

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Faculty of Technology
Degree Programme in Energy Technology

Miskimova Asiya

**WATER CHEMISTRY MANAGEMENT FOR FUTURE
LARGE EXPERIMENTAL FACILITIES**

Examiner: Professor Juhani Hyvärinen
Supervisor: M.Sc. Antti Räsänen

ABSTRACT

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Miskimova Asiya

Water chemistry management for future large experimental facilities

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Examiners: Prof. Dr. Juhani Hyvärinen
M.Sc. Antti Räsänen

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The thesis focuses on the water chemistry of the experimental test facilities and their reference VVER reactors. The main objective of the thesis is to provide recommendations for water chemistry management for laboratory facilities (VEERA, PACTEL) simulating the VVERs and for the large future facilities of the Lappeenranta University of Technology.

In the beginning, the concept of nuclear power generation and the applicability of the nuclear power usage is discussed. Next, different water chemistry and water purification systems in primary and secondary circuits currently used at the power plant have been outlined. Also the construction geometry and design of test facilities PACTEL and VEERA, as well as the operation principles of their main equipment has been described. Finally, the appropriate water chemistry and water treatment system have been proposed for the existing and future experimental facilities of LUT.

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NOMENCLATURE

ACCS	Accumulator Core Cooling System
BWR	Boiling water reactor
CFS	Core Flooding System
CP	Corrosion products
CVCS	Chemical and Volume Control system
DC	Downcomer
ECCS	Emergency core cooling system
ETA	Ethanolamine
FAC	Flow accelerated corrosion
HPIS	High Pressure Injection System
IAEA	International Atomic Energy Agency
LP	Lower Plenum
LPIS	Low Pressure Injection System
LOCA	Loss-of-Coolant Accident
LUT	Lappeenranta University of Technology
LWR	Light-water reactors
NPP	Nuclear Power Plant
ODA	Octadecylamine
PACTEL	Parallel Channel Test Loop
PWR	Pressurized water reactor
RCP	Reactor Coolant Pump
RPV	Reactor Pressure Vessel
SCC	Stress Corrosion Cracking
SG	Steam Generator
SWO	Special Purification Circuit
UP	Upper Plenum
VTT	Technical Research Centre of Finland
VVER	Vodo-Vodjanoy Energeticheskoy Reaktor
WC	Water Chemistry
WCG	Water Chemistry Guidelines
WTS	Water treatment system

1 INTRODUCTION

Power generation is one of the most important branches of economy, including the fuel and energy resources, generation, transformation, transmission and consumption of different energy types. However the global energy consumption is growing much faster than its production. Currently most of the natural resources on our planet are exhausted. The international community faces the global problem of lack of fossil fuels. Nowadays the humanity is at the cusp of environmental disaster due to the global warming on the Earth. The development of the nuclear energy could be an alternative solution to these problems. The cost of energy generated by nuclear power plants is lower the market value of fossil fuels. Consequently, increasing the number of constructed nuclear power plants is an obvious fact. Nuclear energy provides the power generation at low cost, besides it does not produce the greenhouse gases. The amount of commercial nuclear reactors in operation were 438 and their total capacity reached 376.2 GW(e) at the end of 2014 (IAEA 2015, 1). Nuclear energy enables countries with limited natural resources to generate electric power independently on the world fuel market.

Generally, the NPP failures and destruction of equipment are related to operation of auxiliary units. The reliability of equipment under the water chemistry is a basis of safety and stable operation of nuclear power plant. (Kritsky 1999, XI)

2 GENERAL DESCRIPTION OF NUCLEAR POWER

During the process of nuclear fission reactors generate energy - the nucleus splits into two parts. The element with a heavy nucleus, typically uranium-235 is bombarded with a free neutron. Heavy nucleuses are divided into two parts. At this heavy nucleus fission the large amount of energy is released in the form of heat and light. In nuclear power reactors neutrons interacting with the fissile nuclei in the fuel cause fission chain reactions and each fission gives rise to approximately 200 mega electron volts (MeV) ($1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$) of energy, two or sometimes three fission products and two or three neutrons. They bombard other nuclei of uranium-235, split them and form a fission chain reaction. Figure 1 illustrates the process of nuclear fission. (Gofman and Tamplin 1979, 28-30)

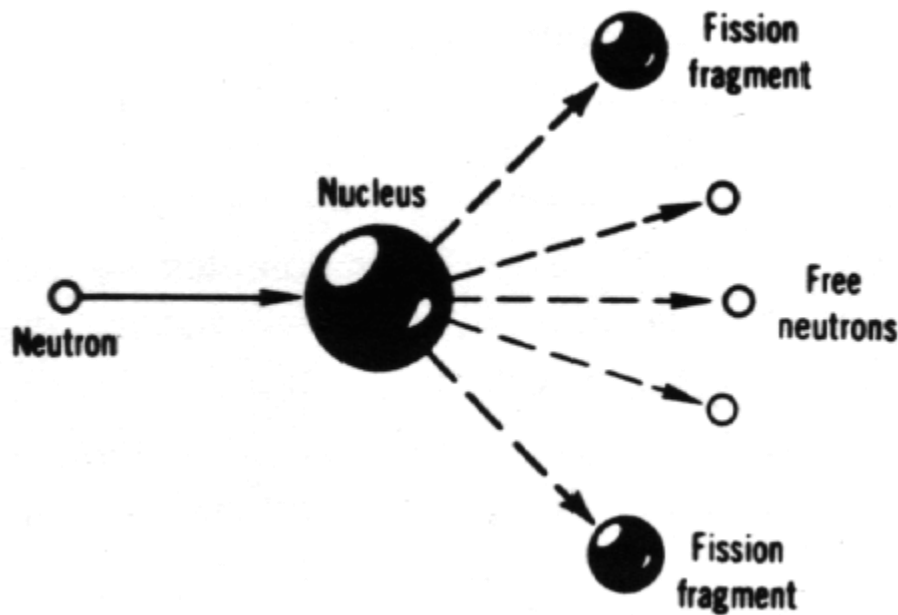


Fig. 1. Nuclear fission. (Gofman and Tamplin 1979, 29)

A nuclear reactor is the device where a sustained nuclear chain reaction is performed and controlled. The reactor must initiate and control the nuclear reaction. The main structural elements of a heterogeneous nuclear reactor are: pressure vessel, core consisting of fuel rods, the moderators, control and protection systems, neutron reflector, heat removal systems, thermal protection,

biological protection, and fuel rod loading/unloading system. Most of reactors use fuel pellets of uranium dioxide. These pellets are packed into the nuclear fuel elements loaded into the core. The core consists of fuel assemblies and control rods. Moderators are used to suppress the excessive reactivity. The control rods adjust the reaction rate. They can speed up, slow down or stop the reaction. The rods are made of materials, which absorb neutrons, cadmium, or boron. The control rods move between the fuel elements absorbing the neutrons to a greater or lesser extent, depending on the desired rate of nuclear reaction. (Dementev 1990, 12-14, 16-17)

To maintain the reactor power at certain level, it is necessary to observe the conditions of the average rate of nuclear fissions, the so-called multiplication factor. The power-producing reactor should operate stable at different power levels. The changes in heat transfer level of the reactor should be made as quick as possible, but gradually without power leaps. The control system is designed in order to compensate the changes in reactivity as a result of mode changes. (Dementev 1990, 12-14, 16-17)

2.1 Classification of nuclear reactors

Depending on different characteristic nuclear reactors can be classified by the following features: purpose, type of nuclear reactions, type of moderator, type of coolant, geometrical parameters of the core. (Dementev 1990, 21-24)

By the purpose of use, the reactors can be classified into experimental, research, isotope and nuclear. The experimental reactors are used to study the physical parameters, their values are necessary for the design and operation; the power of such reactors is less than several kW. The research reactors are used for research in nuclear physics, radiation chemistry and biology. Isotope nuclear reactors are used for obtaining radionuclides, such as plutonium-239 in nuclear weapons, as well as in medicine. Nuclear power reactors are designed to produce electricity, heat, seawater desalination and power units of ships. (Dementev 1990, 21-24)

Also, reactors can be classified by the type of nuclear reactions into the thermal neutron and fast neutron reactors. The reactors differ by type of coolant. There are light water, heavy water, liquid metal and gas reactors. Depending on fuel placement method reactors can be heterogeneous and homogeneous. Thermal-neutron reactors distinguish by the type of moderator in light water, heavy water and graphite reactors. Furthermore, the reactors differ according to geometrical parameters of the core. (Dementev 1990, 21-24)

2.2 Key features of light water reactors

Generally light water reactors (LWR) used in nuclear power industry are of two types: pressurized water reactors (PWR) and boiling water reactor (BWR). LWR uses low enriched uranium fuel allowing the application of a wide range of structural and other materials for the core, including light water serving both as coolant and as moderator. The main difference between PWRs and BWRs is the way of steam production; in BWRs steam is produced in reactor vessel, and in PWRs coolant is maintained under the pressure, preventing it from boiling. Heat generated in the reactor is absorbed by water from the primary circulation loop operating at high pressure. The water circulating in the primary loop transfers the heat to the secondary loop in the steam generator-heat exchanger. The additional shutdown system involves the injection of boron to the reactor primary circuit. Steam produced in the steam generator is supplied to the turbine through the main steam pipes of the secondary circuit, converting mechanical energy into electricity. (Nero 1979, 21)

Figure 2 shows the schematic view of electricity generating process.

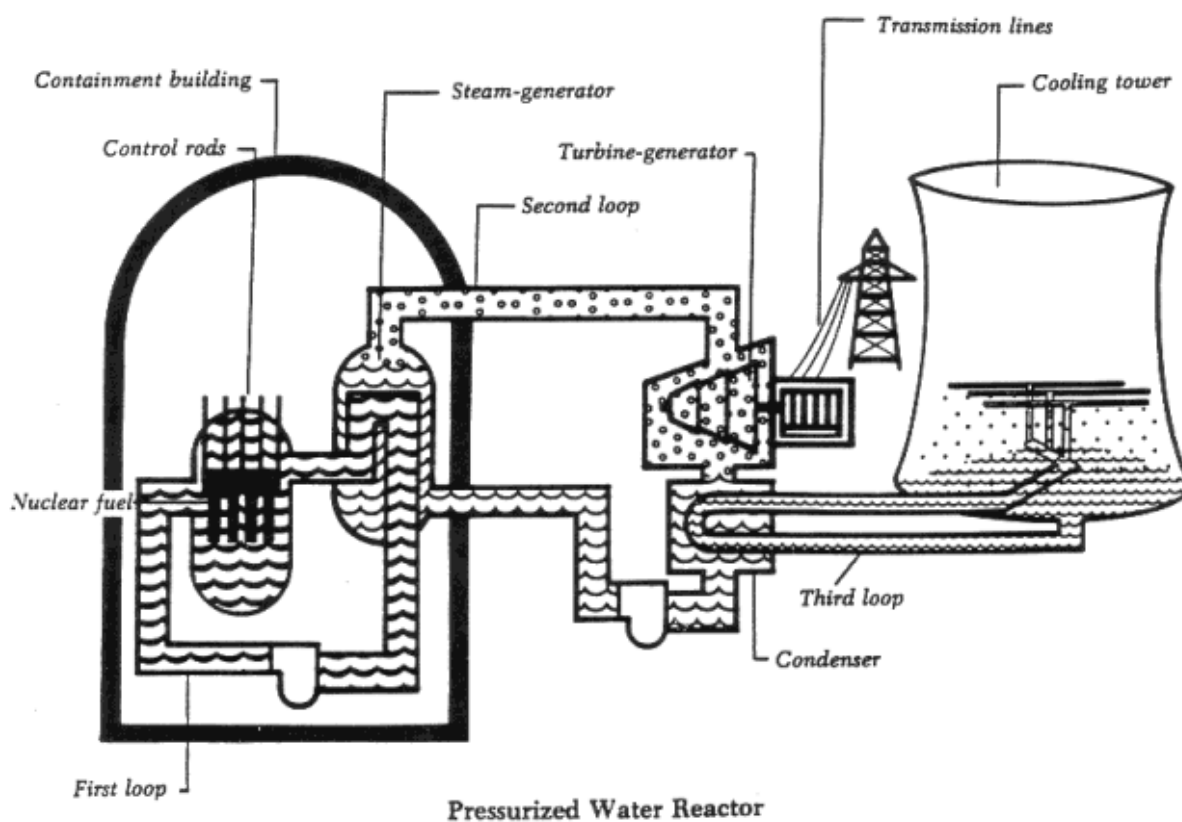


Fig. 2. Construction of pressurized water reactor. (NRC 2012)

Loviisa NPP is a nuclear power plant located on the island of Hästholmen, 15 km to the south-east from the town of Loviisa. There are two units with Soviet pressurized water reactors having a nominal electrical output of 440 MW, hence the trade name, Vodo-Vodjanoy Energeticheskiy Reaktor or VVER 440. The reactors were produced at the Izhora factory. All the other equipment including turbines and generators were produced in the Soviet Union. The station is equipped with security and control systems produced by the western companies. Finnish companies performed the construction of this plant. The first reactor began operating in February 1977, the second in November 1980. As a result of the modernization in 1997-2002, the power of each reactor has risen from an initial 440 MW to 488 MW, and up to 510 MW in 2010s. (Tuomisto 2013, 3-5)

Loviisa-1 uses Westinghouse fuel (BNFL), while Unit 2 utilizes TVEL (Anttila 2011, 69). Some of the experimental facilities in Lappeenranta University of Technology's nuclear engineering laboratory are models of this nuclear power plant (Tuunanen et al. 1998, 4).



Fig. 3. Loviisa nuclear power plant. (STUK 2013)

2.3 VVER-440 characteristics

The first generation of VVER-440 is VVER-440 /V-230. Nowadays, 10 reactors are in operation mostly in Russia. Subsequently, the second generation of VVER-440 is VVER-440 /V-213. The reactor of this type is used in Loviisa power plant. (Gagarinskiy and Saprykin, 2)

Some improvements have occurred in the designing of reactor. Nowadays it is a combination of ordinary VVER- 440 with Westinghouse western-designed equipment (Katona 2011, 158).

