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Water Chemistry in Pressurized Water Reactors – A Gösgen-Specific Overview

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Abstract: The three main water circuits of the Gösgen pressurized water reactor and their chemistries are described. In the primary water circuit the cooling water and its contents undergo chemical as well as radiochemical reactions. Chemical agents – such as boric acid – are used for long-term reactivity control. The boron concentration therefore is dictated by reactor physics and may not be optimal from a chemical viewpoint. Under the given circumstances the chemistry of the primary water circuit cannot be adjusted to a sole optimum covering all the tasks. Nevertheless it is possible to operate the power plant using a chemical regime that avoids excessive corrosion within the expected plant live time of 60 years. The water-steam cycle with its two phases must be conditioned chemically in a way to protect the water and steam side components from corrosion. This is done by adding hydrazine to remove oxygen and to form ammonia, which is the main contributor to water alkalinisation. The cooling water system is open to the atmosphere and supplied by river water with continually changing contents. To avoid deposits on the system surfaces an upstream water treatment plant is used to remove suspended matter and to precipitate calcium and magnesium. Thousands of tons of chemicals are needed to treat the required 20 billions of litres of water each year. Radioactive waste treatment plays an important role in the nuclear industry. Operational waste is divided into three waste streams. Only one of these waste streams (waste water) is really influenced by water chemistry.

Keywords: Pressurized water reactor · Radioactive waste management · Water chemistry

1. Introduction

The pressurized water reactor (PWR) falls, along with the boiling water reactor (BWR), in the class of light water nuclear power plants. In contrast to the BWR, the PWR has a strict separation of the water-steam cycle from the primary water circuit (Fig. 1). In total the PWR has three main water circuits: the primary water circuit, the water-steam cycle, and the cooling water system. The latter can be operated either by a cooling tower or by cooling water pass through. In a PWR only the primary water circuit contains radioactivity.

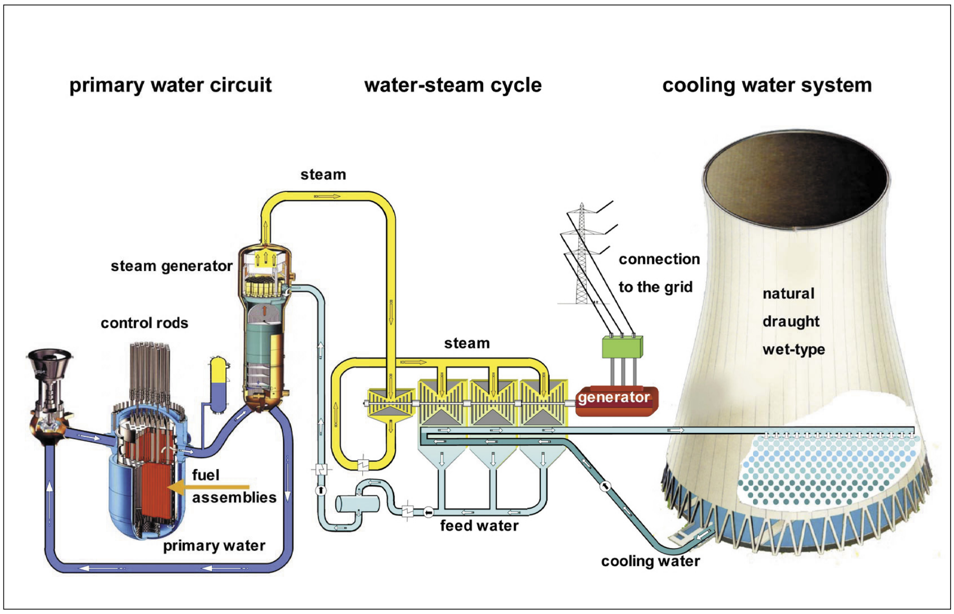

Fig. 1. Basic design of a PWR – overview of the three main water circuits

Heat to generate electrical power is produced by fission of ^{235}U and ^{239}Pu atoms. Small pellets of UO_2, slightly enriched in ^{235}U are collected in fuel assemblies and inserted into the reactor pressure vessel. Pu is generated by neutron capture of ^{238}U, followed by the radioactive decay of the produced ^{239}U atoms or directly inserted as MOX fuel (a blend of UO_2/PuO_2) into the pressure vessel. The water flowing through the reactor pressure vessel transports the heat to the steam generators. In contrast to the BWR, the water is not directly evaporated within the reactor pressure vessel, because it is kept under high pressure (about 150 bars) at operating temperatures (about

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300 °C). In the steam generators the transferred heat is used to produce steam, which flows to the turbine, is condensed thereafter to water and pumped back to the steam generators. Heat that cannot be utilized any further is carried off by the cooling water system.

Changes and developments in water chemistry have occurred since the beginning of nuclear power production [1–4]. In this paper the main chemical aspects of the three water circuits in use today at the Siemens-designed Gösgen PWR are outlined. In addition there will be a short overview of the management of operational radioactive waste. The large number of intermediate cooling and service water systems and water purification systems, in which the chemistry can also play an important role, are not described here.

Generally the water purity standard is very high in nuclear power plants, especially in the primary water circuit and the water-steam cycle. Normally the amount of impurities is in the order of 1 μg/kg or even below. This is to avoid endangered reactor operation due to material corrosion and its consequences. Beside that, the primary coolant is used as a neutron moderator and as a heat transfer medium. Therefore the tasks of water chemistry are quite variable and the principal demands can be expressed as follows [5]:

- Ensure long term reactivity control
- Minimize metal sloughing rate (erosion, corrosion)
- Counteract the occurrence of selective forms of corrosion (stress corrosion cracking)
- Influence the transport and the deposition of corrosion products in a way that the radiological contamination of primary water circuit components remains low
- Avoid depositions on the heat transfer surfaces
- Suppress the radiation-induced production of oxygen
- Keep the pH value in an optimal range
- Monitor and keep up water quality to avoid corrosion and to reduce radiation level
- Monitor and minimize radioactivity discharges
- Monitor fuel conditions
- Monitor compliance with numerous technical specifications and other instructions

As a consequence of these demands there is a relation between material selection and water chemistry. Chemical parameters and specifications have to be derived. This is done by the reactor supplier and the operator. One of the main tasks of power plant chemistry is to ensure the permanent compliance with these specifications, including the implementation of countermeasures if necessary. For a safe plant operation it is necessary to meet the mentioned tasks with the support of up-to-date and effective analytical chemistry.

2. Primary Water Circuit

2.1. *Overview*

The main components of the primary water circuit are the reactor pressure vessel containing the fuel assemblies, the steam generators, the main cooling pumps, and the pressurizer. The Gösgen nuclear power plant (KKG), rated at 1020 MW electrical output, for example, has three coolant loops in the primary water circuit (Fig. 2).

