LCC8 SPECIAL TOPIC REPORT

PWR/VVER Primary Side Coolant Chemistry

Volume II – Water Chemistry Tool to Mitigate the Concerns
PWR/VVER Primary Side
Coolant Chemistry

Volume II
Water Chemistry Tool to Mitigate the Concerns

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Nomenclature

Unit conversion
1 Introduction (Suat Odar)

This Special Topic Report (STR) “PWR and VVER Primary Side Coolant Chemistry” consists of two Volumes. Volume I “Technical Basis and Recent Discussions” was issued in 2012 for the LCC7 program. It mainly covers the information regarding the design and materials of the Reactor Coolant System (RCS), the formation of the protective oxide layers and of the crud and finally the recent discussions with respect to improve the coolant chemistry that is still on-going since several years worldwide in the PWR industry.

This Volume II “Water Chemistry Tool to mitigate the Concerns” is issued in 2013 for the LCC8 program, as continuation of the Volume I and covers the following items:

- The worldwide chronology of the coolant chemistry is explained in Section 2,
- Section 3 explains the basics of the coolant chemistry including the historical data produced in 1960s and 1970s that serves as a basis for the water Chemistry Guideline data.
- Crud in the coolant is the main reason for the problems of the PWR performance, such like fuel clad corrosion and radiation field build-up. The influence of crud on these degradations is explained in Section 4.
- Section 5 covers the information regarding the Coolant Chemistry Guidelines for PWR and VVER plants worldwide.
- In Section 6, the future tendency of the coolant water chemistry programs for PWR and VVER plants is explained.
- In Section 7, the ANT International recommendations for the plant specific application of the coolant chemistry strategies are discussed and the basis for these recommendations is given.
- Section 8 explains the benefits of Enriched Boric Acid (EBA) and summarizes the worldwide unique experience gained in Siemens designed PWR plants with its application.
- The purification systems designed in PWR and VVER plants are explained in Section 9.
- Chemical injection systems used in PWR and VVER plants are described in Section 10.
- Coolant monitoring concept is described in Section 11 including the discussions if isokinetic sampling is needed.
- Finally, Section 12 summarizes and concludes the information given in the Volume II of this STR “PWR and VVER Coolant Chemistry”.

2 Chronology of coolant chemistry (Rolf Riess)

2.1 PWR plants

In Volume I of this STR [Riess et al, 2011], the Section 2 contains some background information regarding coolant chemistry chronology. In the present section more detailed information shall be provided on the captioned subject. When reviewing the developments on coolant chemistry it becomes obvious that the most development steps were performed in the United States. Therefore, the efforts in this country are used as a reference.

The first step was taken in 1943 by selecting water as coolant for large-scale reactors. Such large-scale reactors could be an open cycle system (Boiling Water Reactor - BWR) or closed cycle system (Pressurized Water Reactors – PWR). The first test facility for PWR went in operation 1944. At this time it became apparent that the selection of water is not enough to solve some engineering problems that arose in the operation of these test facilities. The evaluation of literature data and operational test data are the start of reactor water coolant chemistry. By the group of scientists and engineers the key requirements were fixed. This list contains the following items:

- Avoid the radiolytic decomposition of reactor coolant (suppression of water radiolysis),
- Avoid or minimize the crud deposition on fuel rods,
- Maintain the fuel integrity without jeopardizing its compatibility,
- Protect the integrity of RCS material by maintaining the corrosion compatibility of the structural material,
- Control the radiation field at low levels.

Such issues representing negative aspects of H₂O as coolant were compensated by positive aspects, which mainly consist of the possibility to use aqueous solutions and allow some improvements in the design of the plant. In summary, the principles developed in this early phase of reactor development were applied for the design and construction of commercial reactors and the conclusion was that the closed cycle systems had to be operated under slightly alkaline and reducing condition.

An example for solving engineering problems is related to reactivity control. The reactivity varies as a function of temperature and power level. Since the control access of reactivity is necessary, the idea of a variety concentration of dissolved neutron poison became effective. The advantages of the use of dissolved poison are the following:

- The number of control rods can be reduced,
- A better power distribution can be achieved.