New model include addition of emergency core cooling, upgraded accident localization system, and auxiliary feedwater system. Additional development is the use of vapor-suppression containment, a bubbler-condenser tower. There are 6 circulation loops in the reactor with VVER-440. (IAEA 1996, 189)

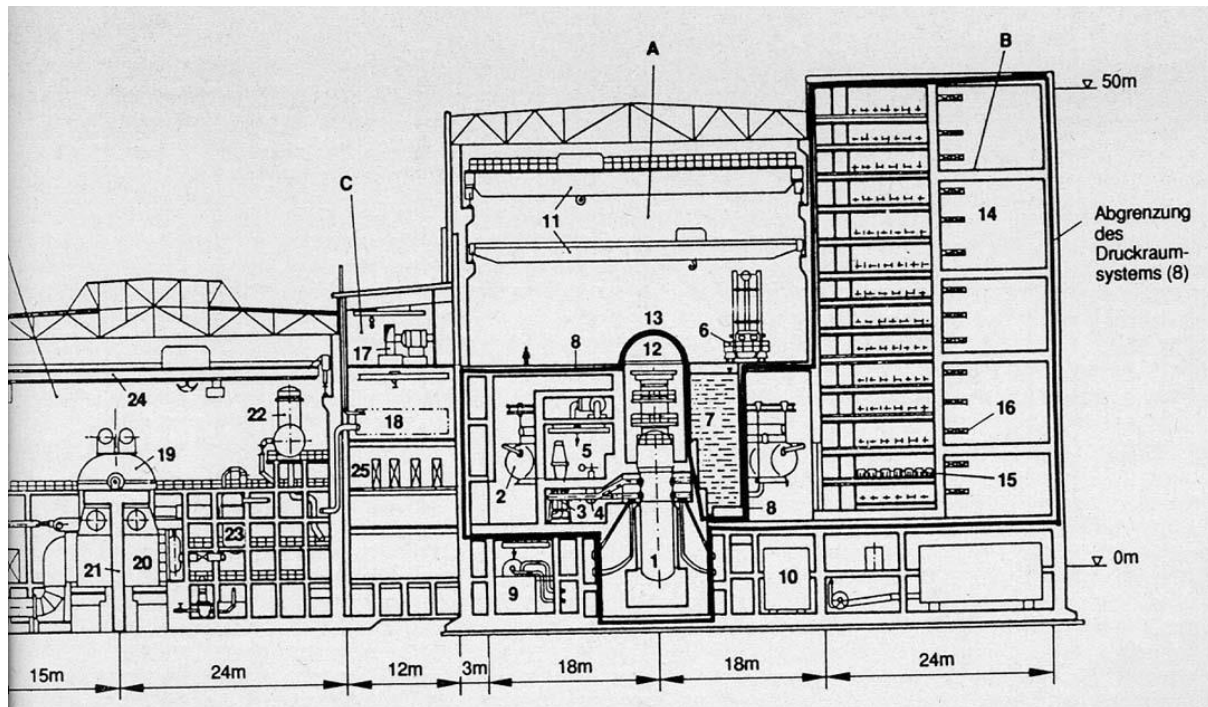


Fig. 4. Cross-cut of VVER 440-213. (Stráský 2007, 4)

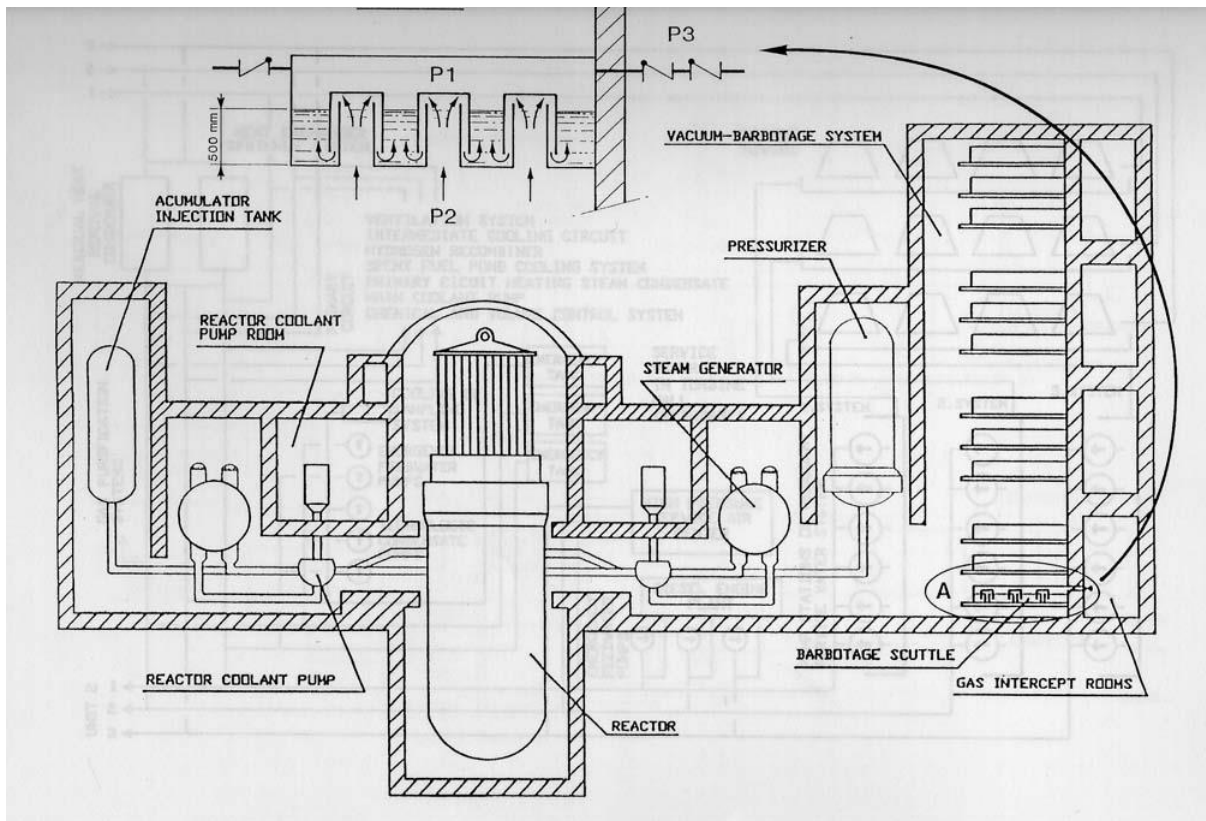


Fig. 5. Cross-cut of VVER 440-213. (Stráský 2007, 5)

The structure of the primary circuit includes the following components: reactor, steam generators, main circulation pumps, pressurizer system, make-up system and feedwater system, emergency cooling systems, chemical and Volume Control System. (Kritsky 1999, 12)

The core is formed from hexagonal fuel assemblies, containing fuel rod-type elements with the core rod made of uranium dioxide in pallet form, coated by the zirconium alloy (Dementev 1990, 34).

The coolant enters the reactor via inlet nozzle, then it goes downwards through the annular space between the reactor pit and the pressure vessel, then it raises up over the fuel assemblies through the holes in the pit support structure. The heated coolant is removed from the reactor through the outlet nozzles. (IAEA 2008, 7-8)

The purification system usually includes: centrifugal glandless axial pump, cooler-heat exchanger for ion exchange filters, cation- and anion-exchanging filters, pipelines and fittings. Pressurized water is supplied to the heat exchanging system and cooled. Then cooled water is supplied to cation exchanging and to the anion exchanging filters and the treated water is returned to the reactor. (IAEA 2008, 11)

VVER-440 V213 units have an emergency core cooling system and several secondary-side cooling systems to remove heat from the steam generators (IAEA 2008, 18-19).

The ECCS includes three systems: high-pressure injection system (HPIS), core flooding system (CFS), the low-pressure injection system (LPIS) (IAEA 2008, 18-19).

ECCS active assembly consists of two independent circuits: emergency cooling and emergency boron injection. Reactor emergency cooling circuit is designed for reactor cooling after ECCS passive unit operation. The circuit includes the emergency cooling pumps and emergency cooling heat exchangers, piping and fittings. (IAEA 2008, 18-19)

Subsystems of EECS prevent severe subsequence of LOCAs. Thus HPIS is used to prevent the core uncovering in a small LOCAs. LPIS supplies low pressure core cooling. Additional of coolant is injected by CFS. The subsystems (CFS and LPIS) operate simultaneous in cases with large LOCAs. (IAEA 2008, 18-19)

The VVER-440/V-213, located in Loviisa NPP differs from regular one because of some innovations, such as installation of external ice-condenser containment cooling concept by Westinghouse. Further developments are additional feedwater systems. Also controls and measuring systems are built following western standards. (IAEA 1996, 233-235)

3 PRIMARY WATER CHEMISTRY GUIDELINES (WCG)

The ensuring of the protective barriers integrity is the basic requirement for VVER water chemistry management. It is achieved by reducing of the coolant corrosive effects to structural materials. (RB 002-97: 1997)

3.1 Structural materials of primary circuit

The main requirements for selection of the structural materials of the reactor primary circuit coolant are: material yield strength, the ability of normal functioning in the conditions of corrosion and the ability to withstand strain aging. That is why the main materials of the reactor primary circuit are stainless steel, low alloy steel and carbon steel. Inconel alloys are resistant to oxidation and corrosion. Inconel forms a thin stable passivating oxide film which protects the surface from further failure. Inconel keeps its high strength and good weldability under a wide temperature range. The most common alloy in the nuclear industry is Inconel 600 (nickel-chromium alloy); it is corrosion-resistant and relatively cheap (Novichkova et al 2010, 3).

Generally, the Russian-type titanium stabilized stainless steel 08Cr18Ni10Ti is used for stainless steel equipment, pipework, SG tubing and the pressurizer. The low alloy steel (15Cr2MFA; Loviisa 12Cr2MFA) is utilized for reactor pressure vessels. The inner layer is made of a non-stabilized stainless steel (Sv-07Cr25Ni13) and the layer, which is in contact with the primary coolant, is a niobium stabilized stainless steel (Sv-08Cr19Ni10Mn2Nb (Loviisa - 07Cr19Ni10Nb), equivalent to AISI 347). (IAEA-NER 2008, 8)

Zircaloy-4 is a structural material for fuel cladding tubes of PWR/VVER (group of high zirconium alloys, zirconium alloy with tin). Zircaloy has a low thermal neutron absorption cross section. Structural materials of reactor coolant system corrode. Moreover, since 1987 it became useful to apply the advanced Russian E110-type Zr1%Nb alloy, which is described with higher resistance to irradiation, creep and corrosion for fuel rod cladding and tubes. (IAEA 2010, 9)

3.2 Discussion of different WC in the primary circuit of NPP

The task of reducing radiation fields from the primary circuit equipment and accumulation of corrosion products is of the utmost importance. WC of the primary circuit should provide: the reduction of the formation of radiolysis products during reactor operation at high power; corrosion resistance of the structural material of core, equipment and pipelines; minimum amount of deposits

on the surfaces of the fuel assemblies in the core and the heat transfer surfaces of SG; the decreasing of accumulation of activated corrosion products on the surfaces of equipment and pipelines of the primary circuit. (Martynova 1983)

The optimal amount of the alkaline components and the content of hydrogen and oxygen at all stages of the fuel cycle are the determining chemical parameters of the existing WC of primary circuit. The alkaline, ammonia and hydrogen components are interrelated (Barmin et al., 2004, 31-33). The ammonia has dual significance in this case. It is used to maintain the required pH of coolant at certain stages of the fuel cycle and to ensure the necessary concentration of hydrogen. WC of the primary circuit is associated with the presence of boric acid in water. Moreover the concentration of boric acid generally depends on the reactor type and fuel burnup. The boron concentration decreases during the operation cycle. Maintaining the required pH requires the alkali addition in the reactor water. (Martynova 1983)

The alkali are used as a correction additive. The selection of alkali is carried out, based on the aggressivity to the zirconium alloys. According to their aggressivity, alkali are arranged as follows:



Therefore, ammonia is the most appropriate additive in regard to zirconium alloys. However, the alkalinity properties of ammonia decrease as the temperature rises, especially when it reaches 300°C. (Martynova and Margulova 1981, 220-223)

NaOH is also not suitable due to two reasons. Firstly, the reason is its strong activation of $^{23}_{11}\text{Na}$ in the reactor. Secondly, the coolant activity increases due to the decomposition of the relatively short-lived isotope $^{24}_{11}\text{Na}$ with a half-life of 15 hours, which emits high-energy γ -quanta. (Martynova 1983)



LiOH is produced from isotope ^6_3Li contained in natural lithium in an amount of 7.5%. The usage of LiOH from isotope ^6_3Li forms tritium. Also there is a way without isotope ^6_3Li utilization, however it is quite costly. (Martynova 1983)



Potassium is also activated by neutrons, forming the radioactive isotope ${}^{42}_{19}\text{K}$ with a half-life of 12.4 hours. (Martynova 1983)



However, the potassium content does not exceed 6.9%, so the activity of potassium in the total coolant activity is not considerable. (Martynova 1983)

Thus, the one of the advantages of KOH is its small contribution of potassium activity to the overall activity. Also it does not form hardly soluble compounds. KOH is not accumulated in the deposits and it is effectively removed on the bypass filter. (Martynova 1983)

However the other alkaline ions in the coolant flow should be taken into account. Na + is entering the primary circuit with feedwater and adjusting additives and Li + is formed in the reactor by neutron irradiation of boron. (Martynova 1983)



Therefore, the normalization is performed not only by the K+ ions concentration, but by the total molar concentration of metal ions: potassium, sodium, lithium. Calculation of total alkalinity is performed by the equation 6.

$$\sum \text{Alk} = \frac{(\text{K})}{39} + \frac{(\text{Li})}{7} + \frac{(\text{Na})}{23} \frac{\mu\text{mol}}{1} \quad (6)$$

where K, Li, Na are the concentrations of potassium, lithium and sodium, respectively [mg/dm³]; 39, 7, 23 are the atomic mass of potassium, lithium, and sodium, accordingly. (Martynova 1983)

Also high lithium concentration is used to maintain the required pH values. Furthermore, some tests in operating conditions have proved that the lithium concentration should be between 3-6 mg/kg, to maintain an optimal level of pH - 7.4 at a temperature of 300°C. This pH value allows reducing the

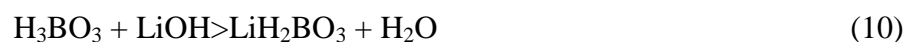
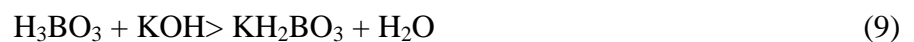
radiation dose. It is necessary to maintain the level of pH = 7.4, with the corresponding lithium concentration equal to 3.5 ppm for the stable operation of NPP. However, such a lithium concentration will lead to stress corrosion cracking of structural material. That is why a new solution has been found: at the reactor start-up, the pH = 6.9 is maintained with the appropriate lithium concentration of about 2.2 and the boron concentration of 2000 ppm, and then the pH value is increased to 7.4. (Nordmann 2004, 521-523)

To limit the oxygen concentration in the reactor water it is required to fill it with well deaerated water. Furthermore a hydrazine is added (not less than 20 mg/l) to remove the residual oxygen containing in the water. The limitation of the radiolytic oxygen concentration is performed by the addition of hydrogen in the reactor water. (Martynova et. al 1980)

Another problem of WC management is the decrease of radiolysis by maintaining the hydrogen concentration in the coolant within the allowable range (Sarkisov and Puchov 1989, 335-336). It is achieved by a continuous or periodic dosing of ammonia or hydrazine hydrate. During past decades the dissolved hydrogen concentration was 25-50 ml/kg, which is allowed to maintain oxygen optimum concentration (Nordmann 2012, 3).