The reactor pressure vessel forms the fixed point of the reactor coolant loops whilst the reactor coolant pumps and steam generators are mounted flexibly due to dilatation.

At KKG the pressure vessel contains 177 fuel assemblies. The cross-section of the fuel assembly is a square matrix with 225 positions occupied by 205 fuel rod positions and 20 control rod guide thimbles. The fuel rods contain a stack of fuel pellets enclosed in a zircaloy cladding tube. The fuel pellets consist of sintered uranium dioxide (UO_2) enriched in the fissile isotope ^{235}U or of a blend of uranium dioxide (UO_2) and plutonium dioxide (PuO_2).

A total of 48 control assemblies serve for reactor power control and reactor trip. They consist of an array of rods made of a neutron-absorbing alloy of silver, indium and cadmium, and are moved in the guide thimbles in the fuel assembly structures. While short-term reactivity changes are counteracted by movement of the control assemblies, long-term reactivity changes are compensated by adding boric acid into the coolant.

The three steam generators are designed as vertical natural-circulation inverted U-tube bundle heat exchangers.

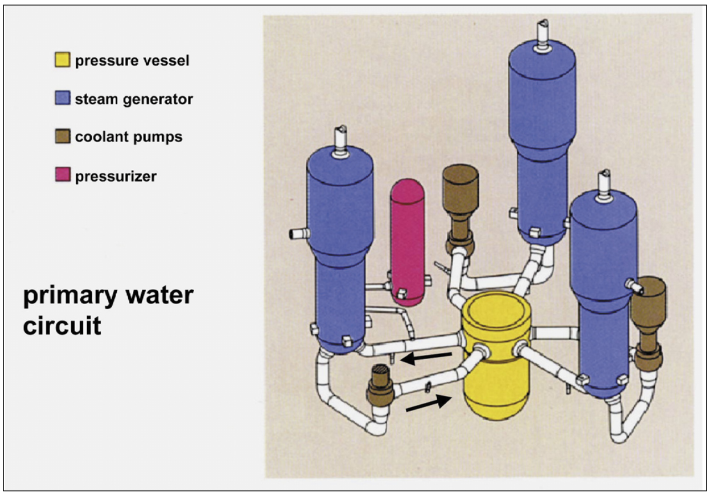

Fig. 2. Primary water circuit at the Gösgen power plant – overview

The reactor coolant pumps are vertical single-stage centrifugal pumps and are driven by an asynchronous motor. The one-piece pump casing is welded into the reactor coolant system piping. The reactor coolant piping interconnects the components of the reactor coolant system.

The pressurizer is a cylindrical vessel partially filled with water. It serves to keep the pressure of the reactor coolant system constant by means of electric heaters and sprays. The pressurizer, which is connected to the reactor coolant system by a surge line, counteracts pressure changes caused by reactor load changes.

While the material of the steam generator tubes is made of Incoloy 800 (an iron-based alloy containing 30–35 weight% of nickel and 19–23 weight% of chromium), the rest of the reactor coolant system is made of carbon steel containing a weld overlay of austenitic stainless steel on the inside surface. At very few points hard metal alloys – like stellites (a cobalt alloy) – are used.

2.2. *Primary Water Chemistry*

As mentioned above, the primary coolant in a PWR is pressurized to ensure that the boiling point remains above the coolant temperature. The coolant reactor inlet temperature in modern power reactors is about 290 °C. This temperature increases to about 325 °C reactor outlet temperature while the coolant is flowing through the reactor core.

The control assemblies serving for short-term reactor power control only have an effect on the neutron flux. They do not influence the primary water chemistry. In contrast, the boric acid added to the coolant to control the long-term reactivity plays a decisive role in water chemistry. At the beginning of a fuel cycle the reactor core has an excess reactivity, which decreases continuously corresponding to the consumption of fissile uranium and plutonium during the cycle. Adding an adequate amount of neutron-absorbing material – such as boron – compensates for the excess reactivity. By neutron capture the isotope ^{10}B absorbs the excess of generated neutrons and is thereby transformed mainly into the isotope ^{11}B without changing the chemical behaviour of the boric acid. During a fuel cycle the initially high boron concentration is decreased in parallel with the decreasing excess reactivity. Thus, the typical PWR primary water chemistry is determined by a variable concentration of boron and boric acid respectively. At the beginning of a fuel cycle the boron concentration is in the order of 1000 to 1500 mg/kg (depending on the fuel cycle length) and decreases during the cycle to only a few mg/kg. The chemical resistance to boric acid has to be taken into account for the choice of the primary water circuit material.

To describe the behaviour of boric acid under primary water conditions, the common formulae H_3BO_3 or $B(OH)_3$ are not sufficient, because boron chemistry is influenced by the occurrence of higher coordinated ions in aqueous solutions (reactions {1} to {4} and Eqns (1) to (8) in Table 1) [6]. From Table 1 one can derive a shift in the chemical equilibrium of the boric acid species while the coolant temperature increases from the reactor inlet to the reactor outlet, respectively decreases from the steam generator inlet to the steam generator outlet. As a result, the chemical environment, especially the pH value, changes within the reactor core and the steam generators. This effect is increased by the pH value dependence of pure water at different temperatures (reaction {5} and Eqns (9) to (10) in Table 2) [7]. For pure water $[H^+] = [OH^-]$ applies. Therefore the pH value as a function of temperature is given by $pH(T) = -½ \log_{10}K_W$. Fig. 3 shows that in the temperature range where modern power reactors are operated (290 to 325 °C), water acidity is nearly at maximum with a considerable gradient as a function of temperature. This has to be taken into account when applying primary water chemistry.

Oxygen often plays a decisive role in corrosion processes – also in PWRs. One of the tasks of water chemistry in the primary water circuit is to ensure the absence of oxygen. On the one hand the intake of oxygen from make-up water (demineralised water added to the whole primary plant to keep the water inventory at a required level) has to be avoided. This is possible by make-up water degassing. On the other hand the production of radiolytically formed oxygen by radiochemical decomposition of water in the radiation field of the reactor core has to be suppressed. By absorption of radiation energy water molecules are decomposed in a primary reaction into $H^{\cdot}$ and $OH^{\cdot}$ radicals. These very reactive radicals can form additional radicals, ions or molecules by secondary reactions (Fig. 4) [5]. All these species may undergo chemical reactions with the primary circuit material resulting in possible material damage. This is avoided by adding a surplus of dissolved hydrogen to the coolant. In order to avoid enhanced fuel cladding material corrosion by accelerated hydrogen pick-up, the hydrogen concentration has to be kept hereby below an upper limit [5]. Under primary water conditions a hydrogen concentration of 2 mg/kg is enough to recombine radiolytically formed oxygen to water [8] without enhancing fuel cladding material corrosion to an unacceptable level. Experience shows that the oxygen concentration can be kept well below 1 μg/kg by this operating mode.

Table 1. Overview of the boron chemistry under primary water conditions.