The earliest considerations on dissolved nuclear poisons were performed by [Breden & Abers, 1953], and [Breden et al, 1955]. They carried out their work in the time frame from 1949 to 1954 at the Argon National Laboratory in the U.S. This was followed by the work of [Shapiro et al, 1953], working in the Bettis Atomic Power Laboratory from 1953 to 1955. The work cited was dealing with a systematic review of employing poisons, evaluation of potential poison materials and preliminary testing of specific poisons under the proposed conditions. The list of potential candidates for nuclear poison materials was the following: boron, cadmium, gadolinium, samarium, and europium. Except for boron, due to their solubility the other candidates could only be handled as solutions with a pH of about 2, which means under strong acid conditions. This means only boron as boric acid, could meet the selection criteria. More details can be taken from Section 3.2.
For unknown reasons, the further investigation of this issue was delayed till 1960. At this time Westinghouse adopted the further development of the pressurized water reactor technology including the development of coolant specifications. This required a thorough investigation of boric acid solutions and the use of lithium hydroxide as a pH control agent. The reducing conditions were established by injecting hydrogen into the system. A precondition for doing this work was the detailed knowledge of the properties of water, see Section 3.1. So the early Westinghouse specifications contained boric acid, lithium and hydrogen as explained above. In addition chloride and sulphate were specified to avoid stress corrosion cracking of the reactor coolant system materials as well as Ca, Mg and Al, which were found in hard fuel deposits.

In the second half of the 1960s one important project was published dealing with the solubility of magnetite by [Sweeton & Baes, 1970]. This work demonstrated that under the foreseen chemistry conditions of PWR a regular solubility of magnetite can be achieved, thus preventing the formation of magnetite deposits on the fuel.

Historically, the starting point for all discussions about the correct pH in PWR Primary Coolant can be found in P. Cohen’s book “Water Coolant Technology of Power Reactors”, 1969, and especially in the chapter “The Physical Chemistry of Water and Aqueous Solutions”. The central point in this document is the work of [Sweeton et al, 1968], who have reported measurements of the solubility of Fe from Fe$_3$O$_4$ and they wrote the general dissolution reaction as:

$$\frac{1}{3} \text{Fe}_3\text{O}_4 (s) + (2-b)\text{H}^+ + \frac{1}{3} \text{H}_2(g) = \text{Fe(OH)}^{(2-b)+} + \frac{4}{3} - b)\text{H}_2\text{O}$$

This equation is valid for the temperature range of interest and applicable to dilute acidic and basic solutions. It also became clear that isotopically pure Lithium-7-hydroxide should be the most suitable pH control agent to be used in the PWR Primary Coolant. A major argument for this consideration is the fact that Li-7 is produced by the B-10(n,α)Li-7 in the PWR core and thus the handling of the pH control chemical becomes easy. The use of Li-7 isotope enriched to 99.9% instead of natural Li, containing 7.42% of Li-6 and 92.58% of Li-7, is based on the fact that Li-6 is producing undesirable tritium according to the reaction Li-6(n,α)T.

The result of Sweeton’s work can be seen in Figure 2-1.
These data suggested that under the conditions of a PWR Primary System, the optimum pH should be pH 6.9 at 300°C. At these conditions, iron solubility from magnetite is at a minimum and thus the transport of iron-based crud should also be a minimum. Furthermore, 2 mg/kg (ppm) of Lithium were sufficient to achieve a pH of 6.9 at BOC (=900 ppm B for a one year of annual cycle). These 2 ppm Lithium were also considered to be low enough to avoid any corrosion attack on the fuel cladding.

An important event for the licensees of Westinghouse was a seminar at Ermenonville, France, 1972, where the status of Coolant chemistry in the US was explained and discussed.

The basic message was that the coolant should stay in an alkaline and reducing condition. The only prerequisite has been to keep the lithium concentration below 2.2 ppm and hydrogen concentration in the range between 2 and 4 ppm. At that time there were no discussions about constant pH or lithium target values depending on the boron content.

However, later on it was recognized, that the contribution of Nickel is much more important to the primary side corrosion product inventory than the iron. Further on, it was found that Nickel ferrite is a major constituent. Consequently the solubility behaviour of Nickel ferrite was investigated and it was found that a pH of 7.4 should be the solubility minimum. However, a pH of 7.4 could not be adjusted at BOC since 2 or 2.2 ppm Lithium was the upper specified limit in order to prevent Lithium induced corrosion of the fuel element cladding. As a consequence, the first two thirds of a cycle, the 2 ppm were kept constant till reaching the pH of 7.4 and then Lithium/Boron ratio was adjusted to stay at 7.4 till end of the cycle.
In order to discuss this transition of the last 35 years it may also be useful to look in parallel to the current Lithium specifications as they are applied in various countries, see Table 2-1. A second question is whether these data are describing the development in the relevant time period.