So the alkaline potassium-boron-ammonia WC is used in the primary circuit. The presence of boric acid in coolant reduces the coolant pH value, so potassium hydroxide or lithium hydroxide are typically used to neutralize the coolant solution acidic properties (Martynova et. al 1980).



3.3 Water quality indexes

The behavior of the main primary circuit impurities, particularly chlorine and fluorine ions, oxygen, hydrogen and ammonia is summarized below in order to perform the proper selection of water chemistry management.

3.3.1 The concentration of chlorine and fluorine ions

Chlorine and fluorine ions are the most dangerous impurities among the all dissolved mineral impurities, because they are the intensive activators of corrosion processes. The newly installed fuel assemblies are the main source of water pollution with fluorine ions in the primary circuit. The fuel assemblies are processed with hydrofluoric acid during the manufacturing process. Chlorine ions are contained in all the additives injected into the primary circuit and trace amounts are left in primary circuit after demineralization. (Martynova et. al 1980)

Chlorine and fluorine ions prevent the protective film forming and increase the corrosion rate of almost all metals. Even small concentrations of chlorines and fluorines in combination with oxygen can cause stress corrosion cracking of austenitic steels, and pit corrosion of zirconium. It was found that at a concentration level of less than 0.1 mg/dm^3 chlorine and fluorine ions do not affect the resistance of construction materials. A further concentration rise increases the porosity of protective film and reduces their protective properties. (IAEA 2008, 26-27)

3.3.2 Oxygen

Oxygen is an active intensifier of corrosion rate of austenitic stainless steels and zirconium alloys under certain conditions. Oxygen is formed as a result of the water radiolysis. Oxygen can also come into the primary circuit with feedwater without thermal deaeration or with poor thermal deaeration of flows. The contribution of oxygen in the corrosion process is very contradictory. On one hand, being an active depolarizer, oxygen increases the metal corrosion; on the other hand, it is included as part of a metal oxide, forming a protective oxide film. The internal stress of the film rises with increasing thickness of the oxide film due to the difference in metal density. It can reduce the passivating properties of films. Oxygen is electrochemical corrosion depolarizer, therefore, the oxygen concentration in the primary circuit is the highly specified value and should be decreased. (IAEA, 2008, 25-26)

3.3.3 Hydrogen

Ammonia is main source of hydrogen, in particular it decomposes in the reactor neutron field, producing hydrogen and nitrogen (IAEA 2008, 29).

The suppression of water radiolysis is one of the ways to maintain a controlled level of oxygen concentration (IAEA 2008, 29). For that purpose it is necessary to maintain the hydrogen concentration in the coolant not less than 2.2 mg/dm^3 . The upper level of the hydrogen

concentration 4.5 mg/dm^3 is limited by the process of hydrogen embrittlement of steels and zirconium alloys. (IAEA 2008, 26)

3.3.4 Hydrogen ion exponent ($\text{pH}_{25^0\text{C}}$)

This parameter is used to specify the acidity or alkalinity of the water. The pH of the reactor water is chosen in terms of structural materials corrosion resistance. The lower level of 5.9 is limited by electrochemical corrosion process with hydrogen depolarization, the upper value of 10.3 is limited by alkali embrittlement of steels and zirconium alloys (Mamet and Yarmanov, 2001, 6).

3.3.5 Ammonia

Ammonia is injected into the coolant to adjust the water chemistry. Its main purposes are a hydrogen synthesis (as a result of decomposition under the influence of neutron flux and beta/gamma radiation) to suppress radiolysis of water and the binding of molecular oxygen (IAEA VIENNA 2008, 29).



(Mamet and Yarmanov 2001, 2).

Consequently, the ammonia concentration in the coolant must be maintained at the level ensuring the hydrogen content in the standardized range of 2.2 mg/dm^3 - 4.5 mg/dm^3 (IAEA 2008, 26).

All materials used for manufacturing of the primary circuit equipment, corrode with varying rate depending on their corrosion resistance and operating conditions in the circuit. Restriction on the corrosion products content in coolant reduces the rate of deposits formation on the different surfaces of the circuit. The deposits on the surface of the nuclear fuel may increase the temperature of the metal shell elements due to their low thermal conductivity. The deposits intensify the processes of non-uniform corrosion. The potential of corrosion products differs from the potential of metals, and corrosive elements appear there as a result. (Horsheva 2000)

Corrosion products are activated at multiple irradiations in the core that leads to the increase of radioactivity in equipment and to the difficulty of repair (Horsheva 2000).

The ability of various compounds to form deposits is primarily determined by the solubility limit on a particular compound. The corrosion products in the coolant can be either in dissolved or suspended state. When a total concentration rises, the percent of suspended corrosion products also increases. The lower is the corrosion products concentration, the less likely is their enlarging and deposition on the surfaces of the primary circuit. (Horsheva 2000)

Previous studies have shown that when the corrosion products concentration (iron, chromium, nickel) is less than 0.2 mg/dm^3 , the probability of deposition is minimal. If the iron concentration in the coolant is less than 0.05 mg/dm^3 there is no need to control chromium and nickel. When the iron concentration in the coolant is more than 0.05 mg/dm^3 it's necessary to control the concentration of chromium and nickel. In this case some measures should be taken to define and eliminate the causes of increasing the corrosion products concentration. (Horsheva 2000)

3.4 Chemical and volume control system

The largest and most important auxiliary system is the Chemical and Volume Control system. It provides boron control, maintenance of complex WC, organized recycling of leaks and primary circuit filling as well as a number of other functions (IAEA 1994, 14). The letdown system performs primary functions continuously withdrawing from the coolant from the primary circuit. Return of this purified water with the appropriate boric acid and certain agent's concentration is called feeding. The system operates in all operational modes. It is composed of 3 powerful makeup pumps with their own oil system. Each makeup pump has a booster pump, providing the necessary operation for cavitation-free operation of the supports for the main pump. Main pumps generate pressure higher than that in the primary circuit. Such parameters are achieved with high rotation speeds and can be continuously adjusted using a fluid couplings. The flow rate and pump pressure are adjusted over a wide range by controlling the fluid coupling regulator. (Wang et al 2010, 33)

Additionally to the pumps the system also includes a large amount of equipment: heat exchangers for various purposes, deaerators, tanks. The feed and bleed system is connected to the primary circuit and a number of auxiliary systems. (Westinghouse Technology Systems Manual 1984, 58-61).

CVCS includes a number of sub-systems, such as letdown cooling system, boron thermal regeneration system, charging pumps, boric acid supply and demineralizers.

The boric acid supply is designed to change the boric acid concentration in the coolant fluid of a nuclear reactor system. It generally accomplishes it by drawing off a portion of the coolant and replacing that portion with an equivalent amount of both demineralized and deaerated water, or water which has been previously blended so as to have a high concentration of boric acid. The system includes numerous pumps and large tanks. (Westinghouse Technology Systems Manual 1984, 60)

The distillate system is used for storage and feeding the added distilled water, that is used to reduce the boric acid concentration in various process systems, including the feed and bleed system. It includes a few tanks and pumps. (IAEA 1994, 89)

Hydrogen is continuously released in the makeup water deaerator, so it must be removed in order to avoid the dangerous concentrations. The hydrogen recombine system is used for this purpose. The oxidation of hydrogen, in the form of combustion, is performed by a platinum catalyst. The system consists of coolers, blowers, heaters, catalytic gas recombiner and water hydraulic hitch. (Westinghouse Technology Systems Manual 1984, 102)

The main aim is maintaining an optimal water chemistry of NPP. The presence of boric acid in coolant can lead to increased corrosion of steel surfaces. Therefore, an alkali such as ammonia and potassium are injected along with boric acid. The water chemistry in this case is called potassium-boron-ammonia.

3.5 Special Purification Circuit and its equipment

Resulting from the corrosion of structural materials and feedwater impurities, the treatment system for the reactor water should be installed. The heat exchangers for cooling treated water, mechanical-wave filters, ion exchange filters and mixed bed ion exchanger are the main components in the purification system for VVER. Mixed bed ion exchanger is commonly used for water treatment with low impurities content, including the reactor water. (Margulova 1978, 128)

There is a plenty of radioactive water to be treated at the plant. The radioactivity of this water requires a special purification circuit, SWO. These coolant purification units have their numbers - from 1 to 7. Among all units, SWO-1 operates continuously and is located near the reactor itself and is the only one connected directly to it. The rest operate periodically and are combined into a single independent tank. SWO-1 and SWO-2 are the main coolant purification systems. (IAEA 2008, 10-11)

The main goals for SWO-1(Primary Coolant Letdown Purification System) are to remove excess alkali metals and boric acid from the coolant during the fuel cycle and to clean up primary coolant impurities and radionuclides. (IAEA 2008, 11)

In VVER-440 V-213 units (including Loviisa 1 and 2) SWO-1 consists of two loops, each connected to three of the primary circuit loops, one loop containing a single mixed bed ion exchange resin in the $K^+ - NH_4^+ / \text{borate}$ saturated form and the second two separate cation and anion ion-exchange resins. To reduce the cost this unit runs at low (compared to the reactor) pressure. Special purification circuit diagram for VVER is shown in Figure 6. There is a regenerative heat exchanger (5) and a restrictor (6) near the reactor. The rest of the system is placed outside the containment. The primary coolant is cooled to 45 to 60°C which is close to the upper limit for ion exchange resin operation by a regenerative heat exchanger, followed by a non-regenerative heat exchanger. Ion-exchange filters 8, 9 and 10 are respectively loaded with cation exchanger in the H-form, cation exchanger in mixed $NH_4^+ - K^+$ -form and the anion exchanger in the OH-form which during the operation transforms into the borate form. After passing ion exchange filters, water can be directed to the mechanical filter 11 for collecting fine fractions of resin in the case of their displacement from the filters 8, 9, 10. The treated water is supplied to the deaerator 14, feeding with a pressure of about 1.2 MPa. The Reactor Coolant Pump (RCP) water leakages also come here via the line 16. The heating steam enters the surface of heat exchanger 15. The water in the tank is heated to the saturation temperature and is partly evaporated. The steam takes away the gas components for hydrogen post-combustion and discharge of other gases through the swept-off gas. (Margulova 1978, 128-130)

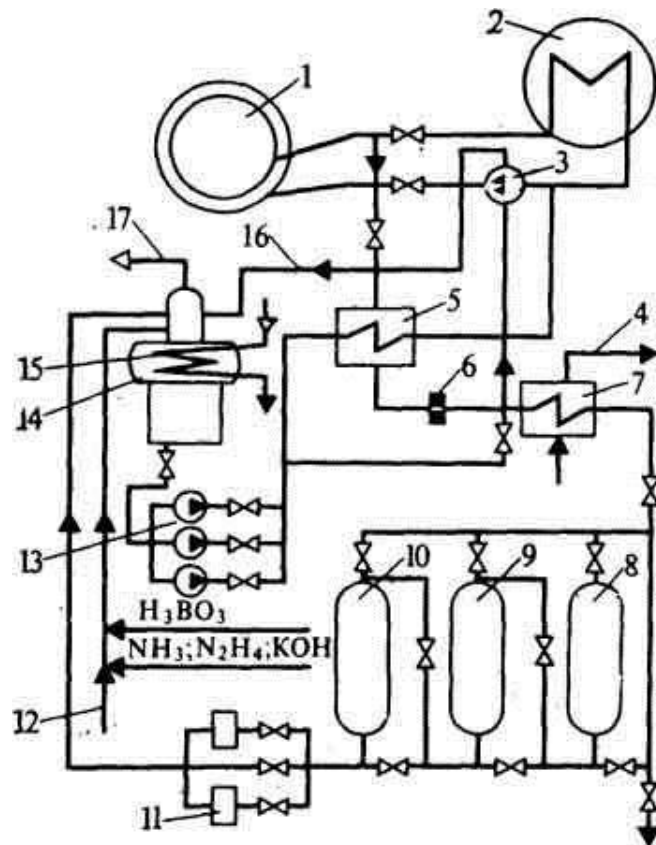


Fig. 6. Special Purification Circuit in VVER reactor with mixed ammonia-potassium and boron water chemistry: 1 - reactor; 2 – steam-generator; 3 - RCP; 4 - non-essential service water; 5 - regenerative heat exchanger; 6 - restrictor; 7 - final cooler; 8 – H-cation exchanger; 9 - NH₄-K-cation exchanger; 10 - anion exchanger; 11 - mechanical filter; 12 - feedwater make-up; 13 -water make up pumps; 14 - make up deaerator; 15 - heat exchanger of deaerator; 16 - seal-water discharge; 17 -deaerator steam. (Margulova 1978, 130)