$B(OH)_3 + OH^-$	$\leftrightarrows$	$B(OH)_4^-$	reaction {1}	
$2\ B(OH)_3 + OH^-$	$\leftrightarrows$	$B_2(OH)_7^-$	reaction {2}	
$3\ B(OH)_3 + OH^-$	$\leftrightarrows$	$B_3(OH)_{10}^-$	reaction {3}	
$4\ B(OH)_3 + 2OH^-$	$\leftrightarrows$	$B_4(OH)_{14}^{2-}$	reaction {4}	
$K_{B1} = [B(OH)_4^-]/([OH^-]*[B(OH)_3])$			Eqn. (1)	
$K_{B2} = [B_2(OH)_7^-]/([OH^-]*[B(OH)_3]^2)$			Eqn. (2)	
$K_{B3} = [B_3(OH)_{10}^-]/([OH^-]*[B(OH)_3]^3)$			Eqn. (3)	
$K_{B4} = \gamma_{B4}^{2}*[B_4(OH)_{14}^{2-}]/([OH^-]^2*[B(OH)_3]^4)$			Eqn. (4)	
γ: activity coefficient				
$\log_{10}K_{B1} = 1573.21/T + 28.6059 + 0.012078*T - 13.2258*\log_{10}T$			Eqn. (5)	T[K]
$\log_{10}K_{B2} = 2756.1/T - 18.996 + 5.835*\log_{10}T$			Eqn. (6)	T[K]
$\log_{10}K_{B3} = 3339.5/T - 8.084 + 1.497*\log_{10}T$			Eqn. (7)	T[K]
$\log_{10}K_{B4} = 12820/T - 134.56 + 42.105*\log_{10}T$			Eqn. (8)	T[K]

Table 2. Dissociation of water.

H_2O	$\leftrightarrows$	$H^+ + OH^-$	reaction {5}	
$K_W = \gamma_W^{2}*[H^+]*[OH^-]$			Eqn. (9)	
$\log_{10}K_W = -14.938 + 0.042*T - 2.103E\text{-}4*T^2 + 6.220E\text{-}7*T^3 - 8.738E\text{-}10*T^4$			Eqn. (10)	T [°C]

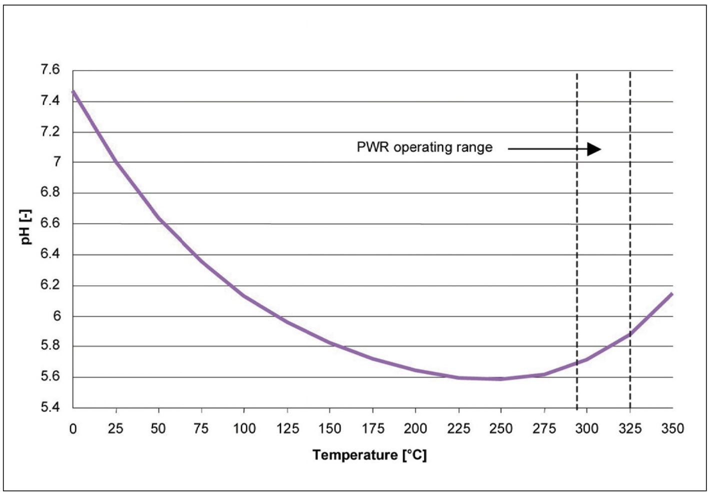

Fig. 3. Temperature-dependent pH value of demineralised water

In the point of view of selective forms of corrosion – intercrystalline stress corrosion cracking for example – the prevention of the intake of impurities into the primary coolant is just as important as the avoid-

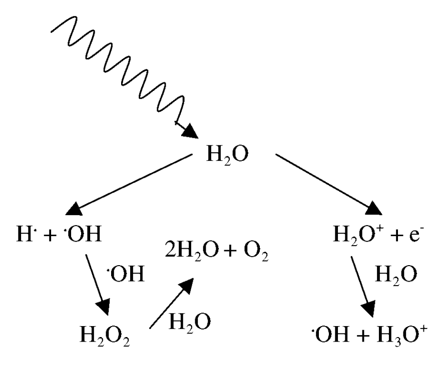

Fig. 4. Radiolytical decomposition of water

ance of oxygen intake. Apart from the absence of oxygen in the make-up water, high standards with regard to ionic and organic impurities are defined [5]. Make-up water conductivities below 0.1 µS/cm are standard in nuclear technology. For the purpose of additional coolant purification a partial flow path purification system containing a mixed bed ion-exchange resin filter is operated continuously. The typical impurity level in the primary coolant is for cationic impurities (*e.g.* corrosion products) as well as for anionic impurities (*e.g.* sulfates and halogens) in the order of less than one to maximum 2 µg/kg.

During operating conditions protecting oxide layers are formed between the coolant and the austenitic weld overlay [9]. The solubilities of the oxide layer species (*e.g.* magnetite or nickel ferrite) depend on temperature as well as on the pH value (Fig. 5 and 6) [9]. For primary water chemistry optimal conditions would predominate when corresponding to the operating temperature the pH value could be adjusted in a way to minimize the solubility of the species of the oxide layers. Fig. 5 shows these conditions in a more or less neutral and slightly alkaline pH range, depending on the species under consideration. In reality the composition of the oxide layers may be different from pure magnetite or nickel ferrite. For the analyzed specific oxide product $Co_{0.05}Ni_{0.5}Fe_{2.45}O_4$ – as one of the possible components – the solubility minimum is at a pH value above 7.7 [5]. Thus and considering all the existing species 'the optimal coolant chemistry' cannot be put into practice.

As shown above, boric acid is one of the decisive chemical compounds in the primary water. Therefore the coolant has to be alkalinized to reduce the acidity and to achieve the required pH range. This is done by adding lithium hydroxide. Lithium, highly enriched in the isotope ^7Li, is used for two reasons. First of all – from a radiological point of view – the unwanted side effect of tritium production according to the reaction $^6Li + n \rightarrow {}^3H + \alpha$ in the neutron field of the reactor core is suppressed. And secondly ^7Li is produced in the neutron field of the reactor core from ^{10}B according to the reaction $^{10}B + n \rightarrow {}^7Li + \alpha$. That means, the coolant is alkalinized by itself.