Table 2-1: Lithium specifications as they are valid in various countries.

<table>
<thead>
<tr>
<th>Country</th>
<th>Lithium Specification in mg/kg (ppm)</th>
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<tr>
<td>Germany</td>
<td>0.1-2.1</td>
</tr>
<tr>
<td>Japan</td>
<td>0.2-2.2</td>
</tr>
<tr>
<td>France</td>
<td>0.4-2.2</td>
</tr>
<tr>
<td>USA</td>
<td>-- (plant specific programs)</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>&lt;0.35 mmol/l Σ K, Li, Na</td>
</tr>
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At a first glance there seem to be little or no changes in the Lithium specification compared to the early days of commercial PWR operation. Also between the different countries negligible differences do exist, except USA, where plant specific specifications have to be applied and where new B/Li-strategies were developed. However, in the specified values of the various other countries, plant specific values are recommended.

To say it in other words: The specified Lithium values are not very helpful to develop consistent worldwide Lithium strategies. It is much more important to look after the Lithium/Boron ratio because changes in the Li/B control were experienced by the industry, especially in the US, establishing specific modes of operation (see also Section 5 of this STR report).

To explain these changes, it is convenient to use the information shown in Figure 2-2. This figure shows, as a first more precise interpretation, the relation between Lithium and Boron in the coolant. This relation is handled in such a way, that the pH at temperature is 6.9, which is called coordinated Lithium/Boron chemistry. It means that the pH₇ is constant over the entire cycle. It is possible for annual cycles of 12 months.

A second approach is the modified Lithium/Boron chemistry, where at the BOC of annual cycles, a concentration of 2–2.2 ppm Li is used and kept constant till reaching a desired pH₃₀°C of e.g. 7.4. Then the pH 7.4 line is followed by the appropriate Li/B-coordination (see Figure 2-2 lower part and Boron values <1000 ppm).

In case of extended fuel cycles, the Lithium concentration at BOC can be higher, e.g. in order not to fall below a pH₇ of 6.9 at 300°C. The chemistry will be operated in a coordinated mode of 6.9 till reaching a Lithium level of 2.2 ppm and will then follow the above description.

The third alternative is to operate with an elevated Lithium/Boron Chemistry where a level of 3.5 ppm Li is used at BOC till reaching a pH₃₀°C of e.g. 7.1. At this pH the Li/B coordination is adjusted to stay at pH 7.1 till the end of the cycle.

The fourth alternative is the constant elevated Lithium-Boron Chemistry where at the BOC a high Li-level of e.g. 5 ppm is adjusted and during the cycle a Li/B-coordination keeps the pH constant throughout the cycle. This case is identical with the first one except that the pH₇ is adjusted at a higher level.

This section is already discussed in great detail in Volume I Section 3.3.1.3.
During all optimisations (new mode) of the PWR primary coolant specifications, a permanent conflict existed between increasing the pH e.g. due to radiation field consideration or prevention of crud accumulation on fuel assemblies and the fear of Zircaloy corrosion caused by Lithium due to a concentration mechanism, see Figure 2-3.
The desire to increase the Lithium-concentration to be applied to the primary coolant requires higher target concentrations as already reported by [Riess & Millett, 1994]. Such modifications however, implied the risk of Zircaloy corrosion. Despite these risks, the modified and elevated Lithium/Boron chemistry were recommended specifically in many US PWRs. But still the radiation field problems and Axial Offset Anomaly, AOA, in plants with high duty cores stimulated to go to even higher Li-concentrations.

The Lithium specification as shown in Table 2-1 on one side and the Lithium/Boron concentration modes on the other hand need some discussion, more country specific. For example, the time frame for chemistry changes in the US is shown in Figure 2-4 [Turnage, 2004].
Regarding the application of all the Li/B-chemistries in non-US operating PWRs there are some differences applied in the various regions and countries. Such variations depend also on the dates of the application. In the early 1970s, worldwide the Lithium concentration was operated between upper and lower specified values. The first step to the coordinated chemistry was made in the late 70s/early 80s in order to reduce crud deposition on fuel rods and to minimize radiation fields. The selected $pH_f$ was 6.9, which was also consistent with the $pH_f$ for iron solubility minimum of magnetite under PWR primary side conditions.