The make-up deaerator diagram is shown in Figure 7. At small loads the chambers (3), (5) and a column (7) are operational. At full load, the chambers (4), (6) chamber and a column 8 are also included. Therefore the make-up deaerator provides the good deaeration at any load. (Margulova 1978, 130)

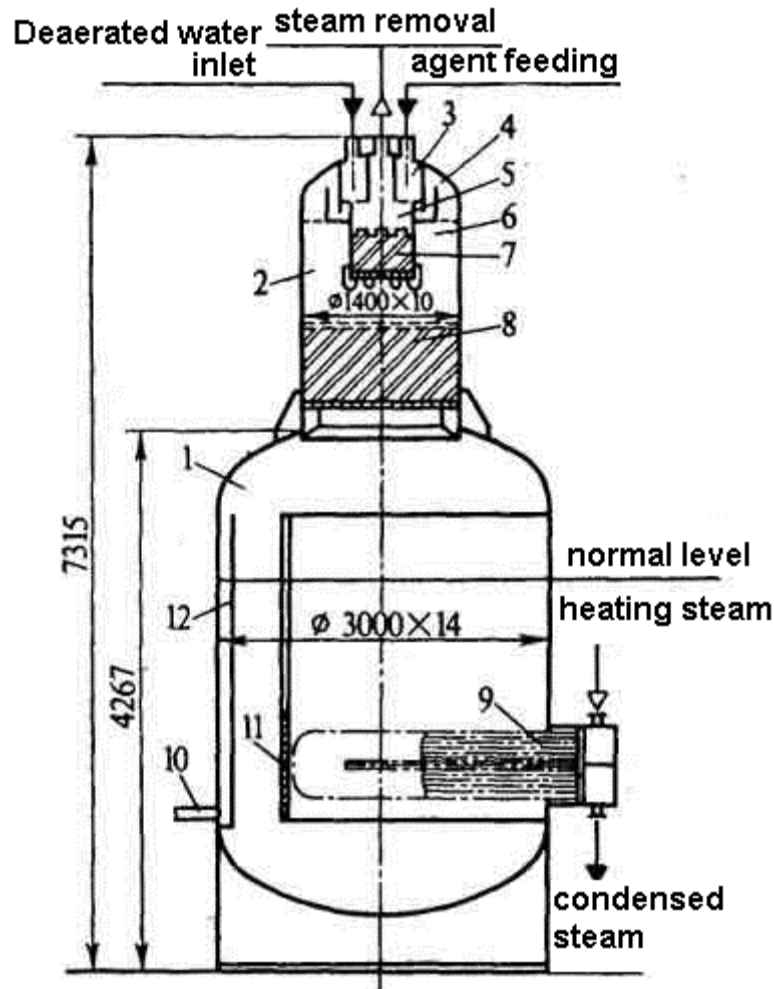


Fig. 7. Diagram of make-up deaerator of VVER 1 – vertical tank; 2 – degassing column; 3, 4 – central and peripheral distribution chambers; 5, 6 – central and peripheral chamber; 7, 8 – columns; 9 – a heat exchanger; 10 – deaerated water removal; 11 - blind shield; 12 – overflow gate. (Margulova 1978, 131)

Ceramic nozzles and the jets ensure the uniform contact of deaerated water and steam. (Margulova 1978, 131)

Water from make-up deaerator returns via the make-up pump to reactor and RCP shaft seal. There are three pumps installed: working, and two in reserve. Deaerator is supplied with all the necessary additives and demineralized water to feed the reactor. Thus, installing a by-pass coolant purification provides the reactor make up. It is noteworthy that by-pass coolant purification is taken off the stream during the NPP blackout. (Margulova 1978, 130-132)

Final purification is performed at ion exchange resins. Resins have a limited heat resistance, thus cooling heat exchangers (regenerative and final cooler) are installed to the treatment systems. (Margulova 1978, 130-132)

A low-temperature system for blowdown water purification of the primary circuit is designed to purify the blowdown water outputted from the primary circuit by the feed-and-bleed, as well as organized leaks of purification system. This system purifies the water from the corrosion products, radionuclides and chemical contaminants. The purification is provided by filtration and ion exchange. It includes two identical loops, each consisting of two parallel included cation exchange filters, anion exchange filters and resin strainer. Various types of ion exchange resins are used as filtering material. (Margulova 1978, 130-132)

The main function of SWO-2 (Letdown Purification System) is the removal of corrosion and fission products from coolant letdown, main coolant and primary make-up coolant pumps. (IAEA 2008, 11-17)

The rest of coolant purification units are placed in a special tank and perform the following functions:

SWO-3 (Leakage and Drains Water Purification System) is designed for the purification of floor drain water received from the water treatment units of reactor compartment, as well as from other places. The SWO-3 uses the techniques of evaporation, degassing, mechanical filtration and ion exchange. The evaporator unit is typically common for two blocks. Typically 18,800 tons of floor drain water come from one unit per year for a purification. (IAEA 2008, 11-17)

SWO-4 (Fuel Cooling Pool and ECCS Tank Water Purification System) is designed for water treatment from the spent fuel pool and borated water supply tank. The purification process is provided by mechanical, hydrogen cation exchange filters and anion exchange filters. The boric acid solution and ECCS tanks are purified by Fuel Cooling Pool and ECCS Tank Water Purification System. The main aim of the system is the removal of chemical impurities and corrosion products during normal operations and after accidents. (IAEA 2008, 11-17)

The boron solution from the ECCS tanks and cooling pools is supplied to SWO-4 pumps and then transferred to ion-exchange filters that consist of two cation-exchanger and one anion ion-exchanger. After purification the boron solution is sent back to ECCS tanks and to cooling pools. (IAEA 2008, 11-17)

SWO-5 is designed for purification of blowdown water and drain water from steam generators (maintaining the secondary circuit WC). SWO-5 has a filter system that purifies the water from corrosion products and contaminants in ionic form and also desalinates water. The system operates continuously. (IAEA 2008, 11-17)

SWO-6 (Boric Acid Concentrate Purification System) is designed to collect and treat the boron-containing water to obtain separate distillate and boron concentrate. Evaporation, degassing, mechanical filtration and ion exchange are used for this purpose. (IAEA 2008, 11-17)

SWO-7 is supplied the active laundry water purification systems. The system uses evaporation, condensation, degassing, mechanical filtration and ion exchange. (IAEA 2008, 11-17)

The main structural material in the SWO-2 and SWO-4 systems are made from 08Cr18Ni9T stainless steel and all auxiliary equipment in the SWO-1, SWO-3 and SWO-6 systems are made from 08Cr18Ni10T stainless steel. (IAEA 2008, 11-17)

3.7 ECCS water chemistry

Boron is used to absorb neutrons and the neutron activity is changed by increasing or reducing the boron concentration. In relation to the stage of fuel cycle the boron concentration in primary circuit progressively changes. The injection and control of boron solution is provided by Chemical and Volume Control System. (Westinghouse Technology Systems Manual 1984, 61)

The flows for high and low injection trains are supplied from tanks, which comprise 40 g/kg and 12 g/kg of boric acid respectively. For all these tanks the boron, fluoride chloride and sulphate concentrations are controlled. (IAEA 2008, 17-19)

In the case of LOCAs the special accumulators with boric acid are fitted to flood the core. Water chemistry of accumulators is considered to be neutral, therefore the potassium hydroxide is dosed to maintain the required pH value. However in Loviisa NPP the dosing of potassium hydroxide is not applied. The fact that the equipment of the system is made of stainless steel provide the limit of chloride and sulphate concentrations to avoid the SCC of stainless steel. The low pressure additive tanks contain the boric acid, potassium hydroxide and hydrazine are dozed. At Loviisa spray additive tank the concentration of hydrazine is 4-6 g/kg and the concentration of potassium hydroxide is 18-22 g/kg. (IAEA 2008, 17-19) The schematic diagram of ECCS is given in the figure 8.

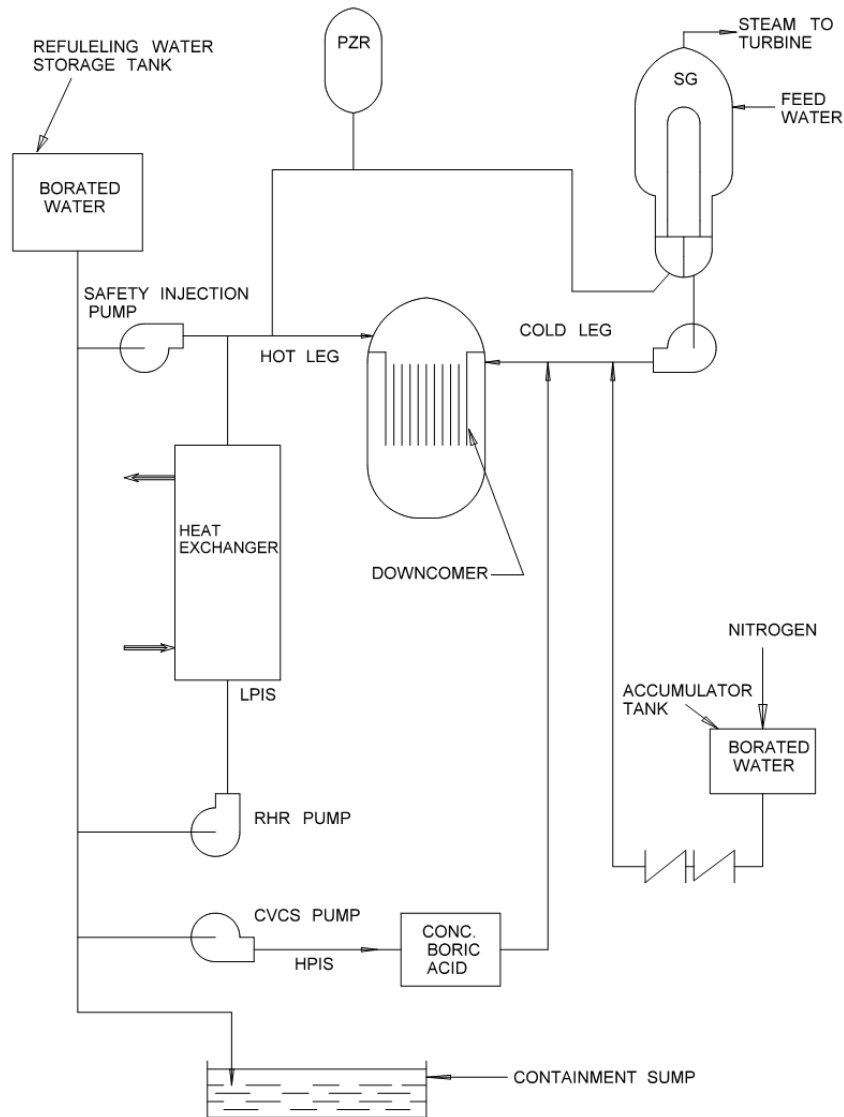


Fig. 8. Emergency core cooling system of VVER. (Rajan, 5)

3.8 Corrosion in the NPP circulation loops

Corrosion can be defined as the degradation of a material due to a reaction with its environment. The main types of corrosion are uniform corrosion, stress corrosion cracking and intergranular corrosion. (Voronov 2006, 63)

The surface effect produced by most direct chemical and electrochemical factors, which affect the rate of uniform corrosion, are: metal structure and physical-chemical properties of its surface, the value of stresses and strain, the aggressivity, temperature and rate of the coolant, the ionizing radiation and NPP operational mode. (Sarkisov and Puchov 1989, 335)

Corrosion aggressivity of the coolant is determined mainly by the composition and concentration of impurities, such as oxygen, hydrogen ions, carbon dioxide and dissolved salts. Oxygen has a double

effect: being a very active cathodic depolarizer, it increases the corrosion (Voronov 2006, 59-60). At a high concentration it also has a passivating effect. However, normal concentration of oxygen in the coolant is quite low in the NPP operating conditions. Therefore, oxygen should be regarded as an active cathodic depolarizer intensifying the uniform corrosion of steel. Neutral salts are of a particular interest. Salts in solutions dissociate into metal cations, chlorine ions and sulfate ions. The chlorine ion displaces oxygen from the iron oxide and a readily soluble chloric iron is obtained; this leads to the destruction of protective oxide films. (Horsheva 2000)

The dependence of the uniform corrosion rate on the coolant speed varies and is determined by water composition (Gerasimov 1980, 5-8). If the water contains oxygen, and there is a very small amount of depassivating additives (chlorine ions) and the speed of coolant increases, then the uniform corrosion rate first increases (oxygen is supplied to the cathodic areas), then reduces (protective oxide film are formed) and then again increases due to mechanical failure of protective films (corrosion erosion). If there is a great amount of depassivating additives, then the uniform corrosion rate rises with the coolant speed increasing. There are various methods to prevent stand still corrosion and different ways of preservation of idle equipment. (Horsheva 2000)

3.8.1 Stress corrosion cracking

Stress corrosion cracking occurs at the complex impact of tensile stresses and corrosive coolant having chlorine ions, oxygen or high concentrations of caustic alkali. Usually there are cracks on the grains of metal perpendicular to the main stretching stresses. Only austenitic steels are exposed to stress corrosion cracking. The electrochemical nature of stress corrosion cracking is generally accepted, but there is no consensus on the reasons of localized electrochemical process appearing. (Sarkisov and Puchov 1989, 338)

The main factors affecting the stress corrosion cracking are stress and strain and coolant corrosion aggressiveness. Scaring, pinchers and other deformation of surfaces become initial places of corrosion cracks (Sarkisov and Puchov 1989, 338-339)

Coolant corrosion aggressiveness is determined by the content of oxygen and chlorine ions. (Voronov 2006, 70-71)

If there are no chlorine ions, the ferric chlorine is not formed and the stress corrosion cracking is not observed. The larger the number of chlorine ions, the faster primary microcracks are formed. The oxygen is an active cathode depolarizer, thus its presence dramatically reduces the time to failure.

