



LCC7 SPECIAL TOPIC REPORT

Introduction to
Boiling Water Reactor Chemistry

Volume I

Introduction to Boiling Water Reactor Chemistry

Volume 1

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1 Boiling Water Reactor (BWR) designs (Wilfried Rühle)

BWRs of western design, which have been constructed in the USA, Japan, Taiwan, Sweden, Spain, Switzerland, Mexico and Germany, are all based on a General Electric (GE) development. A second BWR design family, the RBMK¹ reactors, were developed in Russia and constructed only in countries belonging to the former Soviet Union. This particular BWR design is reviewed in some detail in Section 1.6.

For power plants with BWRs, the main contribution from GE was the reactor or the nuclear island. The Balance of Plant (BOP) is normally constructed by contractors, who specialize on this part of the Nuclear Power Plant (NPP). The reactor design has been changed and improved during the last five decades by GE itself, but additionally by the licence holders from other countries like Sweden, Japan, Taiwan and Germany. Big changes have been made concerning the recirculation system for the reactor cooling water, the construction materials, the Reactor Water (RW) purification systems and the water separators and steam dryers. The difference in design can have a big impact on water chemistry, which will be discussed in Vol. 2.

As the BOP is often constructed by international companies that normally build fossil-fired power plants, the differences in design of the BOP are much greater than those of the reactor system. However, the designers of the BOP had to keep in mind that the Feed Water (FW) that they supply has a direct influence on corrosion and activity built up. The following Sections deal with the reactor cooling circuits and the BOP separately and show the mutual influence.

The BOP is composed of several subsystems. The most important are the FW system, the steam lines, the turbine, and the condensate system. A general overview of a BWR plant is shown in Figure 1-1.

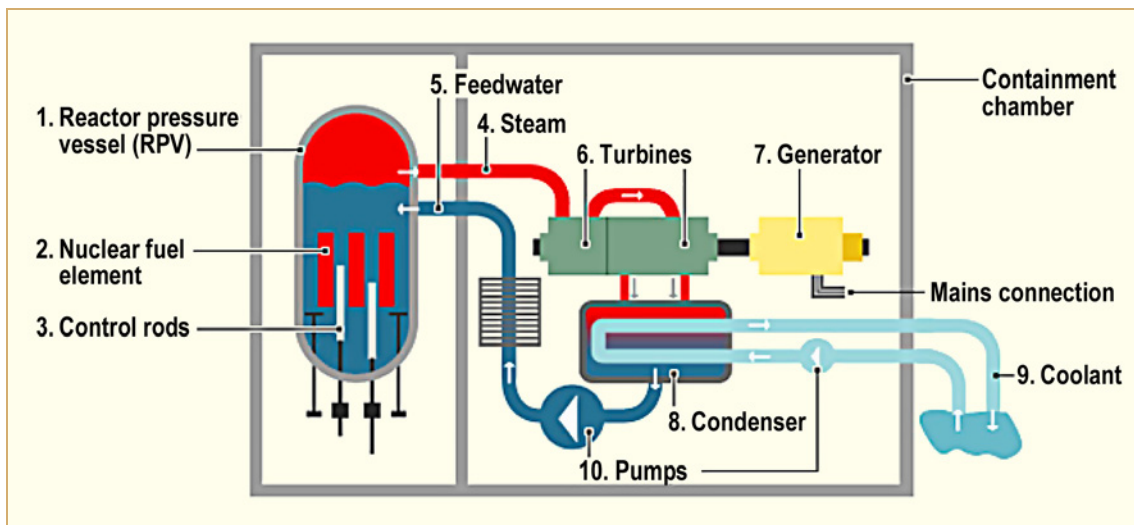


Figure 1-1: Schematic of a BWR, general overview [Wikipedia, 2011].

¹ Reaktor Bolshoi Mozhnosti Kanalov (in English Large Boiling Water Channel)

1.1 FW system

The basic function of the FW system is to supply the reactor or boiler with water. Furthermore, it is very important for the thermal efficiency of the plant. From the viewpoint of thermodynamics, the most important item for the efficiency of the plant is the difference between the steam temperature and the temperature of the condensate in the turbine condenser. The higher the difference in temperature, the higher is the efficiency of the plant. In the BWR, the upper temperature is limited by the materials used and the thermo hydraulic conditions.

Conversion of heat into work is possible according to the Rankine cycle [Rathore, 2010]. In the simplest case:

- The condensate/FW is pumped to high pressure,
- the high pressure water enters the boiler, where it is heated at constant pressure to saturated steam,
- the high pressure steam enters the turbine, expands there and generates work,
- the wet steam enters the condenser, where it is condensed to water.

This cycle would work, but not with high efficiency.

The Rankine cycle can be improved by optimizing the condensate and FW systems by installation of several preheaters, where the condensate/FW is heated gradually using extracted steam or steam condensates from the steam system, especially from different locations in the turbine. The more preheating steps used, the better is the plant efficiency.

Another important role in the plant's efficiency is played by the water separator-reheater. It reduces the droplet concentration in the steam, which can influence the integrity of the low-pressure turbine due to droplet erosion, and it produces a slight superheating of the steam.

As a result of these considerations about the efficiency of the plant, the BOP (and especially the FW system) is designed with a chain of different preheaters (sometimes the preheaters are called "coolers").

However, not only the efficiency of the plant is important. The cost of the plant, its operational features, and safety aspects has to be taken into account. So two construction standards have become accepted: the "forward pumped plants" and the "cascaded plants".

The reason why we have to mention this is that the two designs differ slightly in the water chemistry conditions. Figure 1-2 shows the abstracted schematics of the two production lines.

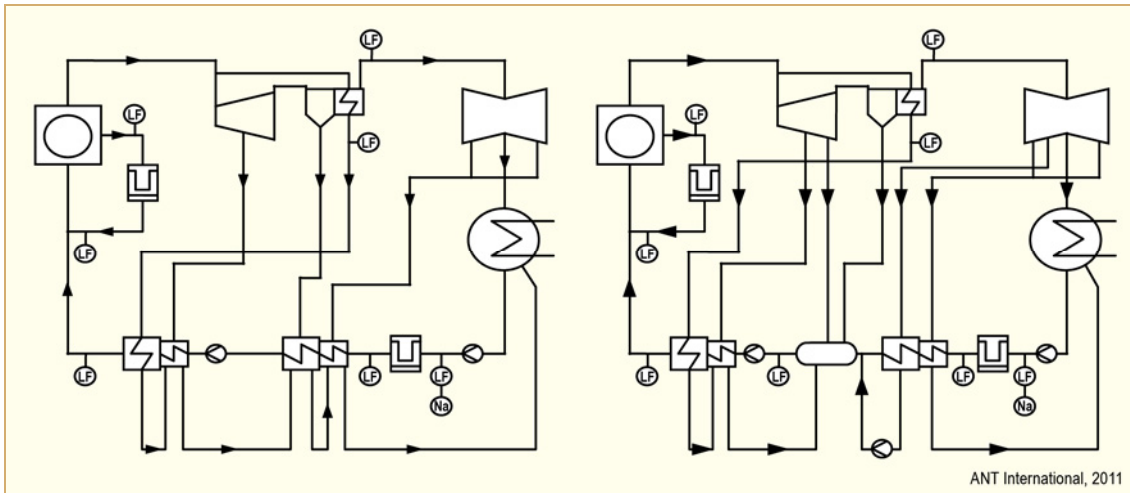


Figure 1-2: Schematic of a BWR with cascaded (left part) and forward pumped condensates.