In the mid 1980s, many PWRs introduced the modified chemistry based on operational experience because at this time high and constant Lithium as a $pH$ strategy produced better result than the coordinated chemistry, as far as crud deposition and radiation fields are concerned.

The German PWRs are still operating today with this type of chemistry and therefore the specification, given by AREVA GmbH and VGB respectively, have an upper Lithium limit of 2.1 mg/kg. Only in very specific cases, utilities can apply Lithium values higher than 2.1 with the consent of the fuel manufacturer.

In the second half of the 1980s in Ringhals (Sweden), an elevated Lithium strategy program with an initial concentration of 3.5 ppm was tested; however, this project was stopped due to concerns for corrosion of Inconel 600 steam generator tubing and Zircaloy-4 cladding corrosion. Despite this kind of “Warning”, several US PWRs increased the cycle length and thereby the Boron concentration at BOC to values of ≈1.500 ppm B. According to the general understanding a $pH_{300^\circ C}>6.9$ can only be maintained when higher Lithium concentrations are allowed. This became operational practice by starting the cycle operation e.g. with 3.5 ppm Lithium, which means an elevated chemistry as described above.

The developments in the last 10-15 years can be taken from Section 5 of this report.
2.2 VVER plants

The fundamental principles of VVER primary water chemistry were developed in the 1960s by Alexeev [Alexeev, 1968] and Chernorotov [Chernorotov et al, 1964] with colleagues in the Kurchatov institute of Atomic Energy in cooperation with other organizations in some Eastern European research centres. In the mid 1960s water chemistry compatibility with zirconium fuel clad was tested in a loop of the MR experimental reactor under the influence of irradiation.

Based on the gained results, ammonia injection was selected to produce hydrogen in situ, in order to avoid the potential risk of hydrogen explosions. Due to the excellent corrosion resistance of the ZrNb cladding material in potassium solution, KOH was selected as pH control agent, as a consequence cation exchanger had to be operated in the ammonia-potassium form, which prevents a rapid potassium increase in case of a potassium hydroxide injection. The use of ammonia in VVER provides radiolysis suppression even in case of low dissolved hydrogen concentration in the coolant.

A second argument for using potassium in comparison with lithium hydroxide is the lower corrosion activity related to zirconium alloys.

Since the 1960s the low alkaline pH of 7.1–7.3 was used to minimize corrosion and corrosion product accumulation on fuel cladding (see [Dragunov & Chabak, 1992]). But in fact there is a variety of alkalizing agents like ammonia, potassium as described before, lithium from the boron-10 n, alpha reaction and sodium from make-up water. All these alkaline forming compounds had to be analyzed in order to generate the correct pH value. The initial boron alkaline mode at VVER 440 is shown in Figure 2-5.

Corrosion tests in the experimental reactor MR have shown a high corrosion resistance of Zr-1% Nb and of titanium stabilized austenitic steels.

In 1971 the ammonium-potassium primary water chemistry was implemented in VVER-440 plants based on good practice of Novovoronezh unit 2. In 1980, the first VVER-1000 unit was put in operation in Novovoronezh and the same chemistry was applied. As of 2012, there are more than 50 VVER plants all operating with the ammonia-potassium coordinated primary water chemistry but some considering using direct hydrogen injection instead of ammonia.
Improvements of VVER primary water chemistry are based on the chemistry impact on radiation field on VVER and PWR in the 1980s. These optimizations are based on updated thermodynamic data and on corrosion products solubility information [Hildebrand & Nikitin, 1988]. A recalculated boron-alkaline-mode for VVER-440 is shown in Figure 2-6 and Figure 2-7.

Figure 2-6: VVER-440 boron-alkaline mode change in 1993 and pH_{270} values.

Figure 2-7: VVER-440 boron-alkaline mode change in 1992 and pH_{290} values.
The optimizations in the first VVER-440 plants are summarized in the following Table 2-2:

Table 2-2: Primary water chemistry at first VVER plants.