Therefore the desalination and dissolved oxygen removal are required for the utilization of austenite steels: content of chlorine and oxygen ions should be no more than 0.02 mg/dm³. (Voronov 2006, 71)

The main ways to reduce the corrosion cracking are: the increase of the austenite stability, the complete removal of oxygen and chlorine ions from the water while also the advancement of technology and construction design. (Voronov 2006, 70-71)

Intergranular corrosion affects only the austenitic steels. It occurs along metal grain boundaries in an aggressive environment. The steel appearance does not change, so the intergranular corrosion is very hard to recognize. Steel becomes fragile as a result of intergranular corrosion. Austenitic stainless steels are exposed to intergranular corrosion under certain combinations of internal (chemical and phase composition of metal) and external (corrosive environment nature, temperature) factors. The heterogeneous electrochemical corrosion on metal surface is the main reason of intergranular corrosion: the anode is the grain boundary, the cathode is the remaining surface. The most widely spread hypothesis is the hypothesis of solid solution chromium depletion adjunct to the grain boundaries. (Sarkisov and Puchov 1989, 339-340)

The higher the carbon content in the steel is, the more chromium carbide is formed. Following that, the propensity to intergranular corrosion increases. Intergranular corrosion does not occur when carbon concentration is less than 0.009 % (in practice, its content is more than 0.005 %). Chromium depletion of grain boundaries does not occur and steel is resistant to intergranular corrosion. (Gerasimov 1980, 48)

There are two general approaches to solve the problem of removing corrosion products from nuclear power circuits. Firstly, the most of the corrosion products are in suspended state, so the purification systems operate in plant operational modes. Secondly, the corrosion products may be removed by chemical circuit flushing with special agent solutions to ensure corrosion products dissolution with minimal corrosion of structural materials.

3.9 General characteristics of primary circuit radioactive contamination

During the NPP operation the decomposition of the activated corrosion products deposited on the surfaces of the reactor circuit make a substantial contribution to the process equipment activation.

Radionuclides determining dose rate are: Co-60, Co-58, Fe-59, Mn-54, Cr-51, Zr-95. These radionuclides are formed in the core. Then they are entered to the circuit by mass transfer of corrosion products. (Severa and Bar 1991, 166-167)

Radioactive contamination in VVERs is basically adjusted by the behavior of cobalt, chromium and iron atoms in the primary coolant. (IAEA-TECDOC-248 1981, 8-10)

The corrosion-resistant alloys are used to reduce the amount of corrosion products in water (IAEA-TECDOC-248 1981, 11-12, 19)

One of the factors ensuring the reliability and safety of nuclear facilities is the corrosion resistance of structural materials to the primary coolant effects. The corrosion process is accompanied by the destruction of metal and the formation of corrosion products that can be transferred around the coolant circulation circuit. Localized corrosion contributes to the formation of cracks and gaps with all severe consequences, such as damaged leaking fuel rods in the primary circuit. The presence of CP in the coolant water has negative consequences for two reasons. Firstly, transfer and depositions on the steam generator surfaces prevents the heat transfer, thus reducing the efficiency of the plant, leading to local overheating and metal destruction to the corresponding parts of the circuit. Secondly, the corrosion products are transferred to the core, and then they deposit in various areas outside the core, increasing the agreed-upon emission level. (Sarkisov and Puchov 1989, 335), (Voronov 2006, 58)

Experience shows that despite of the very low corrosion rate of austenitic steels, the process leads to a gradual increase in the exposure dose during the operation, the main contribution is made by a Co-60 radionuclide in 2-3 years. (Moskvin et.al. 1989)

Special mechanisms reflect the radioactive contamination of the primary circuit with CP. Figure 9 shows the main stages of primary circuit contamination.

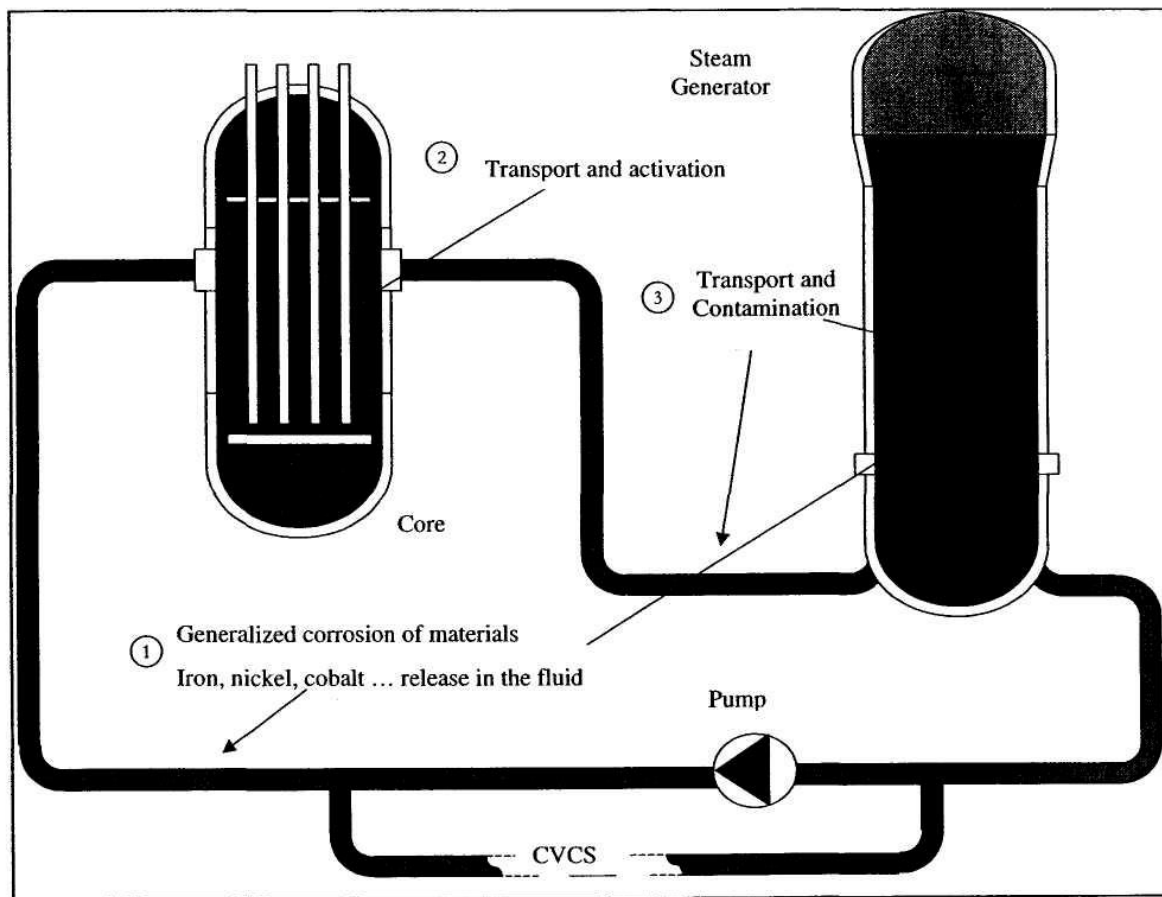


Fig. 9. Diagram of contamination processes with CP at the primary circuit of VVERs. (IAEA 2012, 4)

Generally, the corrosion of structural materials is the reason for the forming of the radioactive corrosion products. Also, metal particles are influenced by various effects occurring in the primary circuit. After the particles enter to the core, they are deposited on the core surfaces and are activated by the neutron flux. After the core radioactive particles move into the circuit and deposit on the surfaces of equipment. (IAEA 2012, 4)

The results of chemical composition control of the radionuclides and the CP in the primary circuit are shown in Table 1 and Table 2. Table 2 shows that the concentration of CP in the coolant fluctuates within several hundred of $\mu\text{g/l}$, having an average concentration of total CP of approximately $50 \mu\text{g/l}$. More than 95 % of the corrosion products are in the form of dispersed particles. (Gusev et.al. 2009, 1-2)

Table 1. Characteristics of the chemical composition of the coolant corrosive impurities. (Gusev et.al. 2009, 1)

Element	Concentration, $\mu\text{g/l}$		
	min	max	Average value
Fe	2	333	45
Cu	0.3	75	4.0
Cr	0.3	22	<1.6
Ni	0.5	17	<1.2
Mn	<1	8	<0.6

Table 2. Typical radionuclide composition of activated crud. (Gusev et.al. 2009, 2)

Radionuclides	Specific activity, Ci/l	
	min	max
Fe-59	4,0 -10	1,0 -7
Cr-51	5,0 -10	5,0 -6
Mn-54	1,0 -10	1,0 -7
Co-58	2,0 -10	5,0 -6
Co-60	1,0 -10	1,0 -7
Zr-95	1,8 -10	1,0 -6

3.10 Decontamination systems used in the primary circuit of the PWR

Removing deposits from the primary circuit is an important task since it determines thermal conditions of the fuel elements and the radiation doses to personnel during the maintenance and repair works, depositing on the internal surfaces of the equipment. The chemical decontamination technology is a traditional solution of the problem of removing CP from the circuit. The chemical decontamination is usually understood as radioactive contamination removal process from surfaces. Sometimes, this term also includes neutralization of radioactive waste. (Sedov et.al. 1985, 84-85, 249)

The chemical decontamination is the traditional technology. The advantages of the chemical decontamination are the possibility of chemical dissolution and subsequent removal of radionuclides in deposits and oxide films on the equipment inner surfaces and the access of

decontamination solutions to any location on the equipment. The chemical decontamination method is based on the fact, that the oxide film with absorbed radioactive substances on it can be removed by the oxidation-reduction reactions. It consists of a subsequent treatment of contaminated sites with alkaline and acidic solutions. Sometimes such solutions can themselves be a reason of corrosion of decontaminated surfaces. In these cases the decontaminated surface is treated with hydrazine (if pearlitic steel are used) or with thiourea (for carbon steel). Chemical decontamination is typically performed by multiple cycles (2-3). A single decontamination cycle consists of four sequential surface processing: caustic treatment, water flushing, acid treatment and water flushing. (Ampelogova et.al. 1982, 89-97)

Another technology - "nonchemical decontamination" is based on the deposits redistribution effects on the circuits of operating NPPs (Ampelogova et.al. 1982, 107-108).

There is another alternative way - to use the electropolishing with phosphate electrolyte to clean the surfaces of NPP equipment from radioactive contamination. The method is characterized by high efficiency, although the development is still at an early stage (IAEA-TECDOC-248 1981, 19).

The selection of the formulation of decontamination depends on the phase composition and water chemistry of the primary circuit. (Ampelogova et.al. 1982, 91)

4 VVER SECONDARY CIRCUIT WATER CHEMISTRY

The reliability and efficiency of any NPP with pressurized water reactor depends on the steam quality which is determined mainly by moisture, salt content and insoluble impurities. The deposited salts and other impurities on surfaces of steam generator and turbine blades may result in an emergency situation. Deposits increase the thermal resistance of the heat transfer surfaces of the steam generator, and the heat transfer decreases. The deposition of salts in the piping and other components of NPP increases the flow resistance and accelerates surface corrosion of steam generators, steam lines, turbines and condensers. The moisture in steam before the turbine leads to decreasing of its efficiency and increases erosion of flow tubes. (Odar and Nordmann 2010, 1)

The insoluble materials (e.g. corrosion products in SG) may enter the steam only with condensed moisture, and the issue of their control is connected with the general limitation of condensed moisture in the steam. Salts enter the steam by two ways: by the condensed moisture with dissolved salts in it or by salt dissolving in the steam. (Odar and Nordmann 2010, 26-30)

4.1 Materials used in the secondary circuit of VVERs

The secondary loop of VVERs has some differences from other PWRs. The main distinctions are the application of horizontal SGs instead of verticals and the utilization of collectors instead of tube sheets. Furthermore, austenitic stainless steels (18 % Cr, 10 % Ni stabilized with titanium) are used in VVERs instead of nickel-based Alloys 600 and 690. Moreover, austenitic stainless steel 08Cr18Ni10Ti is applied as material of SG tubes. This material is used for collectors in VVER-440 to reduce the deterioration mechanisms. (IAEA 2008, 71-73)

Commonly, the rest of the equipment in secondary circuit is made of carbon steel; specifically high alloy steel is a material for turbine blades, while low-pressure heater tubing is made of cupronickel alloy. Finally, condenser tubing is made of titanium alloy. Moreover, the following changes in material selection have been carried out: carbon alloys, which are used as a material for moisture separators, feedwater heater shells, reheater tubes, wet steam lines and high-pressure heater tubes. These have been replaced with stainless steel because of the influence of flow accelerated corrosion (FAC). In some cases, cupronickel alloys are substituted by copper-free ones which allows increasing of pH of feedwater. This innovation allows suppressing the transport of iron to SG and reducing FAC. (IAEA 2008, 71-73)

4.2 Different WC for the secondary coolant circuit of VVER

Hydrazine-ammonia WC has been widely used at NPP for the secondary circuit since the 1970s. Depending on the structural materials of equipment for VVER, there are following modifications of hydrazine-ammonia WC:

- Hydrazine-ammonia WC with a pH of feedwater less than 9.2 (with equipment made of copper alloys. The drawback of such WC is the severity of flow-accelerated corrosion suppression (The equipment and pipelines made of carbon steel and operating in the field of wet steam and two-phase flows).
- Hydrazine-ammonia WC with a pH of feedwater of 9.2 - 9.8.
Hydrazine-ammonia WC with a pH of water of more than 9.8 (if there is no copper alloys equipment of condensate-feeding loop). (Brykov et al. 2003, 1-3)

While dosing the ammonia and hydrazine, the aqueous phase of steam-water mixture has a lower pH due to a high distribution coefficient of ammonia. This does not provide an adequate protection of the steel and results in increased metal corrosion. Moreover at increasing temperature the alkalinity properties of ammonia reduce significantly, leading to a decrease in the pH value of condensate of the high pressure steam. (Brykov et al. 2003, 1-3)

Most of the PWRs use WC with dosing morpholine and other higher amines (ethanolamine and dimethylamine) in order to suppress the formation of flow-accelerated corrosion of equipment and piping made of carbon steel and for neutralizing the anions of strong acids in the two-phase mediums of the secondary circuit. Instead of the hydrazine-ammonia WC for the secondary circuit, where the equipment is made of copper alloys, the morpholine WC is used (with the pH value of the feedwater between 9.2 – 9.4). Morpholine has the excellent properties compared to ammonia due to its low distribution coefficient, especially in the two-phase medium of the secondary circuit, which greatly reduces flow-accelerated corrosion of the secondary circuit equipment. (IAEA 2008, 95-96)

The operation experience indicates that the transition to the morpholine WC provides a significant reduction in the iron and copper concentration in the feedwater thus reducing flow-accelerated corrosion. Also at the transition to a morpholine WC the deposits accumulation rate on heat exchange tubes is reduced and the sludge formation is reduced in SGs. (Dobrovolska et.al. 2006) Morpholine WC is widely used in PWRs in France. Since the middle of 1980s the PWRs in the

United States and Canada have also used Morpholine WC, despite the fact that most of the equipment was not made of copper alloys (TR-102952-R2 1997).