1.1.1 Forward pumped plants

As can be seen in the right part of Figure 1-2, nearly all the extracted steam condensate enters the FW tank, which is used as a mixed pre-heater. From there, the condensates and all the contained energy are pumped forward to the reactor. Only a small amount of condensate from the coldest part of the turbine enters the condenser because of its small energy content. As can be shown by thermodynamic calculations, this condensate treatment should give a little higher plant efficiency than the method with cascaded condensates. In practice, other plant features can compensate for this difference. The comparison of two thermal circuit diagrams for two German BWRs, forward pumped and cascaded, with the same thermal output and from the same supplier, shows, that in this example the cascaded plant has a higher efficiency than the forward pumped plant.

Besides the better efficiency, forward pumping has the advantage that the main condensate system only has to treat 70% of the FW amount, as 30% of it is pumped directly into the reactor as part of the FW. So the condensate system and the condensate purification system can be constructed much smaller, which reduces construction expenses.

The disadvantage of the forward pumped design is that only 70% of the condensed main-steam can be purified by the condensate purification system. The remaining 30% is fed into the reactor without purification. Forward pumping of the condensed steam from lower pressure conditions results in a higher oxygen concentration in the FW system compared to the case of cascading the auxiliary condensates because most of the radiolysis gas leaves the condensate in the turbine condenser (see Section 2.1 on water radiolysis). Therefore, because of the higher oxygen concentration, the concentration of iron (III)-oxide-hydrates in the FW is higher in forward pumped plants than in the cascaded plants. This can result in more deposits on the fuel elements and higher contamination of the reactor cooling system and the BOP (Section 2.2).

1.1.2 Plants with cascaded condensates

The term ‘cascaded condensates’ means that the extracted steam condensates are used to heat up colder condensates. The cooled down condensate heats the next cooler condensate with decreasing efficiency and after several steps, it is feed into the turbine condenser (Figure 1-2, left part). This method is less efficient than the forward pumped method. A positive property of the cascaded plants is that they support a very good FW quality, with achievable conductivities close to the theoretical accessible value and particulate iron concentrations of less than 0.1 µg/kg.

1.1.3 Materials of construction for FW pipes

The connecting pipes and the vessels (or shells) of the heaters and coolers are normally made from standard carbon steels or low alloyed carbon steel. Some often-used materials for FW pipes are shown in Table 1-1.

Table 1-1: Carbon steel types for FW pipes, after [Ilg, 2008].

Material	Composition	Steel type
WB36 mod or 15NiCuMoNb 5	0.15%C, 1.25%Ni	
20MnMoNi55	0.2%C, 1.25%Mn, 1.25%Mo	
22NiMoCr37	0.22%C, 0.7%Ni, 0.7%Mo	
WB35 or 17MnMoV64	0.17%C, 1.5%Mn, 0.4%Mo	Fine grained steel, middle strength steel
15MnNi63	0.15%C, 1.5%Mn, 0.75%Ni	Low strength steel

ANT International, 2011

Basically, the experience with these materials during plant operation under BWR conditions (neutral water, very low conductivity, 10-200 µg/kg oxygen) is very good. However, in some cases local corrosion has been observed in FW systems. Stress Corrosion Cracking (SCC), Strain Induced Corrosion Cracking (SICC), Corrosion Fatigue (CF) and Erosion Corrosion (EC) have been reported. In Germany, some Intergranular Stress Corrosion Cracking (IGSCC) was experienced in the FW system, but much more in steam piping. More details about IGSCC will be presented in Section 1.3.

The piping of the heaters and coolers should be made from austenitic stainless steel, such as Type 347.

1.2 Recirculation systems

The water in BWRs is used for cooling the fuel rods, as means for heat transport to the turbine and as moderator for neutrons. Its moderator function is used for reactivity control of the reactor and thus for load control of the plant. By changing the water flow through the reactor, the size of the bubbles generated by the boiling process can be controlled and thus the density of the moderator. That is why BWRs need a flexible flow control system for the reactor coolant. Early generation BWRs used external pumps to circulate the entire water inventory. Later models combined external pumps to drive jet pumps inside the reactor via external loops. Current designs have the recirculation pumps inside the reactor vessel. In the Russian designed RBMK reactors, external pumps control the coolant velocity.

1.2.1 Plants with recirculation loops

The recirculation systems are only described at an elementary low level. The purpose of the description is the understanding the influence of the systems on water chemistry issues such as local corrosion and activity transport and build up. The information about plants with recirculation loops is predominantly taken from free accessible GE publications, such as the GE Technology Systems Manual “BWR GE BWR4, Technology Manual”, and “BWR6, General Description of a BWR”.

A schematic of the recirculation system for the BWR6 is shown in Figure 1-3. The BWR Vessel Arrangement for the jet pump recirculation system is shown in Figure 1-4. This picture is important for the Sections dealing with activity built up and dose rates as well as for the item “IGSCC” (Volume 2).

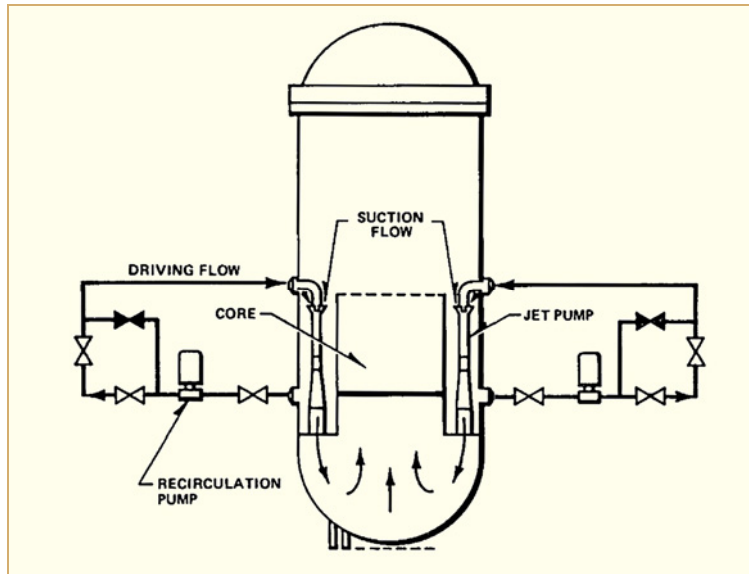


Figure 1-3: Schematic of the recirculation system for the BWR6 [BWR6, 1975].

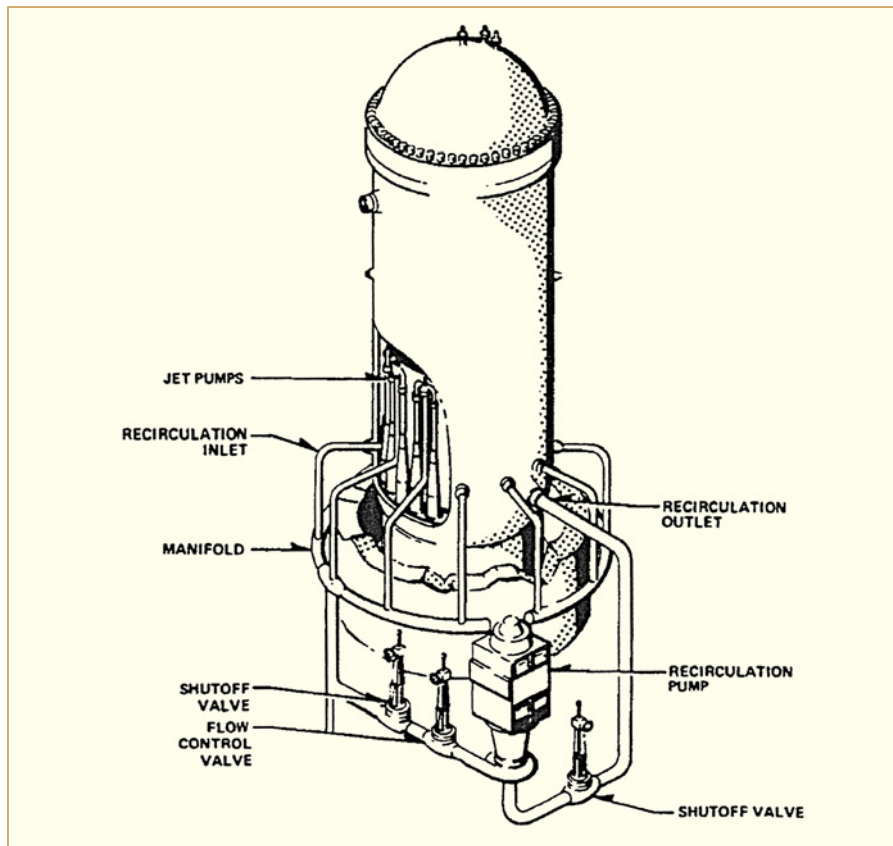


Figure 1-4: BWR Vessel arrangement for jet pump recirculation system [BWR6, 1975].