Because the pH value cannot be measured under operating conditions, it has to be calculated by assuming different lithium concentrations depending on the boron concentration and the temperature. In addition to the chemical equilibriums shown in Table 1 and Table 2, the primary chemistry is defined by the supplementary reaction {6}, the Eqns (11) and (12) and the balances /1/ to /3/ presented in Table 3 [10]. Transforming the Eqns (1) to (4), (9), (11) as well as the balances /1/ to /3/ into a nonlinear equation system of the form $f_i = 0$ ($i = 1 \ldots 9$) and estimating first values for the concentrations of the unknown species ($[H^+]_0$, $[OH^-]_0$, ….., $[B_4(OH)_{14}{}^{2-}]_0$) at a given temperature and at given boron and lithium concentrations, new estimates $[H^+]_1 = [H^+]_0 + \Delta[H^+]_0$, $[OH^-]_1 = [OH^-]_0 + \Delta[OH^-]_0$ *etc.*, can be calculated using the Newton-Raphson algorithm [11]. This algorithm transforms the nonlinear equation system $f_i = 0$ ($i = 1 \ldots 9$) into a linear equation system as shown in Table 4 which can be solved easily. The new estimates are introduced again into the nonlinear equation system $f_i = 0$ ($i = 1 \ldots 9$). This step has to be repeated until a predefined convergence criterion is reached. The calculations show that in the required pH range an optimal lithium concentration should be set to about 0.5 to 3 mg/kg, depending on the existing boron concentration.

Because of possible deposits on the fuel cladding material, followed by an unacceptable reduction of heat transfer, the maximum lithium concentration is limited. For Gösgen this limit is set to 2 mg/kg [5]. That leads to the fact that at the beginning of a fuel cycle (high boron concentration) the chemical regime is not optimal (low pH value). Furthermore the pH value changes – as described above – whilst the coolant flows through the reactor core and shows a temperature increase of about 35 °C. According to the example in Fig. 7, the pH value increases thereby by more than 0.4 units. Reactor inlet and reactor outlet as well as steam generator inlet and steam generator outlet therefore are never exposed to the same chemical conditions. According to

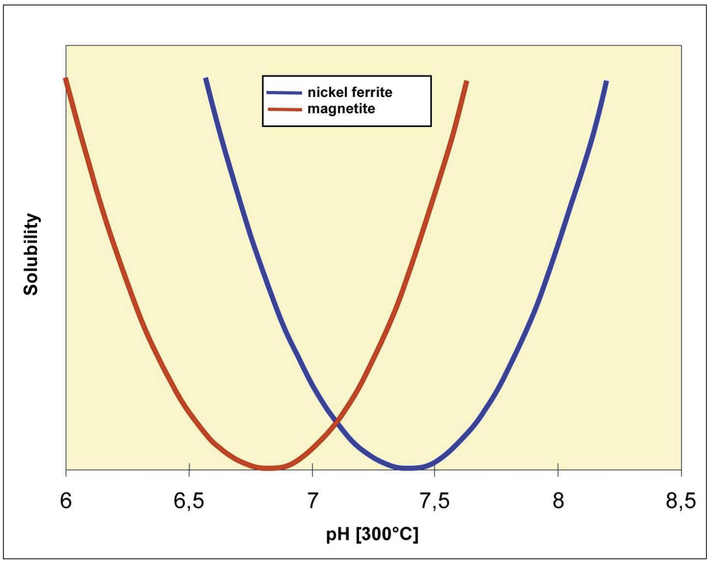

Fig. 5. Qualitative pH-dependent solubility of nickel ferrite and magnetite

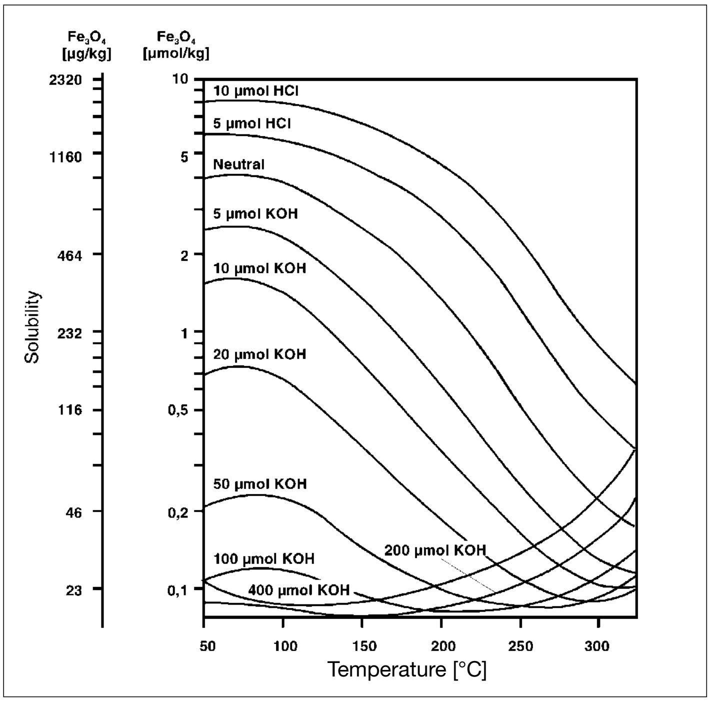

Fig. 6. Temperature-dependent solubility of magnetite in different KOH in HCl solutions

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Table 3. Lithium chemistry, mass and charge balances under primary water conditions

$LiOH \leftrightarrows Li^+ + OH^-$	reaction {6}	
$K_{Li} = \gamma_{Li}{}^2 * [Li^+] * [OH^-] / [LiOH]$	Eqn. (11)	
$\log_{10} K_{Li} = -0.753 - 0.005 * T + 6.746E{-}6 * T^2$	Eqn. (12)	T [°C]
$[H^+] + [Li^+] = [B(OH)_4^-] + [B_2(OH)_7^-] + [B_3(OH)_{10}^-] + 2[B_4(OH)_{14}^{2-}] + [OH^-]$	balance /1/	
$[Li] = [Li^+] + [LiOH]$	balance /2/	
$[B] = [B(OH)_3] + [B(OH)_4^-] + 2[B_2(OH)_7^-] + 3[B_3(OH)_{10}^-] + 4[B_4(OH)_{14}^{2-}]$	balance /3/	

Table 4. Linear equation system for primary water chemistry according to the Newton-Raphson algorithm

$$\Delta[H^+]_0 * \frac{\partial f_i}{\partial [H^+]}([H^+]_0, [OH^-]_0, ..., [B_4(OH)_{14}{}^{2-}]_0) + \Delta[OH^-]_0 * \frac{\partial f_i}{\partial [OH^-]}(....) + ...$$

$$+ \Delta[B_4(OH)_{14}{}^{2-}]_0 * \frac{\partial f_i}{\partial [B_4(OH)_{14}^{2-}]}(....) = -f_i([H^+]_0, [OH^-]_0, ..., [B_4(OH)_{14}{}^{2-}]_0) \qquad i = 1 \ldots 9$$

Fig. 5, corrosion product release, transport, and oxide build up within the primary circuit are inevitable. From a chemical point of view this is not significant as long as heat transfer does not become the limiting factor in power generation. As soon as radiation protection aspects also have to be considered, these release, transport and oxide build up processes become relevant. If the corrosion products contain material that can be easily activated in the neutron field – like cobalt for example according to the reaction $^{59}Co + n \rightarrow {}^{60}Co \rightarrow {}^{60}Ni + \beta + 2\gamma$ – the resulting activity is spread across the primary circuit by the same mechanism. Integrated in spinels like $Co_yFe_{3-y}O_4$ or $Ni_xCo_yFe_{3-(x+y)}O_4$ cobalt is incorporated into the oxide layers of the primary system and contributes significantly to the radiation exposure of the power plant staff.