WC with higher amines (ethanolamine, dimethylamine and triethanolamine) has been widely used along with hydrazine-ammonia WC and morpholine WC in some countries (Korea, South Africa, the USA, Japan) since the 1990s. WC with higher amines (dimethylamine and ethanolamine) is used at majority of PWRs in the USA (TR-102952-R2 1997).

In the past the both units at Loviisa Power Plant WVER-440 utilized the neutral water chemistry in the secondary side, which enabled low content of impurities and lead to absence of tube leakages. However there were some disadvantages in the applied WC , such as the FAC in some parts of the secondary circuit. Other drawbacks were the feedwater line breaks in both units and erosion corrosion in the SG blowdown system. There were lots of discussions about choice of WC of secondary circuit at Loviisa; three optimal decisions of WC were evaluated to be implemented at Loviisa, such as hydrazine WC, ODA WC and morpholine. Moreover, many methods were applied to minimize the erosion corrosion. In the end the neutral water chemistry was replaced by hydrazine water chemistry, at unit 1 in 1995 and unit 2 in 1994. (Mäkelä et.al. 1996, 393-398)

5 WATER CHEMISTRY OF TEST FACILITIES

The cooperation of the VTT Energy (TECHNICAL RESEARCH CENTRE OF FINLAND) and Lappeenranta University of Technology in investigation of thermal hydraulics of power reactors has started in 1976. Lappeenranta University of Technology and VTT Energy had designed a number of facilities during this period: REWET -I, -II, -III, VEERA, and PACTEL. They were intended to simulate the processes in a pressurized water reactors (PWR). The first mutual project was the construction of the single pin plant (REWET-I): this unit was designed to perform the detailed survey of rewetting phenomena during the reflood phase of a large Loss-Of-Coolant Accident. The influence of nitrogen dissolved in coolant on the rewetting phenomenon was also studied but the primary interest was the influence of different injection modes on rewetting of the overheated fuel rods. The next step was REWET-II that was a more realistic model of the VVER-440 reactors. That assembly contained main components of the primary loop and 19 indirectly-heated models of fuel elements. The phenomena which were produced by this unit also represented reactor flooding and rewetting during emergencies concerned with a large loss of coolant. Later the unit has been updated. A steam generator and pressurizer were added to the facility. The facility has been renamed to REWET III. The phenomena in REWET III simulated natural circulation flows at Small Break Loss-Of-Coolant Accidents. (Tuunanen et al. 1998, 4)

There are also two other facilities: PACTEL (Parallel-Channel Test Loop) and VEERA. PACTEL is a large scale (1:305) experimental unit designed to simulate the main components of PWR primary loop during the assumed emergencies with small and medium loss of coolant and the natural circulation in transition modes. VEERA was built for experiments simulating the behavior of boric acid in PWR at long-term cooling of a nuclear reactor during LOCA. VEERA was also used for experiments simulating flooding accidents. (Tuunanen et al. 1998, 4)

5.1 Description of the PACTEL test facility

In the 1980's it was found necessary to develop and construct an experimental facility reproducing all the major components of nuclear reactor in order to get the main goal - a better understanding of the complex systems processes, such as the primary loops of pressurized water reactors. The PACTEL facility was constructed in 1990. Today it is a large-scale test facility constructed for studies of thermal-hydraulics of a VVER-440. VVER-440 with 6-circulation loops is the reference of the experimental facility; it is currently operating at NPP in Loviisa, Finland. Reactors

manufacturers and research organizations implemented similar experimental facilities in many countries. (Tuunanen et al. 1998, 8)

Simulation of the six main circulation loops of the reference reactor includes three separate loops with double power. Each loop has its own loop seals and horizontal steam generators. PACTEL facility is a model with the 6-loop reactor plant with VVER-440, made in the scale of 1:1 in height and 1:305 in volume. (Tuunanen et al. 1998, 10-11)

There are some unique characteristics of VVER-440 at the NPP in Loviisa that distinguish it from other PWRs. VVER-440 has six circulation loops and horizontal steam generators. A driving head for natural circulation at small losses of coolant is considerably small because of the horizontal design of the steam generator. There are loop seals at the primary loops, both in hot and in cold leg of the circulation loop of the nuclear reactor. (Tuunanen et al. 1998, 10)

The schematic design of PACTEL facility is presented in Figure 10. There are three equal (in size) and symmetrically located coolant circulation loops of the primary loop. Each loop is equivalent to two loops of a reference reactor. Downcomer (1), lower (2) and upper (4) plenum in reactor vessel were simulated with the help of the tubes of various diameters, the bypass between was not simulated. Each loop has a horizontal steam generator (6), circulation pump simulating RCP and loop seals in hot (5) and cold (7) legs. This facility also includes a model of the pressurizer (8) connected by the pressurizer line (9) and high and low pressure ECCS systems. (Gudoshnikov et al. 2007, 7-8)

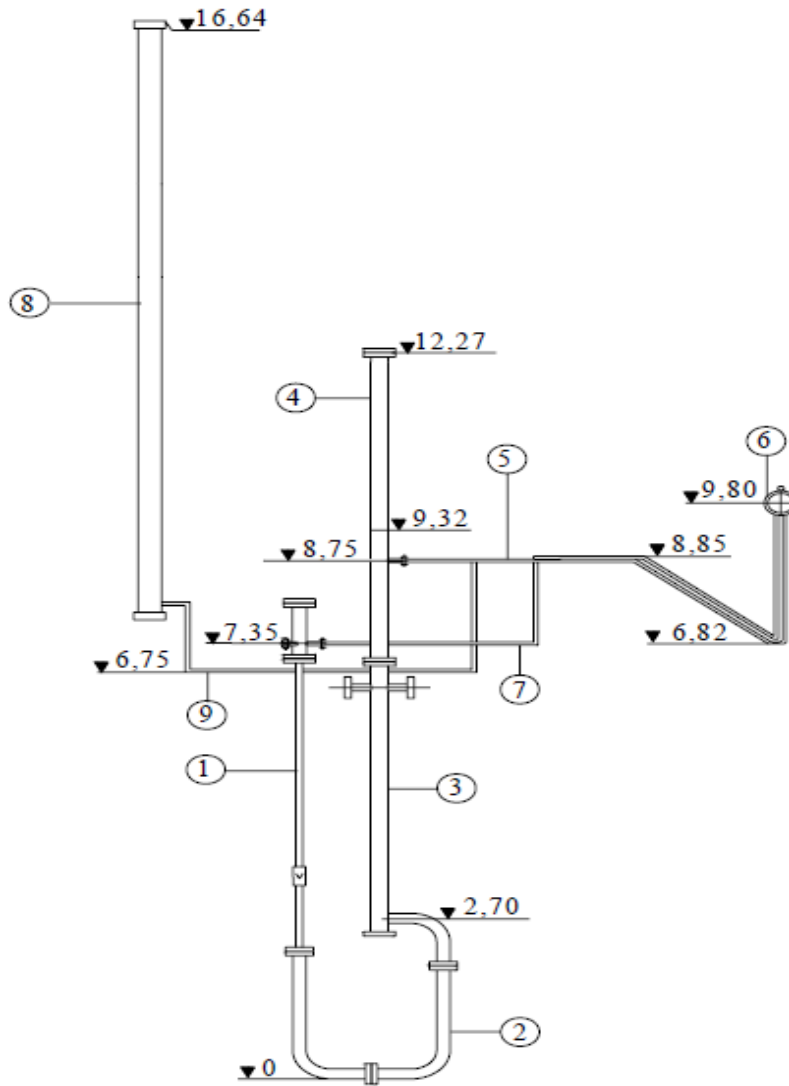


Fig. 10. The PACTEL facility. (Gudoshnikov et al. 2007, 8)

The nominal pressure is 8.0 MPa, while temperature of the liquid is 300°C (Tuunanen et al. 1998, 10).

The stainless steel AISI 304 is the main material for the facility; however the cladding is made of stainless steel AISI 316L. Core (3) includes 144 electrically heated fuel element simulators placed on a triangular lattice. The heated length (2.42 m) and diameter (9.1 mm) of fuel element simulators, as well as the distance between the centers of the fuel elements (12.2 mm) are the same as in VVER-440. Fuel element simulators are divided into 3 sections: A, B and C with 48 rods in each one. They are enclosed into separate casings with a triangular form of passage section. The number and structure of spacer grids is identical to those of real reactor. The gap between the covers (3 mm) forms the bypass channel with the total cross sectional area. (Gudoshnikov et al. 2007, 7-8)

Each section has an independent electrical heating. The total power of the model is 1 MW that corresponds to approximately 20% of the rated power of the reference reactor. (Tuunanen et al. 1998, 11)

The ECCS includes the accumulator core cooling system (ACCS), high and low pressure injection systems (HPIS, LPIS). The four ACCUs in the reference VVER-440 is simulated by two PACTEL accumulators. The HPIS injects water to the cold leg; The LPIS injects water to the downcomer and to the upper plenum. (Tuunanen and Puustinen 1998, 16)

Figure 11 illustrates the schematic view of PACTEL facility.

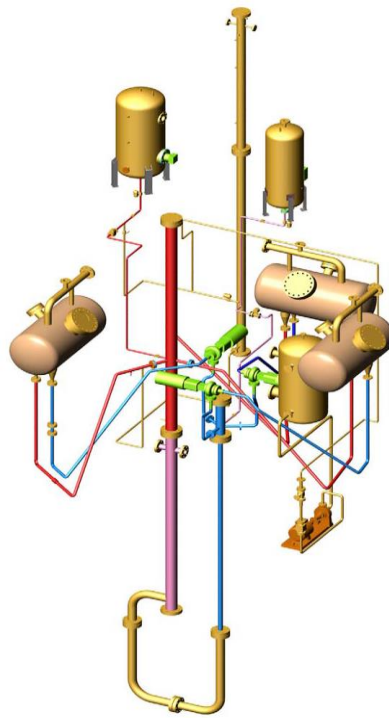


Fig. 11. PACTEL - experimental facility. (Kouhia et al. 2012)

Each steam generator has 118 heat exchanging u-tubes. The tubes are the same size as those of the reference SG, however, the distance between the rows are doubled so that the height of the SG facility differs a little from the height of the reference SG. A common steam line connects the three steam generators at secondary side. The steam is released to the atmosphere. All three steam generators have a separate feedwater injection system and two separate water supply lines. (Tuunanen et al. 1998, 14)

PI-controller is used to control the pressure in all steam generators (Tuunanen et al. 1998, 16).

The main design parameters of the PACTEL facility are presented in Table 3.

Table 3. The Loviisa data in comparison with PACTEL facility. (Tuunanen 1998, 11)

Reference power plant	Loviisa VVER-440	PACTEL
Volumetric scale	-	1:305
High scale	-	1:1
Maximum heating power	1375 MW	1 MW
Maximum operating /secondary pressure	12.3 / 5 Mpa	8 / 5 MPa
Maximum operating /secondary temperature	300 / 260 °C	300 / 260 °C
Maximum cladding temperature	-	800 °C
Number of primary loops	6	3
Number of rods	39438	144
Outer diameter of fuel rod simulators	9.1 mm	9.1 mm
Heated length of fuel rod simulators	2.42 m	2.42 m
Axial power distribution	Cosine	Chopped cosine
Axial peaking factor	1.4	1.4
Feedwater tank pressure	2.5 Mpa	2.5 MPa
Feedwater tank temperature	225 °C	225 °C

5.2 Suggestions for water chemistry management for the PACTEL facility

The objective of the master's thesis is to simulate the management of WC at the PACTEL experimental facility. Choosing the WC, its impact on the core operation, the operation of the primary circuit equipment with the efficiency and reliability of the assembly, safety and convenience of operation and maintenance and the environmental impact should be evaluated. The subjects of consideration for the core are: corrosion, deposit formation and absorption control. The radiolysis of coolant is not present due to the fact that the fuel elements of the prototype VVER-440 are simulated by the assembly of electrically heated rods.

The main objectives of the WC management are to maintain a high level of water quality, to minimize the rate of corrosion and to prevent deposits formation. The proposed WC takes into account the boron control, which is used as a slow-acting system of reactivity compensation as fuel burning up.

In the context of nuclear safety for alkalizing reactor water at PACTEL facility it is permitted to use KOH; it eliminates the possibility of the excess tritium forming (which is possible with the dosing of lithium hydroxide). Proposed WC provides dosing both of KOH and NH₃, this makes the alkalizing technology more flexible and has some advantages over the WC with LIOH. The cation exchanger is used for purifying the reactor water in mixed NH₄-K form and then it gets buffering properties. The cation buffer property helps to regulate the potassium concentration in the coolant and eliminates the danger overalkalining of reactor water. The accepted water chemistry allows to keep a higher pH (than that which is achieved only by means of alkali) value at the decreasing temperature in the loop during the reactor shutdown cooling and strengthening of ammonia properties, thereby reducing the low-temperature corrosion and stand still corrosion.