2 BWR Water chemistry fundamentals

2.1 Water radiolysis (Wilfried Rühle)

In the Annual Report LCC⁵, R. Riess and W. Rühle have dealt very extensively with the behaviour of radiolysis gases in BWRs and PWRs. Great emphasis was given to the international experience with radiolysis gas and the approach for understanding the interrelationships. This book will concentrate on the mechanism of the formation of radiolysis gas in the radiation field, on its behaviour in saturated steam and condensate, and on considerations about its distribution and enrichment in plant systems. The theoretical considerations will be correlated with measurements of radiolysis gases in systems different in temperatures and pressures. From the results, recommendations for safe operation are deviated.

Formation of radiolysis gases in BWRs and the transport of the gases, as a mixture with saturated steam, out of the reactor and into the balance of the plant is well understood and documented. From the viewpoint of thermodynamics, the behaviour of the two gases (non-condensable gases and saturated steam) during part or total condensation of the saturated steam, is also well known. Transfer of this knowledge to an operating system with streaming steam under changing velocities, with heat losses by the enveloping walls connected with changing thermodynamic conditions, condensate formation, condensate dewatering (drainage), changing geometry of the components and flow conditions, raise questions, which are not always easily answered.

Radiolytically generated gases are a topic affecting operations, technical support, maintenance and the chemistry. Because of the complexity of this item and the way it affects nearly all technical departments, it is dealt with by several system engineers and technical experts, each thinking about their part of the problem. Chemistry personnel are normally engaged with this topic to a lesser extent. However, a lack of basic knowledge can result in extremely conservative decisions, leading to expensive... and not always necessary countermeasures.

A better basis for understanding of the radiolysis gas issues can be found by examining the measurements of radiolysis gases concentrations in several steam containing systems of a BWR (with different pressure-/ temperature levels, component geometries and flow conditions, and under different operational conditions) over a period of about 20 years. The following considerations are limited to the description of the normal radiolytic gases produced in a BWR that result in about 20 ppm O₂ and 2.5 ppm H₂ in the main steam at pressures greater than 10 bar and at the temperatures of saturated steam. Higher concentrations of non-condensable gases from other sources and condensation processes, down to pressure values less than 10 bar, would give very different results. Another precondition for this discussion is that there must be a sink where the condensate is degassed to approximately zero before its reuse. This is realized in practice by the vacuum condenser.

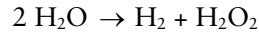
2.1.1 Water radiolysis mechanism

For a better understanding of the behaviour of radiolysis gases within steam, especially their transfer from the water phase inside the reactor into the steam phase, it is useful to know a little bit more about their formation mechanism. We will see that knowing the formation mechanism and the transfer mechanism to the steam is important, especially for the cases of hot stand-by operation and for after shut down, with residual heat removing system is in operation.

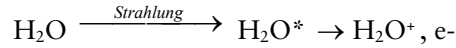
Ionizing radiation, which penetrates a material, interacts with it [Henglein et al, 1969]. Atoms or molecules can be energized to activated conditions or changed into ions or radicals (e.g. H⁺, H⁻). Most of the short-lived intermediate products can undergo versatile reactions with the molecules in its surrounding.

⁵ LWR Coolant Chemistry

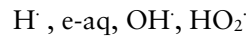
In light water reactors, the most important types of radiation are gamma-, beta-, and neutron-radiation. These radiation types decompose water according to the following equation:



Intermediary products are



and from these products the unstable and very reactive radicals emerge:

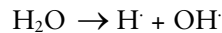


Gamma radiation itself is not directly ionizing. But due to the photoelectric effect or Compton scattering (and in some cases pair production) fast electrons are produced. The fast electrons are slowed down by interactions with water molecules as a result, the water is ionized. By this processes, the fast electrons lose their energy by exciting electrons from the water molecules and the ionization continues to proceed along the so-called “spur”. The ionization density along the spur depends on the energy of the electrons. The slower the electrons are, the higher is its energy loss per unit of travel. The radius of such a spur is approximately 1 E-6 to 1.5 E-6 mm.

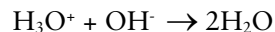
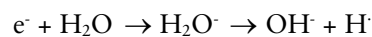
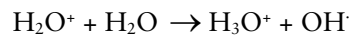
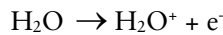
During the slowing down process of fast neutrons by the hydrogen atoms of the water molecule, high energy protons are generated and emerge from the water molecule. Because of their smaller velocity compared to electrons, these high energy protons have a shorter slow down distance and thus produce a much higher ionization density.

Neutrons produce the same radiolysis products in water as produced by gamma radiation but in different concentration ratios.

As the primary process the formation of H^\cdot and OH^\cdot radicals can be taken into consideration:



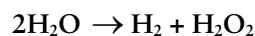
Also other reactions result as a net reaction in formation of H^\cdot - and OH^\cdot -radicals:



The radicals built in a zone with high ionization density react as follows:



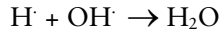
This results in the following sum equation:



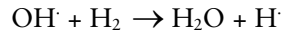
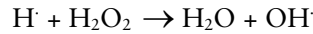
This reaction, leading to the molecular products of the radiolysis process, is called “forward” reaction.

As H_2O_2 in the hot RW is decomposed to O_2 and water, in samples taken from the RW sample lines, only H_2 and O_2 can be found as radiolysis products (Section 2.1.1.1).

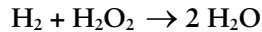
The $\text{H}\cdot$ and $\text{OH}\cdot$ radicals originated during the slowing down process of γ - and β - radiation occur relatively far from each other and so can diffuse out of the spur into the surrounding water before they can react. Here they can react with each other and reform into water:



Furthermore they can react with the molecular radiolysis products transforming those into water:



As net reaction we get the so called **back reaction**.

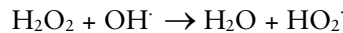


But this reaction is only possible when it takes place in a water phase that is not producing steam such as a PWR, or in a BWR that is in hot standby operation or in the residual heat-removing mode.

The water destruction by radiolysis depends on the following criteria:

- Nature and intensity of the radiation
- Concentration of the just existing radiolysis products
- Purity of the water (ionic pollutants and O_2 increase water destruction)
- Temperature
- Number of phases in the irradiated system

Another primary radiolysis product, which is produced when heavy particles are slowed down, is the $\text{HO}_2\cdot$ radical. Because of the high ionization density, very high concentrations of radicals are generated. Before the radicals have a chance to escape out of the spur, they react within the spur following this reaction equation:

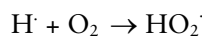


A higher fraction of neutrons results in a decrease of the molecular products and so intensifies the back reaction. This is the reason why the composition of the reactor fuel can influence the amount of produced radiolysis gases.

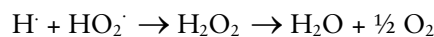
A measure for the yield of radiolysis gases production is the so-called G-value. It indicates the number of atoms, molecules or ions, which are deposited or transformed, when 100 eV of energy are absorbed (e.g. $G(\text{H}_2)$, etc.).