Despite of the fact that the primary coolant chemistry cannot be adjusted to an optimum in view of all the influencing factors, operating experience shows good results in the long-term stability of the primary circuit material. The material combination used at the Gösgen power plant for example (Incoloy 800, austenitic stainless steel) allows, from today's viewpoint, safe operation for at least 60 years.

Also in the field of fuel cladding material, a stage of development was realized in recent years to meet today's significantly increased demands on fuel burnup and neutron economy [12]. In contrast to earlier years, fuel cladding corrosion is no longer a limiting factor.

Future as well as recent developments in the primary coolant chemistry therefore are less focused on the corrosion resistance of used materials. They clearly tend towards optimization of the corrosion product transport and the dose rate build up to reduce the existing radiation fields or to improve operational procedures and emergency preparedness. For example, enriching boron in the isotope ^{10}B (natural boron contains only 20 atom% ^{10}B) enables the enhancement of plant shutdown safety margins and therefore the introduction of higher enriched fuel with lower specific costs. As a positive side effect the total boron concentration can be lowered during power operation, which helps to adjust the chemistry closer to the optimum [13][14]. As another example, which is derived from BWR chemistry, a recent research program has also shown the feasibility of zinc addition to the primary coolant of PWRs, resulting in a noticeable reduction of the existing radiation fields. A couple of power plants – including Gösgen – have actually introduced this new technique to optimize their radiation protection programs [15–20].

The Zn^{2+} ion has more or less the same radius as the Co^{2+} ion, but a much stronger thermodynamic binding energy within the oxide layers. In the presence of zinc therefore, the number of lattice host positions for cobalt as well as the number of lattice vacancies are reduced. In consequence the ion transport from the ground material into the coolant is also reduced. Therefore, the release rate of corrosion products that can be activated in the neutron field decreases as well as the intake of activated material (*e.g.* ^{60}Co) into the oxide layers (Fig. 8 and 9) [21][22].

Very small concentrations of zinc (*e.g.* about 5 µg/kg in the coolant) are needed to achieve a dose rate reduction in the range of 30–50% within a couple of years if zinc depleted in ^{64}Zn is used. The depletion of zinc is necessary to avoid activation of zinc in the neutron field of the reactor core resulting in high ^{65}Zn (a β and γ emitter) activity concentration. At such a low zinc concen-

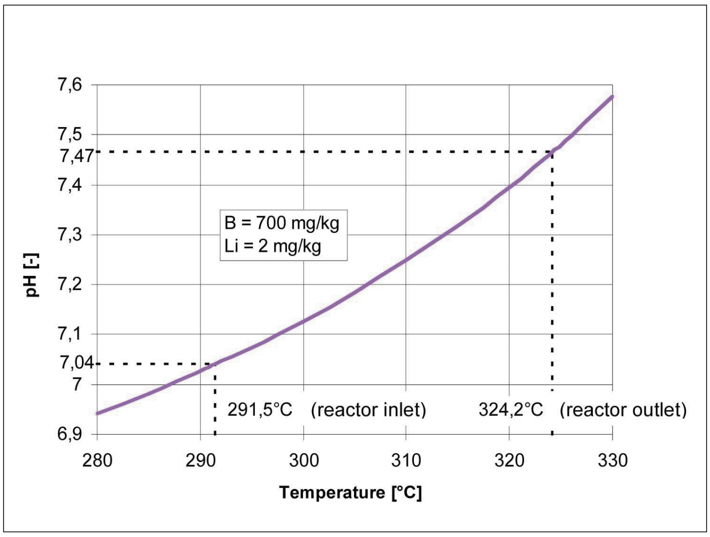

Fig. 7. Example of a typical primary coolant pH curve of a PWR

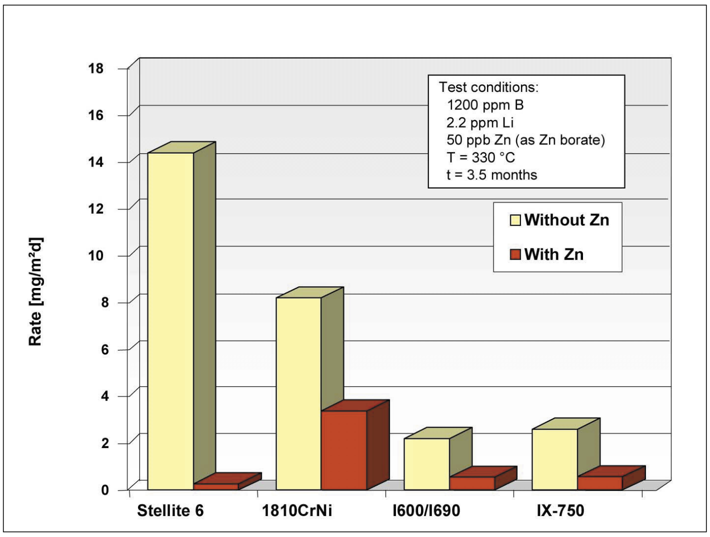

Fig. 8. Corrosion rates of different alloys with and without zinc addition

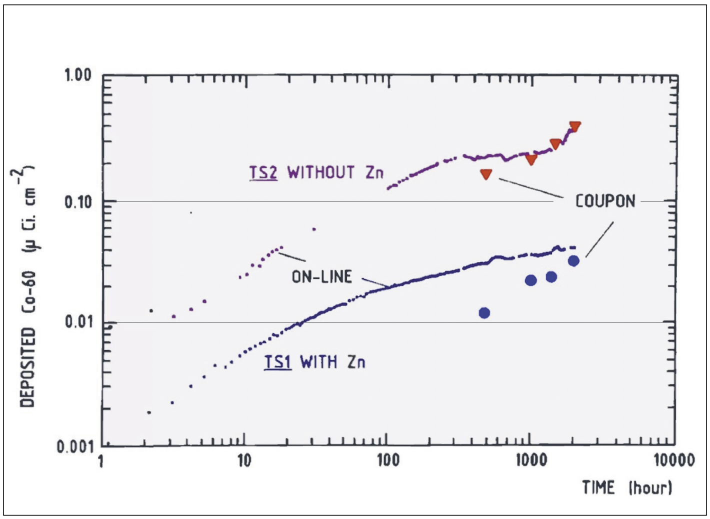

Fig. 9. Activity build up on test sample surfaces with and without zinc addition. Copyright 1990, re-printed with permission of Electric Power Research Institute, Inc. All rights reserved.

tration, chemical consequences – *e.g.* any form of corrosion – can be neglected.