<table>
<thead>
<tr>
<th>NPP, Unit</th>
<th>pH$_{25}$ value</th>
<th>Coolant treatment</th>
<th>Dissolved hydrogen Nml/kg</th>
<th>Dissolved oxygen ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novovoronezh Unit 1</td>
<td>6-7</td>
<td>Hydrazine 0.2-0.3 ppm in feed water</td>
<td>0.5-1</td>
<td>0.02</td>
</tr>
<tr>
<td>Reinsberg</td>
<td>~10</td>
<td>Ammonia up to 35 ppm</td>
<td>Below 60</td>
<td>Below 0.01</td>
</tr>
<tr>
<td>Novovoronezh Unit 2</td>
<td>9.5-10.5</td>
<td>Potassium hydroxide 2-20 ppm</td>
<td>20-40</td>
<td>Below 0.01</td>
</tr>
</tbody>
</table>

As can be seen from this table, the use of hydrazine instead of ammonia is shown for Novovoronezh Unit 1. The attempt was to generate more reducing conditions by the application of hydrazine instead of ammonia. Among the VVER-440 plants there are some units operating without a stainless steel cladding on the inner surface of reactor pressure vessels. This increases the risk for corrosion product release especially during outages. This increased inventory of iron could also generate a delta-p problem over the core of the plant.

In Figure 2-8 the change of actual and calculated values of reactor differential pressure at a VVER-440 is shown. This figure underlines that enhanced ion concentrations are leading to heavy deposits in the reactor core so that critical ∆p values are achieved in a very short time.

![Figure 2-8: The change of actual and calculated values of reactor differential pressure at VVER-440.](image-url)
Yurmanov [Yurmanov et al, 2010] describes the further development of Primary Water-Chemistry Guidelines as follows:

- **Kola NPP and similar plants**
  Since 1980, Kola and other VVER plants have been using hydrazine injection instead of ammonia or their mixture to create more favourable reductive conditions in primary coolants. Hydrogen injection allows to reduce corrosion especially in the case of dissolved oxygen intrusion into the primary system with feed water without deep de-aeration.

  The above water chemistry was recently compared to traditional water chemistry with ammonia injection at similar VVER 440 plants taking into account structural material corrosion rate, hydrogen generation, corrosion product transport, active crud accumulation, radiation field, fuel reliability etc. This study has not revealed any negative impact of hydrazine application on corrosion of structural materials in primary system and in core. As a result, since 2005, VVER primary water chemistry standards have allowed to use ammonia or hydrazine to maintain primary coolant dissolved hydrogen within the specified limits based on the above study.

- **VVER 440 plants**
  In 1973 the Kurchatov Institute of Atomic Energy issued Primary water chemistry guidelines 3-02-73 for VVER-365 and VVER-440. In 1984 the above document was revised taking into account the use of these guidelines at foreign NPPs.

  In 1985 this document was revised to reduce dissolved oxygen limit for primary coolant from 10 µg/kg (ppb) to 5 ppb. Simultaneously, boron-alkaline mode was modified to stabilize coolant pH value during fuel cycle. In 1993 boron-alkaline mode was modified again.

  In 2005 VVER-440 primary water chemistry standards 0621-2005 and 0622-2005 were developed with some changes as compared to previous revision:
  - Allowable range of primary coolant hydrogen was reduced from 2.7-5.4 to 2.2-4.5 ppm
  - Minimum allowable coolant ammonia concentration was reduced from 5 to 3 ppm
  - Boron-alkaline mode was modified.

  In 2007 Primary water chemistry standards 1.1.1.02.005-0621-2007 for the first Russian generation VVER-440 reactors without reactor pressure vessel corrosion resistant lining were introduced to facilitate the above-mentioned actions to prevent reactor differential pressure increase.

- **VVER 1000 plants**
  The first revision of VVER-1000 primary water chemistry standard was issued by Kurchatov institute in 1982. Boron-alkaline mode at VVER-1000 differs from that on VVER-440s because of a higher coolant temperature.

  In 1988, this document was revised to reduce the dissolved oxygen limit for primary coolant from 10 ppb to 5 ppb. At the same time, boron-alkaline mode was modified to stabilize coolant pH value during fuel cycle.

  In 1992, organics control was introduced for primary coolant and boron-alkaline mode was modified.

  In 2001, the current version of VVER-1000 primary water chemistry standard 0004-00 was introduced with some changes as compared to previous version:
  - Nitrate control was introduced in primary coolant taking into account the impact of nitrate on radiolysis behaviour and potential source of nitrates during cation exchanger regeneration with nitric acid;
Allowable range of primary coolant hydrogen was reduced from 2.7-5.4 to 2.2-4.5 ppm;
Minimum allowable coolant ammonia concentration was reduced from 5 to 3 ppm.