Increasing the molecular products H_2 and H_2O_2 accelerates the back reaction (the efficiency of H_2O_2 as a radical catcher, which inhibits the back reaction can be neglected at high temperature because of the instability of hydrogen peroxide).

Molecular oxygen either from H_2O_2 or from air, can be a strong inhibitor for the back reaction by capturing $\text{H}\cdot$ radicals and so accelerate water destruction:



The $\text{HO}_2\cdot$ -radicals again and again produce O_2 :



3 Water chemistry guidelines and technical basis (Robert Cowan)

3.1 Background

The water chemistry limits in the BWR were originally established by the results of extensive laboratory testing by the US Naval Reactor Program [DePaul, 1957] and the GE Company [Vreland et al, 1961]. Original goals were to prevent chloride induced TGSCC of structural materials and to limit extensive scale formation on fuel, as reflected in plant licensing technical specifications and fuel warranty limits. An example of these early chemistry limits are shown in Table 3-1.

Table 3-1: Early BWR technical specifications and fuel warranty limits, after [Cowan, 1994].

	Typical technical specification	Typical fuel vendor warranty limits
FW		
Conductivity, $\mu\text{S}/\text{cm}$	*	<0.065
Total Fe, $\mu\text{g}/\text{kg}$	*	<15
Oxygen, $\mu\text{g}/\text{kg}$	*	20 to 200
Copper, $\mu\text{g}/\text{kg}$	*	<0.5
Zinc, $\mu\text{g}/\text{kg}$	*	<0.6
RW		
Sulphate, $\mu\text{g}/\text{kg}$	*	<100
Chloride, $\mu\text{g}/\text{kg}$	<500	<100
Conductivity, $\mu\text{S}/\text{cm}$	<1.0	<1.0
<small>ANT International, 2011</small>		

3.2 Water chemistry guidelines

With time, the importance of water chemistry parameters on such phenomena as IGSCC, shut down dry well radiation levels, flow assisted corrosion, fuel cladding performance, radioactive waste generation, operating dose rates and radioactive gas release led to the establishment of additional chemistry monitoring parameters as well as tighter limits for the operators, beginning in 1983 with the issue of the BWR Water Chemistry Guidelines by EPRI. Since that time, other consensus organizations (VGB⁹ in Germany, GOST¹⁰ in Russia and the Atomic Energy Society of Japan) have issued recommended operating guidelines that have been adopted by the BWR operators in those countries. This Section will discuss the technical basis for these guidelines and the differences between them. From a general perspective, the EPRI Guidelines differ from the others by also addressing methods that change the inherent oxidizing conditions of the BWR to mitigate IGSCC.

⁹ Vereinigung der Grosskraftwerksbetreiber (Association of big Power Producers, Germany)

¹⁰ Gosudarstvennyy Standart (which means state standard)

Most guidelines have 'Action Levels' which tell the operator what to do when a value exceeds some limit and the reader should refer back to this Section when interpreting the Tables containing the different guidelines in the following Sections. One must visit the original sources to see the complete instructions when an action level is exceeded, as they can be quite complex for some variables. However, a generic summary of the action level guidance is listed below.

3.2.1 EPRI Guideline instructions

Action Level 1: This is the value of a parameter that, if exceeded, may threaten long-term system reliability, as indicated by data or engineering judgment, thereby warranting an improvement of operating practices.

Recommended responses to a parameter exceeding an Action Level 1 value are:

- a) Restore the parameter to the Action Level 1 value as soon as practicable.
- b) Sample and analyze additional sample(s) within 8 hours, 96 hours for integrated samples.
- c) If not restored within 96 hours, perform a review to assess the impact on long-term system reliability. Identify and evaluate corrective actions. Develop and obtain management approval of a written plan and schedule to implement appropriate corrective actions.

Each plant should formalize a management awareness program for prolonged off-NWC conditions. This should include a mechanism for informing appropriate levels of management of the existence of the condition, the implications, and the possible corrective measures over the short and long term.

Action Level 2: The Action Level 2 value of a parameter, if exceeded, indicates that significant degradation of the system may occur in the short term, based on current industry data or engineering judgment, thereby warranting a prompt correction of the abnormal condition.

Recommended responses to a parameter exceeding an Action Level 2 value are:

- a) As soon as practicable, corrective action shall be initiated to reduce the parameter below the Action Level 2 values.
- b) If the parameter has not been reduced below the Action Level 2 value within 24 hours at plants operating with NWC, or with HWC or NMCA+HWC during start-up, an orderly unit shutdown shall be initiated and the plant shall be brought to cold shutdown as rapidly as operating conditions permit. At plants operating on HWC or NMCA+HWC, it may be more prudent to continue power operation with the HWC system in service during an excursion above Action Level 2 if this results in minimized degradation of components during the period of elevated impurity concentrations. As discussed above, if such an approach is adopted, an evaluation of probable impurity ingress scenarios shall be performed prior to occurrence of the event to document how continued operation rather than a shutdown will result in acceptable degradation of reactor materials.
- c) If it is foreseeable that the parameter will be below the Action Level 2 value within the time period required to achieve an orderly shutdown, power operation can be maintained.
- d) (Following an excursion above an Action Level 2 value, a review of the incident shall be performed and appropriate corrective measures taken. If a shutdown was required as a result of the excursion, appropriate corrective measures should be taken before the unit is restarted.

Action Level 3: An Action Level 3 value represents the limit above which it is known that significant degradation of system materials will occur over the short term.

Recommended responses to a parameter exceeding an Action Level 3 value are:

- a) As soon as practicable, corrective actions shall be initiated to reduce the parameter below the Action Level 3 values.
- b) If the parameter has not been reduced below the Action Level 3 value within 6 hours, an orderly unit shutdown shall be initiated and the plant shall be brought to cold shutdown as rapidly as operating conditions permit unless an *a priori* evaluation of the type of the event and its severity has been performed and continued operation has been shown to result in less materials degradation than would occur during a shutdown/start-up sequence. In such cases, power operation can be continued; for HWC or NMCA+HWC plants, the HWC system should remain in service if the decision is made to continue power operation. As discussed above, if such an approach is adopted, an engineering evaluation of probable impurity ingress scenarios shall be performed prior to occurrence of the event to document how continued operation rather than a shutdown will result in acceptable degradation of reactor materials.
- c) If it is foreseeable that the parameter will be below the Action Level 2 value within the time period required to achieve an orderly shutdown, power operation can be maintained.
- d) Following an excursion above an Action Level 3 value, a review of the incident shall be performed and appropriate corrective measures taken. If a shutdown was required as a result of the excursion, appropriate corrective measures should be taken before the unit is restarted.

3.2.2 VGB Guidelines instructions

Action level 1

- a) Efficient evaluation and elimination of the cause for the chemical deviation according to plant specific Technical Instructions within an appropriate period of time.

Action level 2

- a) Minimization of risk for corrosion by time limitation for evaluation of the cause for the chemical deviation and carry out of countermeasures.
- b) Return of concerned parameters into the permitted range within 36 hours, if not specifically defined otherwise.
- c) In case this fails, the plant is to be shutdown according to operation manual. If it is foreseeable, however, that values below Action Level 2 can be reached during the time span to reach 100°C in the reactor vessel, operation can continue.

Action level 3

- a) Initiation of plant shutdown according to operation manual within 12 hours. If it is definitely foreseeable, however, that values below Action Level 3 can be reached during the time span to reach 100°C in the reactor vessel, operation can continue.
- b) Restart of a plant can not occur until elimination of the cause of the incident responsible for the shutdown.