Also, when selecting the optimal WC for reactors with boron control the full range of structural materials types of the primary circuit should be taken into account. The stainless steel was selected as the structural materials for the reactor vessel and piping of the circulation loop for experimental PACTEL facility. AISI 304 stainless steel was applied in steam generator of PACTEL assembly, resistant to stress corrosion cracking.

In order to purify the water circulating in the primary circuit of the PACTEL facility it is proposed that a water treatment system is built.

The water treatment system (WTS) provides the required purity of the coolant and includes cation exchanger and anion exchanger filters and ion exchangers' trap.

It also provides the makeup treatment at WTS, including pretreatment (lime clarification) and three-stage desalting. As the water flow is very small at test facilities, there is no need to install the same equipment as used at the plant. It will be sufficient to choose the filter model simulating the filters used in reactor water cleanup. The dosing of aluminum sulphate or iron sulphate (coagulant) to the pipeline is provided (The water of city water treatment system is provided to use as the makeup for LUT nuclear laboratory. The pH value of the water is 7.4). The flakes begin to form in the pipeline, and then the coolant is fed to the tanks, where the flakes formation process ends. After the tank the water is sent to the cartridge filters (simulation of three-stage desalination). Cartridge filters are designed for a small volume of water and are loaded with ion exchanging resin. The use of the cartridge filters enables to avoid costly and challenging wastewater treatment. Figures 12 and 13 provide a schematic diagram of primary circuit without water chemistry and with proposed water chemistry respectively.

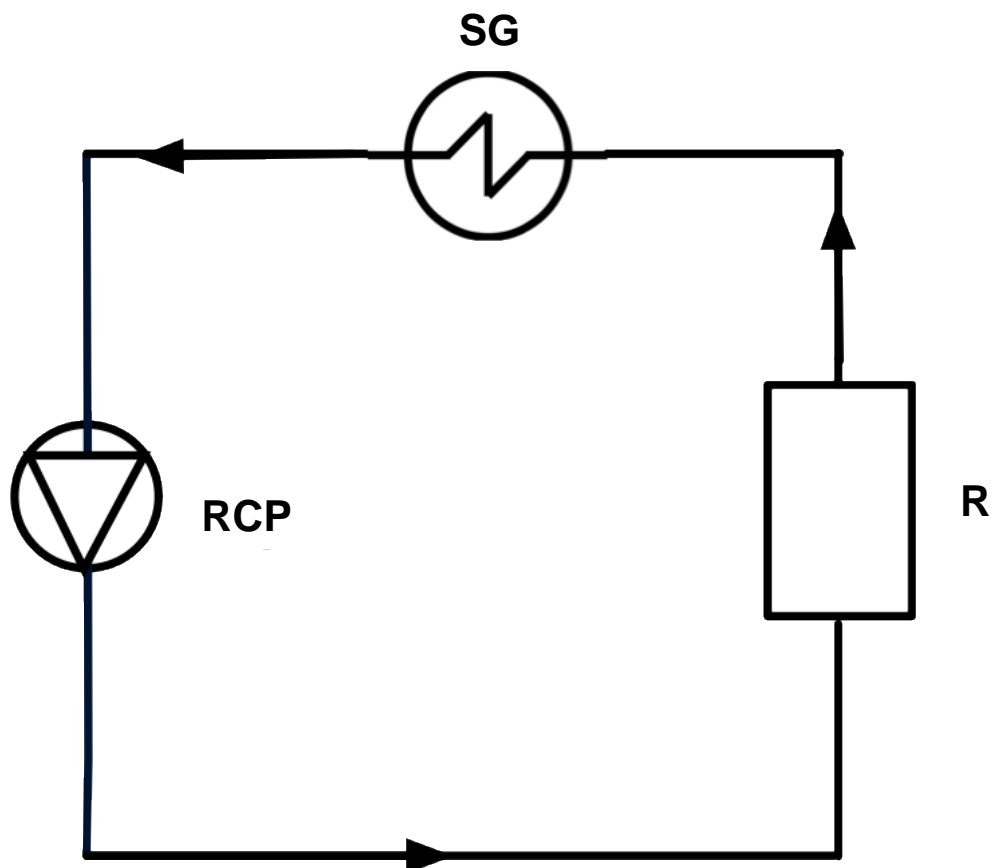


Fig. 12. The flow diagram of the PACTEL primary circuit.

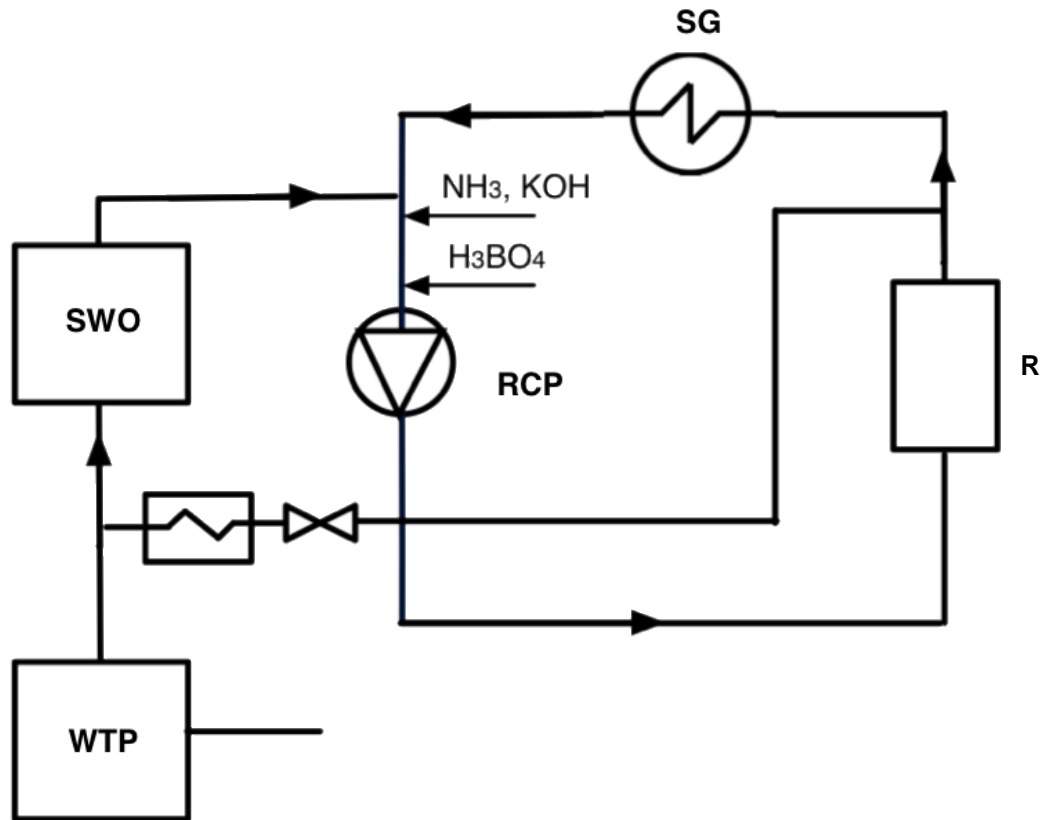


Fig. 13. The flow diagram of the primary circuit PACTEL. Proposals for the water chemistry management.

5.3 Description of the VEERA test facility

The main purpose of VEERA experimental facility was to simulate the behavior of boric acid in the NPP with PWR during the long-term cooling period of the LOCA. The loss of the coolant in primary loop takes a special place among all the accidents at the NPPs as this type of accident results in the maximum damage. As for the dangerous radiation impact on the environment, the failures in the NPP operation associated with the loss of coolant differ from all other emergencies. Usually such accidents start with the damage of one of the safety barriers. A threat of destruction of all safety barriers appears later. (Puustinen and Tuunanen 1994, 7)

A modified VVER-440 nuclear power plant in Loviisa is the reference reactor for the VEERA experimental facility. The design brief of this experimental facility is to perform accurate simulations in order to test the processes of mixing and concentration of boric acid solution and to examine the impact of the boric acid crystallization on the coolant flow in the core. The horizontal steam generator of the primary loop was not implemented in VEERA test facility. The models of circulation pumps, pressurizer or a secondary loop are not provided for these experiments either. (Puustinen and Tuunanen 1994, 7-14)

The reactor vessel is made of stainless steel, and is represented by a U-shaped tube, comprising a downcomer, a lower plenum, a core, a throttle at the core output and at the upper plenum. All heights in the reactor model are located below the hot leg of the circulation loop of a nuclear reactor is in the scale of 1:1 (Puustinen and Tuunanen 1994, 9.) The scale of volumes and flow cross section is 1:349. Schematic diagram of VEERA is shown in figure 14.

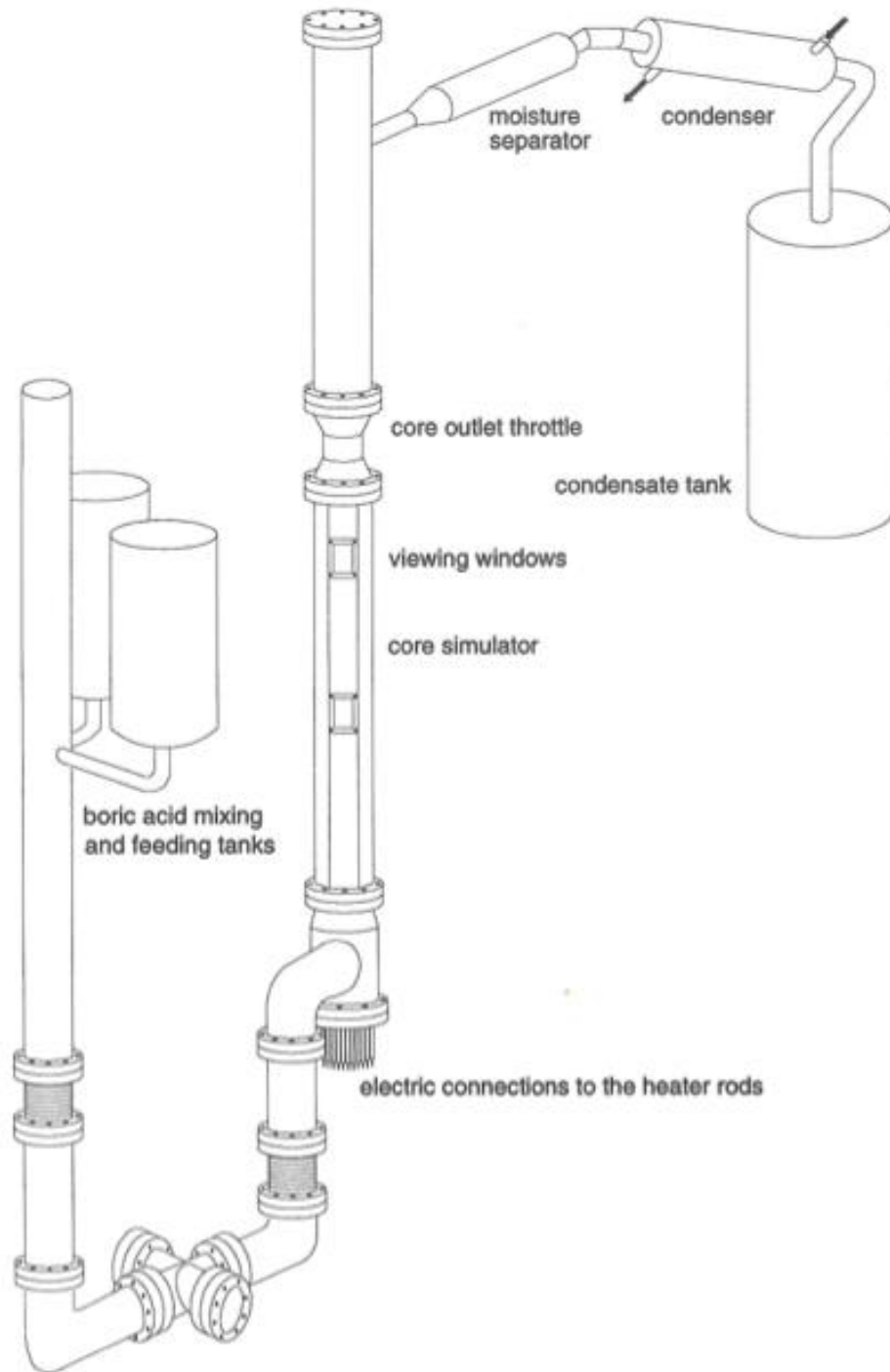


Fig. 14. The diagram of VEERA experimental facility. (Puustinen and Tuunanen 1994, 10)

The experimental section includes the copies of rod bundles of VVER-440 in the scale of 1:1. It also includes 126 full-size models of electrically heated rods and one unheated rod. The rods are placed in a thermally insulated hexagonal shroud. The boric acid crystallization can be observed by special viewing windows. It is also possible to take pictures or record events on camera. The viewing windows area is significantly smaller than the dimensions of the shroud. Small size windows are used to avoid heat loss and surface cooling. (Puustinen and Tuunanen 1994, 10-12)

Two tanks are connected to the DC to feed with the boric acid. The exhaust steam line includes moisture separator, condenser and condensate tank. (Puustinen and Tuunanen 1994, 10)

The total capacity of the heater surface is 8833 Watts. The housing of the experimental facility, except of viewing windows, is thermally insulated with mineral wool (thickness: 100 mm). Electric heaters with a capacity of 200-250 watts are fixed to the outer surface of DC. (Puustinen and Tuunanen 1994, 14)

The constructions at the top of the core as well as the nozzles at the outlet of the core are simulated very precisely. The condenser is made of two tubes. The cold water flows in the intertube space and the hot water flows through the inner pipe. The condensed steam is collected in the condenser tank where distribution ratio of boric acid, i.e. concentration ratio in vapor and in water can be measured by measuring the concentration of the boric acid. (Puustinen and Tuunanen 1994, 13-14)

In December 1987 the first larger scale experiments with the VEERA facility were started and by the middle of 1988 they were finished. Then after experiments it was decided to modify VEERA facility. The goal was better mixing of the boric acid between the core and lower plenum. It was achieved by modifying the core's lower structure. (Puustinen and Tuunanen 1994, 9-14)

5.4 Experiments with boric acid in the VEERA test facility

The water level was on the top of the core in the beginning of the experiments. All of the tests were started with the same concentration of boric acid. Water losses in the system were compensated with boron solution from one or two large tanks with feedwater connected to downcomer, and thus the water level remained constant during the test. The generated steam flows to the condenser tank through moisture separator and condenser. The concentration of boric acid in the core is increasing during boiling, and the generated steam has a low concentration of boric acid (close to 1 %). The concentration of boric acid was measured in the core, the condensate tank and the lower plenum at fixed time intervals. The heating power, the boric acid concentration, pressure and the water level in

the core were measured during the experiment. Sometimes 2.5 % concentration was used instead of 1 % concentration to cut down the duration of the tests. (Puustinen and Tuunanen 1994, 28)

Diagram of the VEERA experimental facility during testing with boric acid is shown in Figure 15.