VVER-1000 primary water chemistry standard could be particularly revised following power uprate programs, fuel cycle extension to 18 months and implementation of manoeuvred operation mode.

In 2003 VVER-1000 primary water chemistry standard 0009-03 was developed especially for pre-start activity.

Primary water chemistry optimization performed by Nuclear Research Institute (Rez, Czech Republic) during hot functional tests at Temelin NPP was taken into account in the above document, [Zmitko et al, 2000].

Some new improvements are used in primary water chemistry documents elaborated for VVER-1000 plants in China (Tianwan), India (Kudankulam), Iran (Bushehr), Bulgaria (Belene, construction still pending) versus the above Russian standards, i.e. total organic carbon and sulphate control. Some improvements are also implemented in primary water chemistry documents for future VVER-1200 and VVER-1500 plants.

Development in the Ukraine

Four Ukrainian NPPs are currently operating: two VVER-440 reactors and 13 VVER-1000 units. From 2002 to 2007 the Ukraine issued its own standards. At the end of 2007 new standards were issued based on IAEA and WANO recommendations. In this document new issues were included like:

- Total organic carbon
- Recommendation on chemical control techniques
- Requirements to primary chemistry support systems
- Requirements to on-line chemical control system.

Currently there are ongoing discussions to consider some modifications in the Primary Coolant Chemistry, e.g:

- Gaseous hydrogen injection (as of 2012, still under investigation)
- Zinc addition (probably will not implemented; however, still open issue)
- Introduction of Lithium-hydroxide injection instead of Potassium-hydroxide (as of 2012 still under investigation)
- Implementation of enriched B-10 (project was cancelled after recognizing the huge amount of uncontrolled leaks containing boric acid due to system design).

Further activities

Another activity is related to corrosion tests performed by “Kharkov Institute of Physics and Technology” (KIPT) investigating the compatibility of Primary Coolant Chemistry with fuel cladding, stainless steel corrosion and crud build-up. This investigation has been performed in conjunction with the IAEA FUWAC-Program.
3 Basics of coolant chemistry (Rolf Riess, Suat Odar)

Deminerlised water is used as reactor coolant in the PWR plants to moderate the fast neutrons to thermal neutrons, which is needed for the nuclear fission reaction to produce energy in the core. Another function of the reactor coolant is to transport the heat of nuclear fission energy produced in the core to steam generators (SG). In addition boric acid is added to the reactor coolant as chemical shim to control the core reactivity. Based on field experience gained during the early PWR operation in 1960s at several research and power plants, an operation with reactor coolant without further chemical treatment may result in several serious problems with respect to safe plant operation, radiation field control and compatibility of the structural materials. This is due to the fact that the coolant is exposed to radiation field in the core, where it decomposes by radiolysis. As a result of this, radiolysis products are generated, some of which are extremely strong oxidants and can jeopardize the compatibility of the structural materials by corrosion. Oxidizing conditions can cause enhanced fuel cladding corrosion or Primary Water Stress Corrosion Cracking (PWSCC) in nickel base alloys like Alloy 600MA that is used as SG tubing material or in numerous reactor penetrations in many PWR plants designed and constructed by US vendors or their licenses worldwide. However, oxidizing conditions are also detrimental (SCC) for stainless steels as well at high temperature. In addition, oxidizing conditions enhance corrosion product (so called “crud”) deposition on fuel rods, which may cause crud induced fuel clad corrosion and increase the radiation field exposure.

In addition to these problems that are created solely by coolant radiolysis, the insufficient alkalinity of the reactor coolant, which would happen if only boric acid is added to coolant as chemical shim, similar problems again with respect to fuel performance and radiation field control would occur. This is because, boric acid as a weak acid, it undergoes poly-condensation processes with increasing temperatures. Thereby the pH-value is increasing, but this pH increase is not sufficient to minimize the metal release and corrosion rates of the structural materials at operating temperatures. The result is, as confirmed by old-field experience in the 1960s and early 1970s, the heavy deposition on fuel rods with a consequence of possible crud induced fuel clad corrosion and radiation field increase.