4 Water chemistry related systems (Wilfried Rühle)

4.1 Condensate filtration and demineralization

The FW quality of the BWR is much higher than that of other boilers because of: a) the potential corrosion risk associated with trace pollutants and b) the activation of the pollutants in the neutron field. As cleaning of the FW directly before the water entry in the reactor is not possible because of the high enthalpy content of the water, the condensate has to be cleaned at the beginning of the preheaters line. Because of the limited temperature stability of the ion exchange resins, the condensate temperature should be as low as possible (about 35°C). For economic reasons the temperature should be higher, but the upper limit of about 80°C should not be exceeded. In such cases, special, thermally stable resins should be used.

4.1.1 Comparison of condensate purification methods

For purification techniques, two methods are used, deep bed filters and precoat filters. Occasionally, the deep bed filters are supplemented with mechanical filters (4.1.3). The advantages of deep bed filters are:

- Their high capacity for ionic pollutants removal and
- that they enable plant operation with small condenser leakages for long time.

A weak point of deep bed filters is their limited ability to remove particulate products, such as iron oxides. This can increase corrosion product depositions in the reactor and especially on the fuel rods [Eickelpasch & Lasch, 1985, 1986, 1988]. Furthermore, the resins (after exhaustion) have to be regenerated with bases and acids. Great emphasis has to be given to avoiding entry of these regeneration chemicals into the reactor.

The poor efficiency for particulate removal can be ameliorated by back fitting the deep bed filters with mechanical filters.

In 2006 EPRI published the results of the “EPRI BWR Chemistry Monitoring Database in 2005” [Tran et al, 2006], where the performance of the different condensate polishing systems of 39 BWRs were reported. This paper is a well-substantiated comparison of the available condensate polishing systems and their efficiency against ionic and particular pollution. Therefore, some details out of this paper have to be repeated here:

The condensate polishing systems of the plants examined were equipped with:

- Deep bed demineralizers only with limited capacity to remove insoluble crud particles,
- deep bed demineralizers with upstream backwashable filters as prefilters with a good capacity for particulate and ionic species,
- filter demineralizers with pleated or wounded septa and precoated with filter aids made from flocculated mixtures of cation and anion powder resins, sometimes protected with an inert filter aid.

4.1.1.1 BWR FW iron control

The main purpose for FW iron control is minimizing crud formation on the fuel rods, minimizing activity built up by Co-60 in case of zinc addition, avoiding excess deposition of zinc on the fuel rod surfaces. The efforts made in the 39 plants to reduce corrosion product input into the reactor in the years 1997 to 2005 showed a reduction by more than a factor of two. As shown in Figure 4-1 the lowest values were gained by the combination “filter and deep bed”, but the results concerning the precoat systems were very similar.

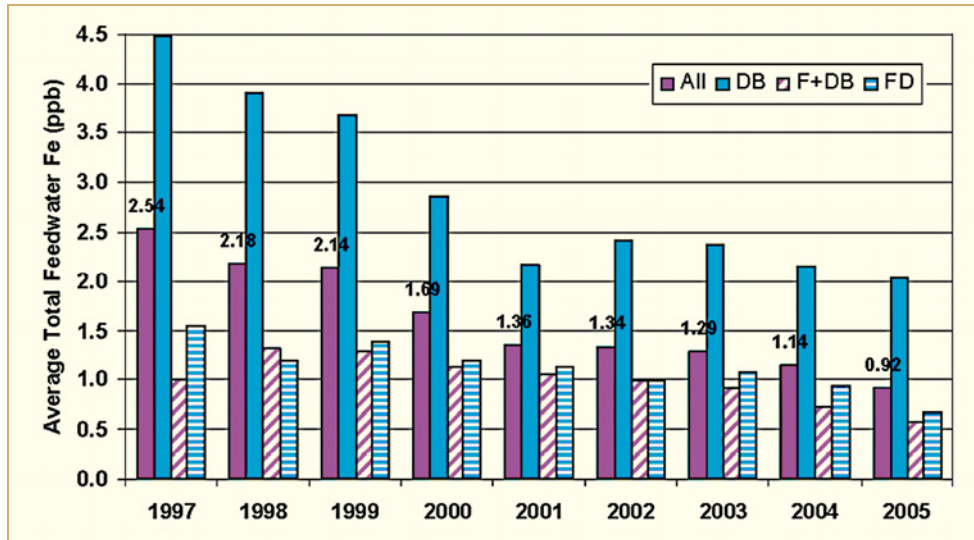


Figure 4-1: BWR FW iron trend from 1997-2005 for 39 BWRs by condensate polishing system [Tran et al, 2006].

For the particles retention efficiency with deep bed filters a dependency on water viscosity, according to variations in water temperature, was observed. Higher viscosity enhances the drag forces against adsorbed particles and so can remobilize them.

4.1.1.2 BWR FW copper control

Plants with brass as the material for condenser tubes normally have more copper in the RC than those with stainless steel or titanium. Because of the influence of copper on local corrosion, its concentration in FW should be as low as possible. The plant comparison has shown that plants with filter-deep bed combinations reach the lowest, extremely small copper concentrations in FW with values less than 0.05 µg/kg (Figure 4-2).

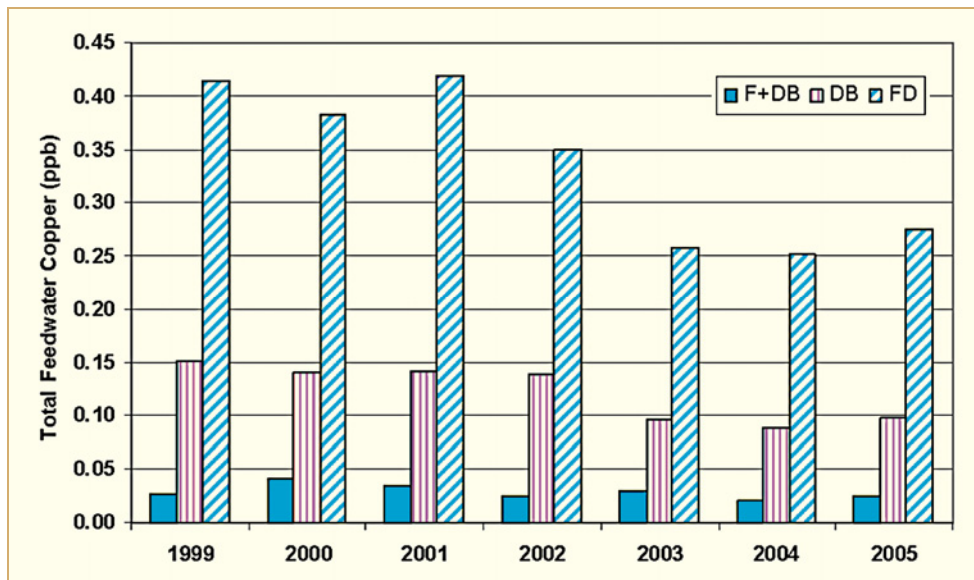


Figure 4-2:: 1999-2005 Average FW copper differentiated by condensate polisher type (for North American plants with copper alloy condenser tubes) [Tran et al, 2006].

4.1.1.3 Alternative precoat material for copper control

One German BWR had a pronounced copper problem, which was solved by a new, unconventional condensate purification method. Because of high steam velocities in the turbine condenser, EC problems at the brass tubing occurred, resulting in rather high copper and zinc concentrations in both the condensate and in the RW. In RW, copper increased up to 15-20 $\mu\text{g}/\text{kg}$ and zinc up to 5-10 $\mu\text{g}/\text{kg}$. By optimizing the filter precoat using other resins, these values were reduced by about 25%. Nevertheless, the RW conductivity in this plant was higher than in the other German BWRs. To avoid expensive hardware optimizations, the plant management decided to watch out for other precoat products [Roßkamp, 1998].

The product should be:

- Insoluble in water up to 50°C,
- after the reaction with the impurities in water, no soluble species must be produced,
- the product should be mixable with filter resins and inert materials,
- it should form flocks, which could be precoated.

As the most suitable product, chitin, (Poly [1 \rightarrow 4]- β -N-acetyl-D-glucosamine), was identified (Figure 4-3). This product was first used for the RW purification filters and later for the condensate polishing system.

