is due to the high efficiency of the power unit and the relevant reduction of specific capital investments into numerous NPP systems, their cost depending essentially on the reactor thermal power, as well as reduction in the amount of the equipment due to the reactor design simplification. Reactor facility, refueling complex, as well as safety systems are arranged within a leak-tight containment.

INNOVATIVE CHANNEL SUPERCRITICAL REACTORS (2)

Fuel channel is being made as the Fielde tube cooled by coolant, which permits maintaining of graphite stack and metal structure temperature at acceptable level. The use of ceramic-metal fuel (similar to successfully used in the steam superheating channels of AMB) permits reduction in fuel temperature, higher burnup, as well as restriction of fission products release from the fuel. Design of the VGERS safety systems was based on a balanced combination of passive and active systems. It allowed to improve stability of the reactor facility in the modes requiring safety system actuation. VGERS reactivity coefficients defining the reactor dynamics are negative.
Reactor has 2 independent shutdown systems: FPR (fast power reduction) and EP (emergency protection), each featuring efficiency adequate for reactor scram and maintaining the reactor in subcritical state.
Specific capital investments into VGERS of the proposed power will make up approximately $1000/kW. Estimates of emergency and transient conditions made using the RELAP code allowed to evaluate dynamic features of the reactor facility and make conclusions regarding sufficient safety. The research has shown satisfactory temperature conditions of the reactor structural elements in all the examined modes. R&D for the project support should be mainly aimed at selecting structural materials for the reactor core featuring improved resistance to corrosion, deformation and swelling at high temperatures and pressures and substantiation of their applicability. The issues of the coolant purification and water chemistry are highly important.

INNOVATIVE CHANNEL SUPERCRITICAL REACTORS (3)

A concept **of** a fast reactor has been proposed based on the following provisions:

- operation with a breeding coefficient in excess of unity;
- use of annular fuel elements cooled by coolant from the inside;
- development of a core design with a dense lattice with high uranium content;
- minimization of void content within the core;
- use of dispersion (cermet) fuel.

The core largely contains fuel elements and is accommodated in an isolated reactor cavity ventilated by either chemically passive or inert gas (Ar, N_2 or other). Use of tubular fuel elements places certain constraints on the fuel assembly design and excludes refueling on the operating reactor. The concept under consideration employs single-circuit, once-through cooling of the reactor with supercritical water. Coolant pressure has been increased to raise plant efficiency up to 45%, which improves considerably the power unit economic performance, reduces the specific investments in equipment, installation and construction and improves reactor fuel utilization. Concept relies on proven range of supercritical turbine sets 300-1200 MW.

The basic layouts have been studied as well as components and operation modes of the normal operation systems and safety systems have been defined.

Ref.: A concept of the fast pressure-tube power SCW reactor BKER
S.V. Barinov, V.K. Vikulov, V.Ye. Gmyrko, I.I. Grozdov, A.A. Petrov (NIKIET)

WATER CHEMISTRY OF INNOVATIVE CHANNEL SUPERCRITICAL REACTORS

While designing once-through water-graphite supercritical reactor VGERS or fast channel power reactor BKER-300 with supercritical parameters (24.5 MPa, 540^0C) selection of reactor materials and water chemistry optimization are critical issues in view of long design life up to 60 years.

It appears expedient to exclude copper containing alloys and use a titanium condenser.

It is necessary to preclude deposition on fuel and in once-through section of the turbine by minimizing corrosion products and silica deposition.

Crud deposition in the turbine is dependent on reactor chemistry.

Neutral water chemistry with demineralization of turbine condensate in a condensate polishers seems to be the proprietary option.

Neutral oxygen water chemistry with oxygen injection into condensate to reach concentration of 200 ppb will allow to reduce transport of corrosion products.

Water coolant radiolysis could be suppressed by gaseous hydrogen, ammonia or hydrazine injection into feedwater.

WATER CHEMISTRY OF CHANNEL TYPE SUPERCRITICAL WATER COOLED REACTOR

At the early design stage, the following requirements to feedwater are proposed:

- conductivity < 0.1 µS/cm
- chloride, sodium, copper < 2 ppb
- silica, dissolved oxygen < 20 ppb

pH value at 25ºC   6.8-7.1

- iron < 5 ppb
- oil < 100 ppb

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

WATER CHEMISTRY OF CHANNEL TYPE SUPERCRITICAL WATER COOLED REACTOR
(continued)

The following challenges need to be addressed at the further design stages:

- Optimization of chemistry.
- Selection of coolant purification techniques.

Substantiation of balance-of-plant equipment servicing under the condition of transport of radioactive corrosion products from the reactor with a steam flow.

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.

Adsorbents like titanium-based thermoxide that can operate at up to 350ºC could be used as a filter material for a high temperature filter.

These adsorbents could be periodically cleaned from corrosion sludge and hydraulic overloads.

Physical and chemical characteristics of Thermoxide type adsorbents

Indicator	Adsorbent Grade	
	Thermoxide 3A	**GDT- M**
Physical configuration	**Glass-like spherical white colored granules**	**Light yellow grains of irregular shape**
Physical configuration	**0.4 – 1.8**	**0.4 – 2.0**
Size of granules, mm	**1.05**	**1.85 – 1.95**
Bulk density of granules, kg/dm^3	**12 - 18**	**49 - 98**
Mechanical strength of granules, MPa	**2.6 – 2.8**	**-**
Static exchange capacity with pH=7.0	**-**	**30 - 40**

CONCLUSIONS

1. At the design stage, it is proposed to implement neutral water chemistry with full flow condensate demineralization and feedwater high temperature filtration.
2. A condenser with titanium tubing is recommended for use to minimize cooling water in-leakage into condenser.
3. Optimal filter material should be selected to allow effective high temperature coolant filtration.
4. Reactor coolant radiolysis can be suppressed by increasing hydrogen content by hydrogen, ammonia or hydrazine injections.
5. Micro additives of depleted zinc into the coolant could minimize corrosion processes and reduce active cobalt accumulation.