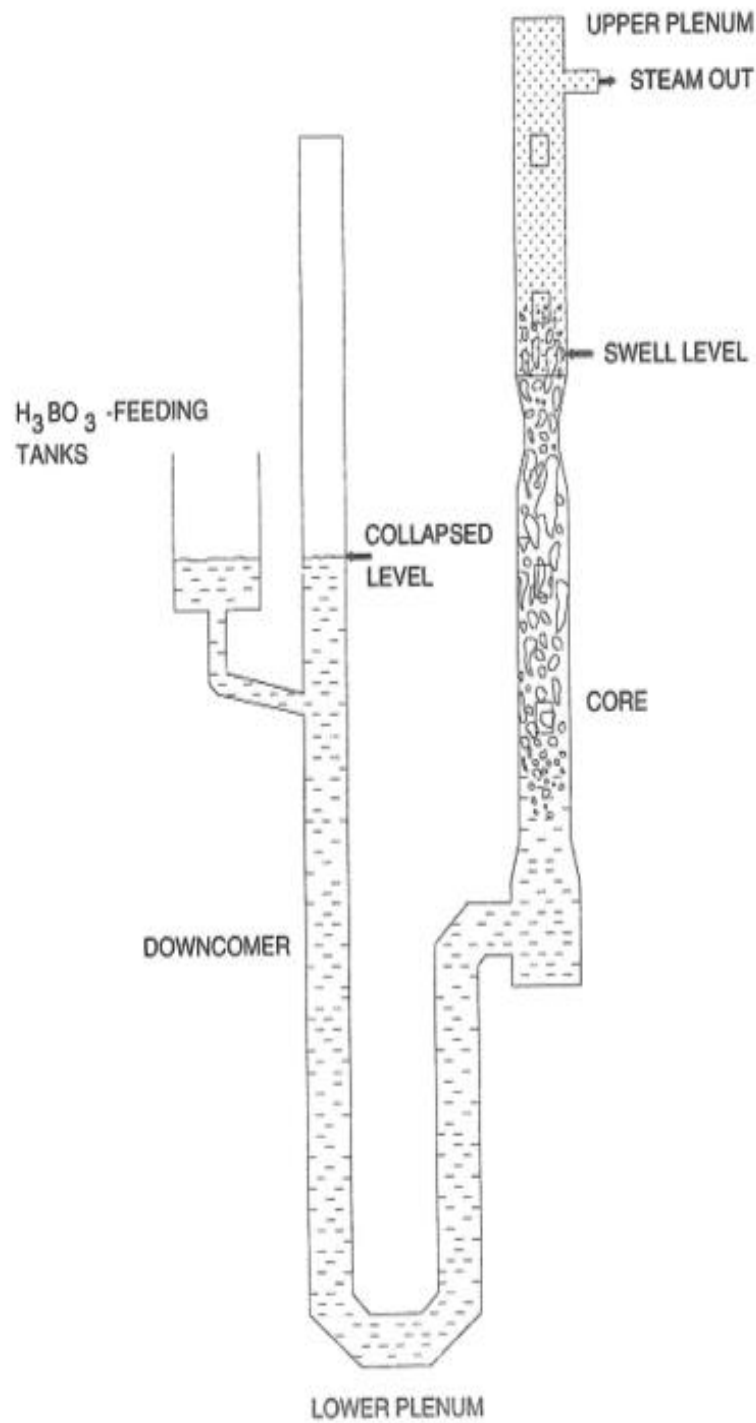


Fig.15. VEERA - experimental facility during testing with boric acid. (Puustinen and Tuunanen 1994, 28)

The main design parameters of the VEERA facility are presented in Table 4.

Table 4. The VEERA facility characteristics. (Puustinen and Tuunanen 1994, 9)

Reference power plant	VVER-440
Volumetric scale	1:349
High scale	1:1
Rod arrangement	triangular
Bundle geometry	hexagonal
Shroud tube geometry	hexagonal
Maximum cladding temperature	900 °C
Cladding material	stainless steel
Number of rods	126
Outer diameter of fuel rod simulators	9.1 mm
Heated length	2420 mm
Insulator material	MgO
Heating coil material	NiCr
Axial peaking factor	1.4
System design pressure	0.5 MPa

5.5 Suggestions for water chemistry management for the VEERA test facility

The ammonium potassium WC with dosing of boric acid was proposed for VEERA facility as well as for PACTEL facility. Experiments with different concentrations of boric acid allow to studying and identifying the correct geometry of fuel rods placement in the core during LOCAs.

The test facilities at LUT nuclear laboratory have not provided the dosing of alkali to maintain the pH level in the desired range. It was suggested to dose KOH and NH_3 . Figure 16 shows the diagram of VEERA with suggestion of proper water chemistry.

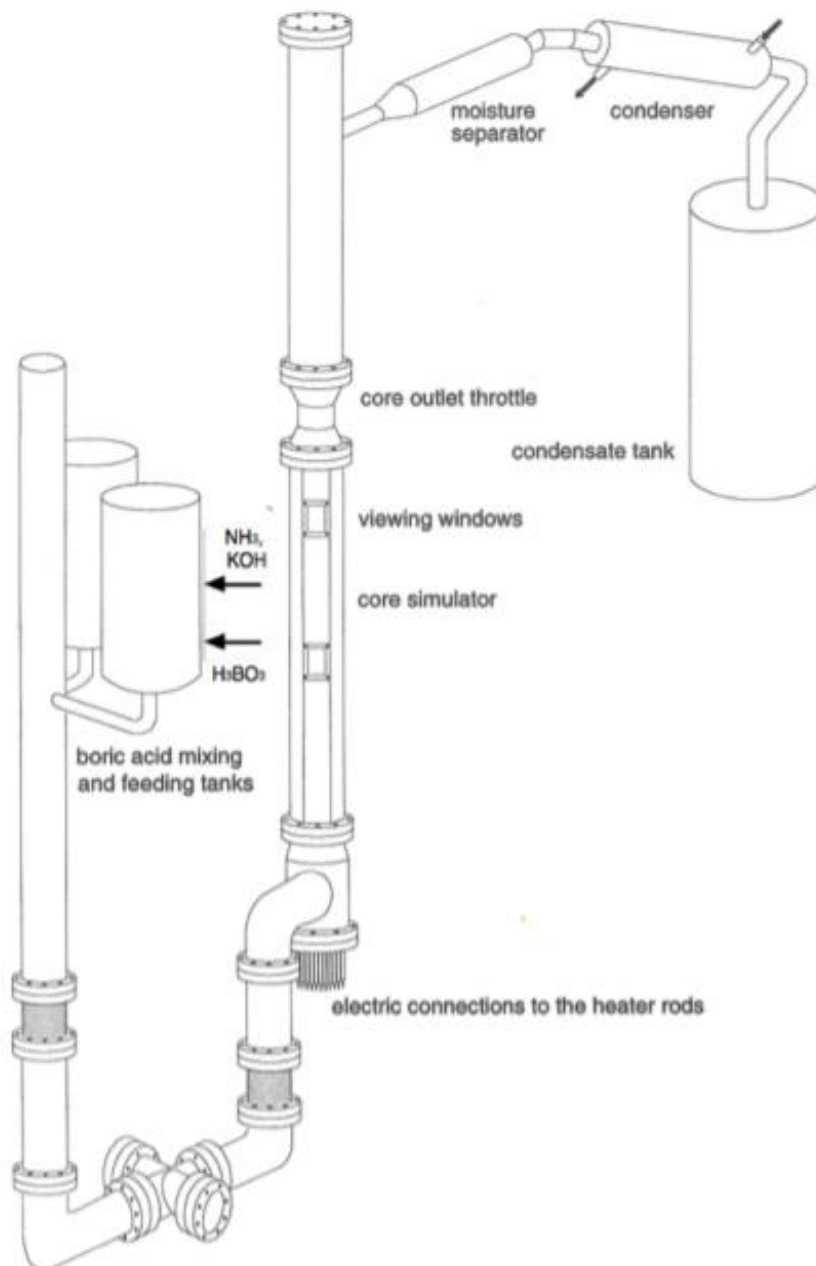


Fig. 16. The flow diagram of VEERA experimental facility. Suggestions for the water WC management.

5.6 Selection of water chemistry for future large test facilities

The laboratory of LUT is planning a series of facilities for further thermal-hydraulics researches. The correct primary and secondary water chemistry selection is one of the designing factors. VVER-1200 would be the prototype reactor for the development of future experimental facility. It is noteworthy that the configuration, as well as structural materials and operational conditions of future laboratory units would be similar to the existing test facilities.

It was mentioned in the previous chapters that regular water chemistry of primary circuit of existing VVER-440 and VVER-1000 reactors is potassium-boron-ammonia; however, the following improvements should be carried out for the further applications of newest reactors (Kritsky 1999, 161, 172-173, 179):

- Soft absorption control of nuclear reactor core.
- Increasing the efficiency of contamination removal by optimizing the coolant cleanup systems.
- Reducing the concentrations of corrective additives (potassium, boron) and reduction of their proportion in wastes.
- Application of new approaches of demineralizing, such as electrolytic process and membrane methods.
- Increasing the efficiency of automation in chemical control systems.
- Decreasing the operational expenses of ionite regeneration by reducing the amount of ammonia.
- Simplifying and reducing the number of the auxiliary equipment in WC management.

The boron injection to the coolant in primary circuit is needed to maintain the reactivity control for future power plants. The concentration of boric acid is neutralized by the addition of potassium hydroxide and ammonia, which allows keeping the pH on the required level. However, the typical water treatment is not always enough to ensure the stability of physicochemical conditions. The modified water chemistry provides the maintenance of alkali concentration on the maximum permitted level of 0.5 mmol/l at the beginning of reactor cycle. When the desired pH_{300} is reached, the alkali concentration is retained on a level to provide the pH_{300} of 7.1.

The alternative is to replace the ammonia with dissolved hydrogen. The main advantages of this approach is stability augmentation of WC maintenance under reduced power conditions, while simplification of water chemistry management during the startup and shutdown cooling is also

achieved. Moreover, it allows reducing the ionite regeneration costs and disposal costs. (Vatsuro 2013, 26)

Consequently, the modified potassium–hydrogen water chemistry with the boron regulation is proposed for the primary circuit of future large-scale test facilities.

Water chemistry of secondary circuit ensures the minimum amount of deposits formed at steam generator surfaces. Localized corrosion and cracking of the secondary circuit equipment could lead to compromising the safe operation of the test facility. Generally, the corrosion rate can be decreased by increasing the pH value. The most appropriate secondary WC for the future large facilities is ethanolamine, which ensures stabilized high pH of feedwater and blowdown water of SG, as well as decreases the flow-accelerated corrosion.

A water treatment system for future test facilities of LUT nuclear laboratory has been designed. Classical WTR based on chemical demineralization are technically, ecologically and economically imperfect. The newest approaches of demineralizing, such as membrane methods have become widely accepted over the last years. Taking into consideration recent developments, a modified scheme of WTS is proposed. In the first stage of demineralizing the water is fed to a clarifier. Next the treated water is filtered by osmotic membranes. The last stage of purification is a mixed bed ion exchanger. This simulation scheme of WC management would allow decreasing the final costs of facility, while ensuring the high quality of coolant. (Suharev 2013, 31)

6 SUMMARY

Nuclear energy makes a significant contribution to the energy balance of the industrialized countries. It is associated with the equipment reliability, the low cost of generated power and low environmental pressure under normal and safe operation of nuclear power plants. However, history knows several examples where inadequate technical solutions in NPP design and operation has led to huge accidents and even world-wide disasters. Therefore, the safety of nuclear power is of paramount importance.

One of the ways to improve nuclear safety is to reduce the radiation exposure of the nuclear industry workers at the power plants and apply measures to reduce the amount of radioactive deposits on the surfaces of the primary circuit equipment.

Water chemistry has a significant impact on the equipment reliability, and the incorrect management of the water chemistry may lead to premature equipment shutdown. Reasonable and rational WC helps to decrease the impurities concentration that adversely affect the radiological situation and reduce the heat exchange in the core of a nuclear reactor. The transfer of impurities into the steam turbine is accompanied by impurities deposition on the turbine blades and the reduction of turbine's internal efficiency factor.

It's necessary to monitor WC to ensure the integrity protective barriers and to follow the radiation safety standards. The structural material corrosion, mass transfer, corrosion product deposition, accumulation of radioactive substances and their removal from the circuit are the main reasons of mechanical damage of the equipment. Furthermore, corrosion products are the largest source of radiation dose. The radiation fields are formed as a result of activated corrosion products.

Different WCs of the primary circuit were examined in this Master's thesis. One of the primary goals of the thesis was to develop the WC for a LUT nuclear engineering laboratory's test facilities.

It is proved that the optimal WC for the current laboratory facilities is a potassium-ammonia with the boric acid addition. WCs used in the secondary circuit of VVER, such as ammonia-hydrazine chemistry and WC with amines dosing, were considered. SWO for water purification of the primary circuit of PACTEL facility is also proposed. For future large test facilities, the potassium-hydrogen water chemistry with the boron regulation has been proposed for the primary circuit, while ethanolamine water chemistry has been suggested for secondary circuit. Finally, modified WTS equipped with osmotic membranes has been selected.

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