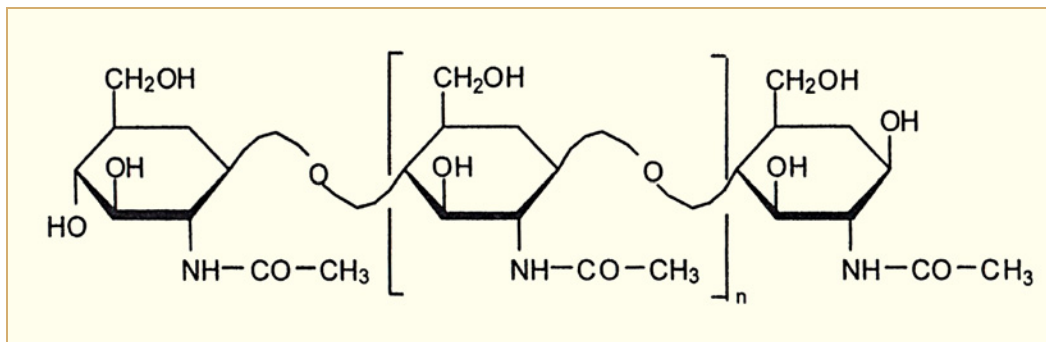


Figure 4-3: Chitin, precoat product for copper removal (Poly [1 \rightarrow 4]- β -N-acetyl-D-glucosamine).

When the product was used at the RWCU system, an immediate reduction of RW conductivity was observed. Furthermore, the decontamination factor for iodine was improved. After additionally using the product at the condensate polishing system, the RW conductivity reached the intended value of 0.08 $\mu\text{S}/\text{cm}$.

5 Cold shutdown and long term lay-up methods (Wilfried Rühle)

Plant shutdown is extensively described in the LCC5 Topic report “Start-up and shutdown practices in BWRs and in primary and secondary circuits of PWRs, VVERs¹³ and CANDUs¹⁴”. In the case of BWRs, shutdown measures in preparation for an outage are included. For a normal outage lasting for about 3 to 6 weeks, no further measures besides those described in this paper are necessary. For longer time special lay-up measures are recommended. The following contribution to long-time lay-up of BWRs is based on a procedure for the German Plant KKP1 of EnBW, which was based on plant experience, but written by AREVA NP GmbH [AREVA/EnBW, 2007].

5.1 Reasons for plant lay-up

Shutdown of a plant might result in indefinite conditions concerning rest water content, humidity in drained systems, oxygen and carbon dioxide in rest water and corrosive chemicals such as chloride and sulphate. These conditions can cause surface corrosion and local corrosion, which can be starting points for other corrosion types during start-up and plant operation.

5.2 Materials and corrosion phenomena

Corrosion sensitivity is different concerning stainless steel, copper alloys and carbon or low alloy steel. In the case of stainless steel, we need not fear any corrosion at low temperatures. Nevertheless higher concentrations of chlorides and sulphates should be avoided, as these ions can be accumulated in preferred regions of the steel surfaces, such as micro cracks and welding failures. For the case of stainless steel systems, which cannot be drained during lay-up, like the reactor vessel itself, avoiding introducing contaminants is very important. During restart of the plant and temperature increase, these locally adsorbed corrosive agents can cause crack propagation.

Limitations for the water quality during lay-up have been established in many countries and from different plant suppliers. In Germany, these are the VGB guidelines, Table 5-1.

Table 5-1: Chemical specification for RW in case of water temperature <100°C, after [VGB, 2006].

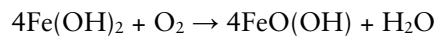
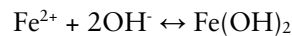
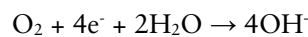
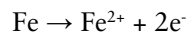
Control parameter	Normal value	Action level 1
Chloride [$\mu\text{g}/\text{kg}$]	<20	>50
Sulphate [$\mu\text{g}/\text{kg}$]	<20	>50
Diagnostic parameter	Normal value	Action level 1
Conductivity at 25°C [$\mu\text{S}/\text{cm}$]	<1	>2*)
Silica [$\mu\text{g}/\text{kg}$]	<200	
*) If conductivity >2 $\mu\text{S}/\text{cm}$, pH should be 5.5 to 8.5		
ANT International, 2011		

¹³ Voda Voda Energo Reactor (Russian type PWR)

¹⁴ Canadian Deuterium Uranium

In the case of copper alloy turbine condenser tubes, the cooling water side has to be managed carefully. If the layer is in good condition, it is protected with a smooth, glossy protective layer consisting of fine-grained minerals and biologic components. If this layer dries out, it shrinks, forming cracks. The cracked protective layer is the reasons for local corrosion during and after start-up. The solution to this problem is either a) keep the layer wet during the whole shutdown period or b) remove the protective layer by corundum coated rubber balls before the final shutdown.

The most critical materials in terms of lay-up are carbon and low alloy steel. Normally these materials are components of the balance of the plant are protected or passivated with a layer consisting of magnetite and hematite. In cold water und high oxygen concentrations, these protective layers are not permanently stable. Fe(II) in magnetite will be oxidized to Fe(III) witch reacts with water to form FeO(OH) and its hydration products. The corrosion process can be described as follows:



These products are not protective and enable further corrosion of the base metal. From personal experience, more than 6 weeks of lay-up without special measures are not recommended. The loose corrosion products can make problems during start-up, so that intensive rinsing measures should be used. Because of the small diffusion coefficient of oxygen in water, the most important region for this corrosion is that close to the boundary line of the water-air-pipe wall. The corrosion mechanism can result in a uniform corrosion or as shallow pit corrosion. Shallow pit corrosion can be aggravated by aggressive chemicals such as chlorides and sulphates. These ions can induce local pH-decrease, and that promotes the local corrosion.

5.3 Lay-up procedures

To find the optimal procedure for shutdown and lay-up some basic items have to be checked:

- Duration of lay-up
- Sections of the plant, which have to be opened for scheduled work
- Materials and material conditions in this Sections
- Technical possibilities and temporal conditions for draining, drying and refilling
- Possibilities for shutdown procedures on lay-up planning
- Checking the lay-up procedure because of side effects (e.g. release of radionuclides)

For systems made from carbon steel and low alloyed steel there are two different lay-up methods available:

- Dry lay-up by removing all the rest water and humidity from the components, which have to be protected.
- Wet lay-up with demineralised and oxygen free water.

For systems made from stainless steel, both dry and wet lay-up are possible. In the case of wet lay-up, there are high demands for the water quality. For RW, the specification is shown in Table 5-1.

5.3.1 Dry lay-up

Corrosion is only possible if water is in contact to a material. Therefore, without water or humidity, corrosion is impossible. Preconditions for successful dry lay-up are:

- Short duration time for the dry out process,
- a pure system free from corrosive ions in the rest water, because trace pollutants are concentrated to saturated solutions before the residual water is completely evaporated,
- the drying equipment must not release any pollutants into the system, which has to be dried.

Drying a system is not only removing the water from the system, but the humidity in the air inside the system has to be reduced beneath the dew point.

The dew point is the temperature to which moisture containing air must be cooled, until the humidity in the air starts to precipitate. The dew point is reached, when the relative humidity in air arrives at 100%.