2.3. *Chemical and Radiochemical Monitoring*

An important operational aspect is to ensure compliance with the defined chemical parameters. To this end the essential parameters (like boron, lithium, hydrogen, impurities (Cl^-, SO_4^{2-}, *etc.*)) are monitored regularly. Changes in the primary coolant – like the intake of impurities for example – are detected very quickly so that appropriate countermeasures can be taken within reasonable time.

In addition to the chemical monitoring, radiochemical monitoring enables the observations of trends concerning the transport of activated corrosion products with the prospect of the optimization of radiation field build up. It enables also to judge the condition of the fuel assemblies during power operation. Normally the fission products are enclosed in the fuel rods. If one of the rod cladding tubes ruptures, a fraction of the volatile and soluble parts of the fission products are released into the primary coolant. This results in a change in the ratio of long-lived and short-lived radioisotopes of noble gases (^{133}Xe and ^{135}Xe for example according to Fig. 10). A broken fuel rod is not a safety problem, nevertheless the knowledge of such a defect is very helpful for scheduling refueling outages, because in most cases maintenance work and radiation protection measures have to be adapted. Sometimes some additional work is necessary.

3. Water-Steam Cycle

3.1. *Overview*

The main components of the water-steam cycle are the steam generators, several heat exchangers, the turbine, the condenser, and the feed water tank (Fig. 1).

Heat from the reactor is transferred to the water-steam cycle in the steam generators. From there at the Gösgen power plant, for example, the produced main steam flows to the turbine building through three parallel pipes at a pressure of about 65 bars and a temperature of about 290 °C. In the turbine building, the three main steam lines are subdivided into four trains and connected to the double-flow high-pressure section of the turbine-generator unit. The exhaust steam from the high-pressure turbine is dried and superheated as it flows through the two combined moisture separator reheaters standing on either side of the high-pressure turbine to reduce the final moisture at the inlet of the low-pressure turbines. Each of the three low-pressure turbines has its own condenser arranged underneath. The turbine exhaust steam is condensed at a temperature of about 45 °C and at a pressure of about 0.1 bars. The condensing heat, which cannot be utilized any further is discharged to the atmosphere *via* the cooling water system. The condensed water is supplied by the main condensate pumps through the low-pressure preheating plant into the feed water tank. The main feed water pumps convey the feed water through the high-pressure preheating plant back to the steam generators.

3.2. *Water-Steam Cycle Chemistry*

The complete separation of the water-steam cycle from the primary water circuit in PWRs means that all the tasks can be dropped that arise from the interaction of gamma and neutron radiation with the coolant and the substances in it. However, the existence of the two phases, water and steam, leads to new terms of references. The chemical conditioning has to be chosen in a way to protect the system against the different forms of corrosion in both phases. At best such a task is met by using a single chemical agent. Among the given conditions (temperature and pressure) this agent has to be water-soluble on the one hand and should have volatile properties on the other hand to be transportable in the steam. In many power plants – including Gösgen – water treatment is done by hydrazine. This enables the three main tasks in the water-steam cycle to be fulfilled. First of all, hydrazine binds oxygen, which is taken in from the main condensate or the make-up water according to the reaction $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$. Secondly, hydrazine forms ammonia – as the main alkalinization contributor – by thermal decomposition at temperatures above 150 °C according to the reaction $3N_2H_4 \rightarrow N_2 + 4NH_3$. And thirdly, hydrazine already promotes the formation of protective magnetite layers at temperatures below 200 °C.

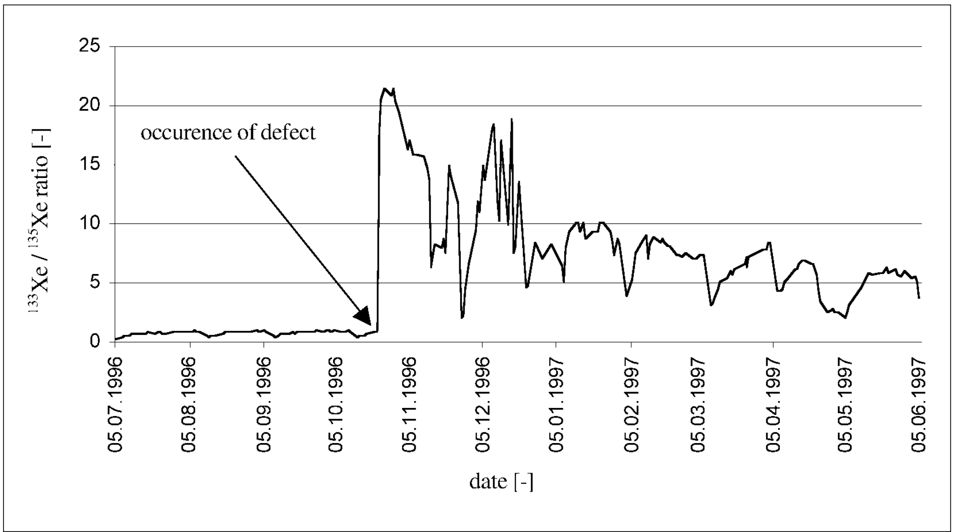

Fig. 10. Example for the detection of a fuel rod defect using the ^{133}Xe/^{135}Xe ratio

The hydrazine chemistry enables the pH value to be maintained above 9.8 in the feed water and even above 9.5 in the steam generator water. Therefore the components of the water-steam cycle can be made from low-alloy steels without suffering material losses by erosion-corrosion (Fig. 11) [5]. In order to avoid drop impact erosion, the condenser tubing however is made out of stainless steel or titanium. Only the inevitable absence of good heat conducting copper alloys due to the lack of chemical resistance to ammonia and the toxicity may be seen as a disadvantage of the hydrazine chemistry. The concentration range of hydrazine in the water-steam cycle is very low at about 30–70 µg/kg, which eases the toxicity aspect.

Like in the primary water circuit the absence of impurities is an essential requirement in the water-steam cycle. Local corrosive conditions may occur in the steam generators, if by an intake coming from a condenser leakage, impurities (*e.g.* Na^+, Cl^-, SO_4^{2-}) reach concentrations up to saturation in transition zones between stagnant steam bubbles and the steam generator water. Stagnant steam bubbles exist in certain parts of the steam generators, *e.g.* on deposits of corrosion products. Beside avoiding impurity intakes an accumulation of corrosion product deposits has to be kept at a low level in the steam generators. This is done by operating the chemistry within the predefined regime and by removing existing deposits mechanically during refueling outages.

3.3. *Chemical Monitoring*

During power operation the chemical monitoring is focused on the condensers and the steam generators. Online conductivity and oxygen measurements are supported by measurements of ionic impurities on a regularly basis. Impurities concentrate in the steam generator water and are therefore more easily detectable. This way small leakages in the condensers in the range of about 0.1 kg per hour can be detected using mass balances within the water-steam cycle. No immediate measures have to be taken in the case of such small leakages because the impurity concentration does not exceed a few µg/kg in the steam generator water. But they allow plant operators to plan and realize the necessary countermeasures carefully. In this sense, the sensitive chemical analyses are an important contributor to a safe and careful plant operation.