The relative humidity is defined as follows:

$$\text{Relative humidity [\%]} = p_w(t)/p_s(t) \times 100$$

$p_w(t)$ = Partial pressure of vapour in air at temperature (t)

$p_s(t)$ = Saturation pressure for vapour in air at temperature (t)

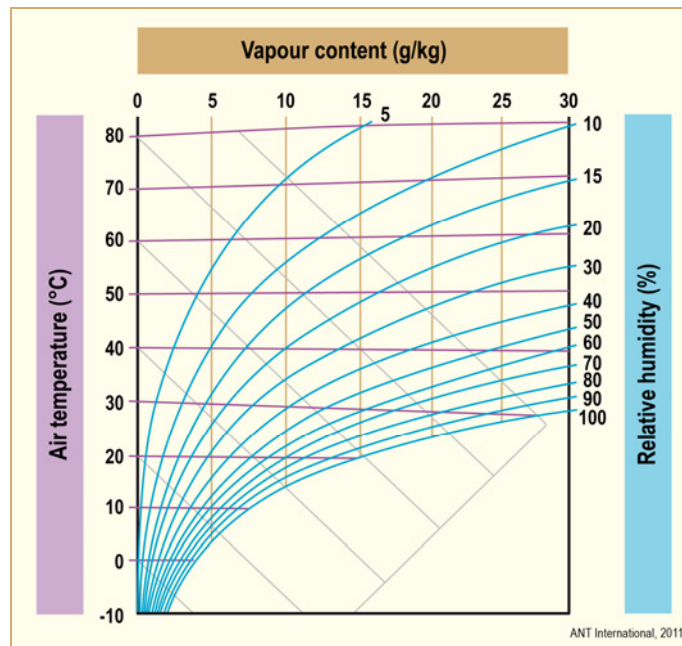


Figure 5-1: Correlation between relative humidity and temperature, after [AREVA/EnBW, 2007].

The above graph clarifies the correlation between dew point and relative humidity (Figure 5-1).

For dry lay-up, we can see from this diagram, that decreasing temperature increases relative humidity until we have reached the dew point at 100% humidity. If we have for example in our system a humidity of 40% at 32°C (point A) and we decrease temperature to about 15°C, we reach 100% humidity and so the dew point. In practice, if we have a save lay-up situation with 40% humidity at an environmental temperature of 32°C and we have to open the building in winter for special work, we very easily can fall below the dew point.

6 Data base for some BWRs (Robert Cowan)

Table 6-1: Operating Asian BWRs.

NPP	Type	MWe	Condenser tube material (a)	Condensate treatment type (b)	RWCU type (b)	RWCU % of FW flow	FW Zn injection	IGSCC mitigation applied (c)	Heater drains
Japan									
Tsuruga Unit 1	BWR2	357	Cu	DB	F/D+DB	7%		HWC	Cascaded
Tokai No.2	BWR5	1100	Cu	DB	F/D	2%	DZO	HWC*	Cascaded
Fukushima I (Daiichi) Unit 5	BWR4	784	Cu	HFF(33%)+DB	F/D	1%		HWC	Cascaded
Fukushima I (Daiichi) Unit 6	BWR5	1100	Cu	HFF+DB	F/D	2%		HWC	Cascaded
Fukushima II (Daini) Unit 1	BWR5	1100	Ti	PF+DB	F/D	2%		HWC+TiO ₂	Cascaded
Fukushima II (Daini) Unit 2	BWR5	1100	Ti	PF+DB	F/D	2%			Cascaded
Fukushima II (Daini) Unit 3	BWR5	1100	Ti	F/D+DB	F/D	2%		NMCA	Cascaded
Fukushima II (Daini) Unit 4	BWR5	1100	Ti	PF+DB	F/D	2%			Cascaded
Hamaoka Unit 3	BWR5	1100	Ti	F/D+DB	F/D	2%	DZO	HWC	Cascaded
Hamaoka Unit 4	BWR5	1137	Ti	HFF+DB	F/D	2%	DZO	HWC	Cascaded
Hamaoka Unit 5 (d)	ABWR	1380	Ti	HFF+DB	F/D	2%			FPD
Higashidōri Unit 1(Tohoku EPCO)	BWR5	1100	Ti	HFF+DB	F/D	3%			Cascaded
Higashidōri Unit 1(Tokyo EPCO)	ABWR	1385	Ti	HFF+DB	F/D	2%			FPD
Kashiwazaki-Kariwa Unit 1	BWR5	1067	Ti	PF+DB	F/D	2%		HWC	Cascaded
Kashiwazaki-Kariwa Unit 2	BWR5	1067	Ti	F/D+DB	F/D	2%			Cascaded
Kashiwazaki-Kariwa Unit 3	BWR5	1067	Ti	HFF+DB	F/D	2%			Cascaded
Kashiwazaki-Kariwa Unit 4	BWR5	1067	Ti	HFF+DB	F/D	2%			Cascaded
Kashiwazaki-Kariwa Unit 5	BWR5	1067	Ti	F/D+DB	F/D	2%			Cascaded
Kashiwazaki-Kariwa Unit 6	ABWR	1315	Ti	HFF+DB	F/D	2%			FPD
Kashiwazaki-Kariwa Unit 7	ABWR	1315	Ti	HFF+DB	F/D	2%			FPD
Ohma (d)	ABWR	1383	Ti	HFF+DB	F/D	2%			FPD
Onagawa Unit 1	BWR4	524	Ti	F/D+DB	F/D	3%			Cascaded
Onagawa Unit 2	BWR5	825	Ti	HFF+DB	F/D	3%			Cascaded
Onagawa Unit 3	BWR5	825	Ti	HFF+DB	F/D	3%			Cascaded
Shika Unit 1	BWR5	540	Ti	HFF+DB	F/D	2%			Cascaded
Shika Unit 2	ABWR	1358	Ti	HFF+DB	F/D	2%			FPD
Shimane Unit 1	BWR3	460	Cu	F/D+DB	F/D+DB	7%		HWC	Cascaded
Shimane Unit 2	BWR5	820	Ti	F/D+DB	F/D	5%		HWC	Cascaded
Shimane Unit 3 (d)	ABWR	1373	Ti	HFF+DB	F/D	2%			FPD
India									
Tarapur Station Unit 1	BWR1	160	Adm. Brass	DB					Cascaded
Tarapur Station Unit 2	BWR1	160	Adm. Brass	DB					Cascaded
Taiwan									
Chinshan Unit 1	BWR4	604	Titanium	DB	F/D	1.3		HWC	Cascaded
Chinshan Unit 2	BWR4	604	Titanium	DB	F/D	1.3		HWC	Cascaded
Kuosheng Unit 1	BWR6	948	CuNi	DB	F/D	1		HWC	Cascaded
Kuosheng Unit 2	BWR6	948	CuNi	DB	F/D	1		HWC	Cascaded
Lungmen Nuclear Unit 1 (d)	ABWR	1350							
Lungmen Nuclear Unit 2 (d)	ABWR	1350							
* OLNC scheduled									
(a) Ti = Titanium, Adm. Brass = copper zinc alloy, CuNi = copper nickel alloy and SS = stainless steel									
(b) DB = deep bed demineralizer, F/D = filter demineralizer, HFF = hollow fibre filter, PF									
(c) NWC = normal water chemistry, HWC = hydrogen water chemistry, NMCA = noble metal chemical application, OLNC = on-line noble metal chemical addition, TiO ₂ = titanium oxide treatment									
(d) still under construction as of 2011									
ANT International, 2011									

Table 6-2: Operating European BWRs.