4. Cooling Water System

4.1. *Overview*

At the Gösgen power plant, a circulating water system with a cooling tower reduces the heat flowing into the river Aare. The system transfers almost 2000 MW of heat. The circulating water flows from the cooling tower basin to two pumps, which deliver it through the turbine condensers back to the cooling tower. The tower is a natural draught wet-type with a reinforced concrete shell.

4.2. *Cooling Water System Chemistry*

The cooling water system is open to the atmosphere. Water losses by continuous evaporation have to be replaced by adding river water. Therefore the initial chemical parameters of the cooling water are variable as decreed by nature, but can be adjusted as far as possible by an upstream water treatment plant. This is not possible for airside pollution particles, which are washed out into the water phase without exception.

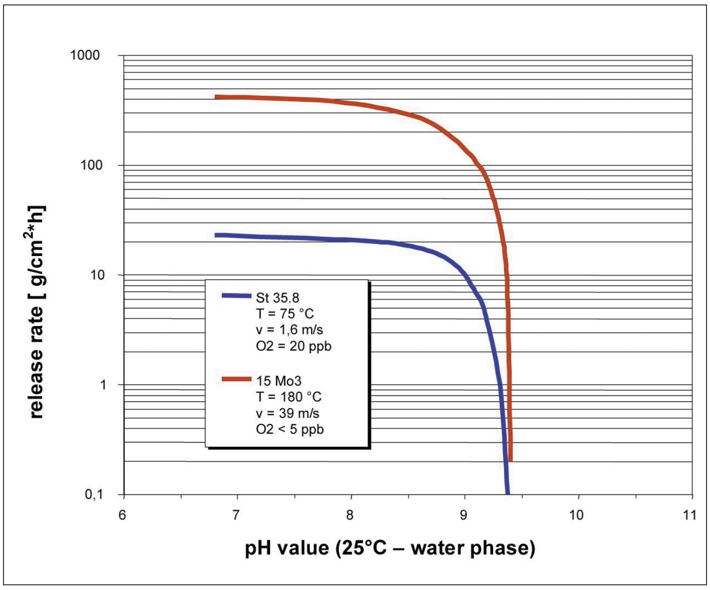

Fig. 11. pH-Dependent erosion-corrosion of two examples of low-alloy steels

In spite of these less than optimal conditions, the cooling water system has the important task of transferring the power plant waste heat to the environment. This works most efficiently with heat-transfer surfaces free of deposits. The presence of deposit-forming substances – in particular lime, microorganisms, and slime-forming bacteria – has to be limited by an adequate chemical conditioning, taking into account the chemical compatibility of the system compounds. In addition one has to consider the concentration process of the water contents due to the continuous water evaporation, which makes a partial system water blow down into the river necessary. Therefore, compliance with regulatory aspects in water pollution control is indispensable. Thus, the operation of the upstream water treatment plant has to take place within clearly defined limits together with an adequate monitoring.

Essentially, it is necessary to precipitate calcium and magnesium and to remove the suspended matter from the river water. By adding a soluble iron salt, iron hydroxide precipitates in the alkaline medium of the water treatment plant according to the reaction $2FeClSO_4 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 + 2CaSO_4 + CaCl_2 + 6CO_2$. The suspended matter absorbs on the iron hydroxide flakes and is removed by sedimentation. Lime milk is used as a precipitant so that soluble calcium and magnesium hydrogen carbonates are converted and precipitated as insoluble carbonates according to the reactions $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ and $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$ respectively.

To increase the sedimentation rate of the precipitated lime flakes a flocculant (a high-molecular acrylamide copolymer) is added to enlarge the flakes. Sulfuric acid is added at the outlet of the water treatment plant to adjust the pH value to the regulatory aspects in water pollution control and to protect the cooling water system components from corrosion. To keep the residual hardness of the cooling water in solution, a stabilizer (a polycarboxylic acid) is added. The temperature of the cooling water varies – depending on the season – between 20 and 35 °C at the condenser inlet or 35 and 50 °C at the condenser outlet respectively. These are ideal conditions for biological growth. A biocide treatment is usually necessary. For reasons of environmental care at Gösgen a non-chlorine, hydrogen peroxide based biocide is used [23].

For a 1000 MW power plant – like Gösgen – about 20 billion litres of water have to be treated each year. This means that a considerable amount of chemicals is necessary. At Gösgen, for example, 1700 tons of iron chloride sulfate (13%), 8000 tons of lime milk (35%), 1000 tons of lime powder, 20 tons of flocculant, 20 tons of stabilizer, 200 tons of sulfuric acid and 20 tons of biocide are used. 12 000 tons of lime sludge are discharged from the water treatment plant as a waste product. About 4 billion litres of water are released back into the river *via* the partial system water blow down. There is no measurable temperature increase of the river water due to the water release, because heat carried off by the cooling water system is released into the atmosphere. There is only a minor increase of the chloride and sulfate content in the river water due to the water release. On the average the chloride and sulfate concentrations in the river water increase by about 0.02 mg/kg and 0.12 mg/kg respectively. This has to be compared with the existing river water concentrations of 5 to 15 mg/kg for chloride and 15 to 30 mg/kg for sulfates.

In terms of a careful treatment of resources, of environmental care, and of economical optimization, the operators of the Gösgen power plant have created synergies for chemical procurement and waste disposal with other industries. Lime milk, for example, is a waste product coming from acetylene factories and is reused in the Gösgen water treatment plant. On the other hand lime sludge from the water treatment plant can be reused as a raw material in cement factories or as an additive in agriculture. And last but not least the fact that 750 billion cubic meters of air are cleaned and washed out in the cooling tower should not be underestimated from the point of view of environmental care.

5. Radioactive Waste Conditioning

In a nuclear power plant the routinely treated radioactive operational waste can be separated into three main waste streams.

- Liquid waste
- Ion exchange resins
- Incinerable and solid non incinerable waste

Hereafter the treatment processes of the waste streams are outlined. Thereby, one has to take into account the Swiss requirements for the planned final repository which demand an immobilization of the waste. That can be done either by concrete, bitumen, or an equivalent matrix.

5.1. *Liquid Waste*

Waste water produced in the controlled area of a nuclear power plant has to be considered as potentially radiologically contaminated. The release into the environment has to be accompanied by release measurements and if necessary by treatment steps. Typical for a PWR is that liquid waste sometimes contains boron with a limited solubility. The various sources of liquid waste consist of:

- Water from building sumps containing drains of intermediate cooling systems
- Water from laboratories
- Decontamination solutions
- Laundry water
- Water from the regeneration of the secondary side steam generator blow down purification system

The treatment of this waste water is normally done by dividing it into three sub streams:

- Waste water containing potentially no activity
- Laundry waste water
- Boron-containing waste water

At Gösgen, for example, an average of about 8000 m^3 of waste water arises each year in the controlled area. The biggest part (60%) has its origin in the secondary side steam generator blow down purification system. Up to now Gösgen has never experienced a severe steam generator leakage so that this part of waste water contains no radioactivity and can be released after chemical treatment (in general pH adjustment by adding sulfuric acid or sodium hydroxide) for reasons of river water protection. About 1200 m^3 of waste water contains boron and some 2000 m^3 is laundry waste water. The waste water is treated by evaporation. During evaporation the boric acid, the radioactivity, and the impurities (soluble and insoluble ones) are retained and concentrated in the evaporator sump. Therefore, it is very important to keep the chemical regime at a point where the solubility of the solution contents and especially of the boric acid is optimal. According to Fig. 12 [5], this is the case at a pH value of about 7. In addition, a small amount of EDTA solution is added to the sump to keep the impurities in solution. The evaporated water is collected in discharge tanks. After a radioactivity check and – if necessary – adjustment of the pH value, the purified water is released from the discharge tanks into the environment.

The amount of waste water concentrate is small (6 m^3 per year of boron-containing waste water concentrate, 7 m^3 per year of laundry waste water concentrate and 1 m^3 per year of decontamination solutions). A continuous treatment of these concentrates is not necessary. Usually every second year the concentrates are treated in a campaign. The concentrates are fed into a bitumen extruder through a feed pump. The contained water is evaporated in the extruder and the remaining solid particles are physically mixed with bitumen. After condensation the evaporated water is transferred back to the waste water treatment system. At the extruder outlet 200-liter drums are filled with the waste-bitumen mixture.

Treating waste water by evaporators and embedding the residual waste in bitumen is quite a satisfactory process. It leads to low amounts of activity discharges and, as long as the steam generators are tight, to a low amount of waste. Within 26 years of operation in Gösgen only 850 drums (or 170 m^3) containing bituminized waste water concentrates have been generated.

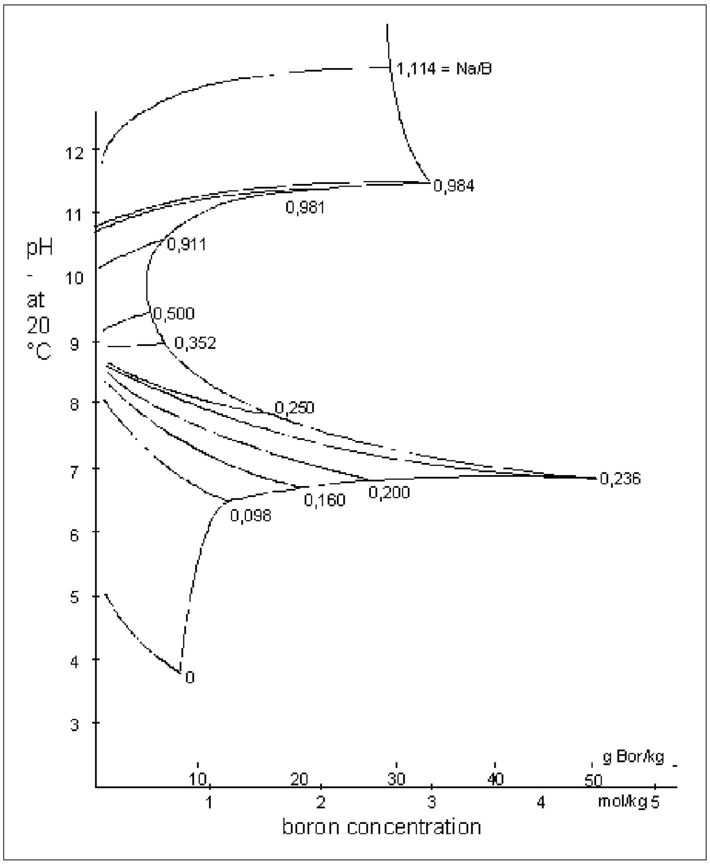

Fig. 12. Solubility of boron in waste water

5.2. *Ion Exchange Resins*

In PWRs ion exchange resins are used in mixed bed filters within systems like primary coolant purification, primary coolant storage and recovery, and spent fuel pool water purification. The resin consumption in the primary systems of PWRs is small compared to other types of nuclear power plants. At Gösgen, for example, the consumption averages 1.3 m^3 per year. On the other hand, the radioactivity concentration in the resins can be orders of magnitude higher than in waste water concentrates. This results in high dose rate waste drums with a need for an adequate handling. Therefore resin management is an important task, which starts with application engineering and application optimization.

The treatment of ion exchange resins is quite simple compared to liquid waste treatment. In a first step used resins are transferred to the waste resin storage tanks for intermediate storage. After homogenization of the tank content by blowing in nitrogen, samples can be taken for a radiological waste characterization. Batches of about 450 litres of wet resins are then transferred to the drying device of the treatment system. Drying takes place by blowing hot air (80 °C) through the resins in a closed circuit. The air condensate as well as the water from the integrated scrubber can be treated in the waste water treatment system. After completion of the drying process a cellular wheel sluice transfers the resins to the bitumen extruder where the waste is mixed with bitumen. The temperature level inside the extruder is lowered compared to the waste water treatment because water has been removed in the drying device and anion exchange resins tend to decomposition at temperatures above 150 °C. At the extruder outlet the waste is filled into 200-liter drums – analogous to bituminized concentrates.

Thanks to the efficient resin management, only 300 drums (or 60 m^3) of bituminized resins have been produced in 26 years of operation in Gösgen. In contrast to the waste water treatment the chemistry does not play an important role for the treatment of waste resins.

5.3. *Incinerable and Solid Nonincinerable Waste*

Beside liquid waste and ion exchange resins various operational waste arises with different chemical and physical properties. Nevertheless all this waste can be considered as a single waste stream, because the majority of this waste arises from maintenance work, has a similar nuclide spectrum and possesses, with a few exceptions, a low specific radioactivity level. Transportation to an external treatment facility is possible without exceptional efforts (like shielding for example). The treatment of such waste streams has been centralized therefore in Switzerland at the ZWILAG. After treatment in a plasma arc furnace [24] the waste is packed into 200-liter drums for intermediate storage. Also this waste stream is not influenced by chemical factors.

6. Conclusions

Demands for chemistry in the different systems of a PWR are multi-layered. In general the coordination between the chemical regime and the materials used is established nowadays in a way that hardly ever a component has to be exchanged due to excessive corrosion. Therefore, no basic changes in the chemical regime of the power plants have to be expected in future. However, selective optimizations in the field of radioactivity build up and local corrosion process control are still possible and partially in the stage of implementation.

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