NPP	Type	MWe	Condenser tube material (a)	Condensate treatment type (b)	RWCU type (b)	RWCU % of FW flow	FW Zn injection	IGSCC mitigation applied (c)	Heater drains
Finland									
Olkiluoto Unit 1	BWR75	860	Ti	F/D	DB	2			Cascaded
Olkiluoto Unit 2	BWR75	860	Ti	F/D	DB	2			Cascaded
Germany									
Gundremmingen Unit B	Type 72	1344	1.4439 (Alloy 317 LN)	DB	F/D	2			FPD
Gundremmingen Unit C	Type 72	1344	1.4439 (Alloy 317 LN)	DB	F/D	2			FPD
Isar (d)	Type 69	912	Cu28Zn1Sn1As	F/D	F/D	1			FPD
Krümmel (d)	Type 69	1402	Cu28Zn1Sn1As	F/D	F/D	1			FPD
Philippsburg (d)	Type 69	926	Cu28Zn1Sn1As	F/D	F/D	1			Cascaded
Brunsbüttel (d)	Type 69	806	Cu28Zn1Sn1As	F/D	F/D	1			Cascaded
Spain									
Cofrentes	BWR6	1096	Titanium (orig. Adm. Brass)	F/D	F/D	1.1	DZO	OLNC	FPD
Santa María de Garoña	BWR3	466		F/D + DB	F/D + DB	6.7	DZO	HWC	Cascaded
Sweden									
Forsmark Unit 1	BWR69	1010	Titanium (orig. Al/Brass)	F/D	DB	2.7			Cascaded (FPD planned 2010)
Forsmark Unit 2	BWR69	1010	Titanium (orig. Al/Brass)	F/D	DB	2.7			Cascaded (FPD planned 2010)
Forsmark Unit 3	BWR75	1190	Titanium	F/D	DB	2.8			FPD
Oskarshamn Unit 1	BWR	494	Titanium	F/D	DB	2	DZO		Cascaded
Oskarshamn Unit 2	BWR	661	Titanium	F/D	DB	2	DZO	HWC	Cascaded
Oskarshamn Unit 3	BWR75	1450	Titanium	F/D	DB	2			FPD
Ringhals Unit 1	BWR	830	Titanium (orig. Adm. Brass)	F/D + standby DB	DB	4		HWC	Cascaded
Switzerland									
Leibstadt	BWR6	1220	Titanium	F/D	F/D	1	DZO	OLNC	FPD
Mühleberg	BWR4	385	Titanium (orig. Adm. Brass)	F/D	F/D	1	DZO	OLNC	Cascaded
<p>(a) Ti = titanium, Adm. Brass = copper zinc alloy, CuNi = copper nickel alloy and SS = stainless steel</p> <p>(b) DB = deep bed demineralizer, F/D = filter demineralizer, HFF = hollow fibre filter, PF = pleated filter</p> <p>(c) HWC = hydrogen water chemistry, NMCA = noble metal chemical application, OLNC = on-line noble metal chemical application, TiO₂ = titanium oxide treatment</p> <p>(d) Out of operation currently</p>									
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Table 6-3: Operating BWRs in the Americas.

NPP	Type	MWe	Condenser tube material (a)	Condensate treatment type (b)	RWCU type (b)	RWCU % of FW flow	FW Zn injection	IGSCC mitigation applied (c)	Heater drains
Mexico									
Laguna Verde Unit 1	BWR5	682.5	Titanium (was Cu-Ni)	Filter + DB	F/D	0.95	yes	OLNC	FPD
Laguna Verde Unit 2	BWR5	682.5	Titanium (was Cu-Ni)	Filter + DB	F/D	0.95	yes	OLNC	FPD
United States									
Browns Ferry Unit 1	BWR4	1065	SS	F/D	F/D	1.15	DZO	NMCA	Cascaded
Browns Ferry Unit 2	BWR4	1118	SS	F/D	F/D	1.15	DZO	NMCA	Cascaded
Browns Ferry Unit 3	BWR4	1114	SS	F/D	F/D	1.15	DZO	OLNC	Cascaded
Brunswick Unit 1	BWR4	938	Titanium	Filter + DB	F/D	0.85	DZO	HWC	FPD
Brunswick Unit 2	BWR4	900	Titanium	Filter + DB	F/D	0.85	DZO	HWC	FPD
Clinton	BWR6	1043	304 SS	Partial filter + DB	F/D	0.9	DZO	NMCA	Cascaded
Columbia	BWR5	1131	Adm. Brass/ Copper Nickel	F/D	F/D	1	DZO	NMCA*	Cascaded
Cooper	BWR4	760	SS	F/D	F/D	1	DZO	OLNC	Cascaded
Dresden Unit 2	BWR3	867	304 SS	Partial filter + DB	DB	2.8	DZO	OLNC	Cascaded
Dresden Unit 3	BWR3	867	304 SS	Partial filter + DB	DB	2.8	DZO	OLNC	Cascaded
Duane Arnold	BWR4	581	304 SS	F/D	F/D	1	DZO	OLNC	Cascaded
Edwin I. Hatch Unit 1	BWR4	876	Titanium	F/D	F/D	1	DZO	OLNC	Cascaded
Edwin I. Hatch Unit 2	BWR4	883	Titanium	F/D	F/D	1	DZO	NMCA*	Cascaded
Enrico Fermi Unit 2	BWR4	1122	Titanium	F/D	F/D	1.1	DZO	OLNC	FPD
Grand Gulf	BWR6	1266	304 SS	DB	F/D	1	DZO	OLNC	FPD
Hope Creek	BWR4	1061	Titanium	Filter + DB	F/D	1	DZO	NMCA*	Cascaded
James A. Fitzpatrick	BWR4	852	Admir. Brass w/ Ti impingement	DB	F/D	1.11	DZO	OLNC	Cascaded
LaSalle Unit 1	BWR5	1118	304 SS	F + DB	F/D	0.9	DZO	OLNC	FPD
LaSalle Unit 2	BWR5	1120	304 SS	F + DB	F/D	0.9	DZO	NMCA*	FPD
Limerick Unit 1	BWR4	1134	Adm. Brass	Filter + DB	F/D	1.1	DZO	NMCA	Cascaded
Limerick Unit 2	BWR4	1134	Adm. Brass	Filter + DB	F/D	1.1	DZO	NMCA*	Cascaded
Monticello	BWR3	572	304 SS	F/D	F/D	1	DZO	HWC	Cascaded
Nine Mile Point Unit 1	BWR2	621	90Cu/10Ni/Super SS	DB	DB	5.14	DZO	OLNC	Cascaded
Nine Mile Point Unit 2	BWR5	1135	Admir. Brass /Periphery70/30 Cu/Ni	DB	F/D	2	DZO	OLNC	FPD
Oyster Creek	BWR2	619	Titanium	DB	F/D + DB	4.6	DZO	NMCA	Cascaded
Peach Bottom Unit 2	BWR4	1112	Titanium	F/D	F/D	1.2	DZO	NMCA*	Cascaded
Peach Bottom Unit 3	BWR4	1112	Titanium	F/D	F/D	1.2	DZO	OLNC	Cascaded
Perry	BWR6	1231	SS	Filter + DB	F/D	1	DZO	OLNC	FPD
Pilgrim	BWR3	685	Titanium	D/B	F/D	1.5	DZO	NMCA*	Cascaded
Quad Cities Unit 1	BWR3	867	SS	F/D	F/D	2	DZO	NMCA	Cascaded
Quad Cities Unit 2	BWR3	867	SS	F/D	F/D	2	DZO	NMCA*	Cascaded
River Bend	BWR6	967	Adm. Brass	Filter + DB	F/D	1	DZO	OLNC	FPD
Susquehanna Unit 1	BWR4	1300	304 SS	Filter + DB	F/D	0.94	DZO	HWC	Cascaded
Susquehanna Unit 2	BWR4	1140	304 SS	Filter + DB	F/D	0.94	DZO	HWC	Cascaded
Vermont Yankee	BWR4	620	92% Admir. Brass/ 8% 304 SS	F/D	F/D	0.8	DZO	NMCA*	Cascaded
* OLNC scheduled									
(a) Ti = titanium, Adm. Brass = copper zinc alloy, CuNi = copper nickel alloy and SS = stainless steel									
(b) DB = deep bed demineralizer, F/D = filter demineralizer, HFF = hollow fibre filter, PF = pleated filter									
(c) NWC = normal water chemistry, HWC = hydrogen water chemistry, NMCA = noble metal chemical application, OLNC = on-line noble metal chemical application, TiO ₂ = titanium oxide treatment									
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