Therefore, application and control of coolant chemistry is indispensable by adding additional chemicals to avoid the problems explained above. The objective of the coolant chemistry in PWR plants for safe plant operation is in detail to

- Avoid the radiolytic decomposition of the reactor coolant (suppression of the water radiolysis).
- Avoid or minimize the crud deposition on fuel rods.
- Maintain the fuel integrity without jeopardizing its compatibility.
- Protect the integrity of Reactor Coolant System (RCS) by maintaining the corrosion compatibility of the structural materials.
- Control the radiation field at low levels.
- Optimize the quantity of released wastes and the operating costs.

To fulfil these objectives, alkaline water chemistry under reducing conditions is selected for the reactor coolant. For this purpose, hydrogen gas is added to the reactor coolant to suppress the coolant radiolysis (the net decomposition of the water), which also provides sufficient reducing conditions. Adequate alkalinity is achieved by adding depleted Lithium-7-hydroxide (~Li depleted LiOH; i.e. ^7LiOH). Since the last fifteen years, many PWR plants are also injecting zinc to their RCS with the aim to reduce their radiation field exposure and improve the PWSCC resistance of the nickel base alloys like Alloy 600MA/TT if that is used as SG tubing material and for reactor system penetrations.
In this section, the basics of the reactor coolant are explained. Basics of the PWR reactor coolant chemistry as it is applied today was established in the late 1950s and 1960s, based on the theoretical and experimental work performed mainly in North America. In the following sections, these fundamental aspects are discussed.

Even though, similar coolant conditions exist in VVER plants, different chemicals are used to control the VVER coolant chemistry but for the same objectives and having similar characteristics. This is explained in Section 5.3.

3.1 Properties of water (Rolf Riess)

The background of water chemistry in the early days of installation of commercial PWRs was presented by P. Cohen [Cohen, 1972] in Ermenonville, France. As water is used in various functions in a nuclear plant as e.g. in the PWR primary system, it has to fulfil the following requirements:

- Heat transport medium in primary loop of PWRs,
- Working medium in steam-water cycles (Secondary side of PWRs), or
- As plain coolant.

A precondition for the application in all these functions is the knowledge of the properties and the behaviour of aqueous solutions. In addition, water is requested not to corrode the system materials.

In the current section there will be two aspects of importance in the discussion:

- Are the data of some relevance for material corrosion, and
- Will these data be of importance for PWRs?

Water as a liquid has unusual properties when comparing it with other liquids. In such a comparison it becomes apparent that there are fundamental differences between such liquids and water. Unusual properties are for example the high melting point and the high boiling point, the high heat capacity and the decrease in the molar volume during melting and the adjacent contraction between 0°C and 4°C.

Looking to the di-electricity constant as a function of temperature, it has to be recognized that there is a decrease (see Figure 3-1). The di-electricity constant is an important value for the solubility capacity of the coolant.
4 Crud behaviour in the coolant (Rolf Riess)

Crud is involved in all areas of concern. This includes the formation of deposits in the core and is thus generating a corrosion risk for the fuel cladding and it enhances the formation of radionuclides. Another phenomenon is the Axial Offset Anomaly (AOA), which is described in Volume I of this STR. Therefore, this section on crud in this Volume II deals with all crud aspects, which were not yet covered in Volume I.

Crud in the coolant can have several negative consequences on the operational performance of PWRs like fuel element corrosion and activity build-up. Corrosion deposits are playing a key role in this area. When describing the relevant subjects, it is assumed that corrosion products do exist already. Under this precondition, the following items will be evaluated:

- Formation of deposits
- Fuel Crud characteristics
- Role of Crud
- Axial Offset Anomaly
- Circulating Corrosion Products
- Interferences with inspection necessities
- Build-up of OUT-of core Radiation Fields
- Additional Issues influencing crud properties

4.1 Formation of deposits

According to some authors, most of the corrosion products determined in the primary water are in the form of particles, whereof the main bulk (approx. 60%) is in the range of 3-4 µm and a substantial amount (approximately 25%) larger than 2 µm, [Vanbrandt & de Regge, 1980], [Comley et al, 1989] and [Bolz et al, 1996]. Unless well-specified and reliable methods of sampling and determination are known to have been employed, results should be treated with caution. An interesting observation is that the amount of larger particles increases significantly with the age of the plant, at least during the first 3 cycles [Comley et al, 1989]. The increase is mainly due to formation of larger particles, reportedly >8 µm. Of course, during transients, especially start-up and shutdown, the number and density of particles can increase by 3 orders of magnitudes [Comley et al, 1989].

One of the first reactions that can occur is the formation of a layer of crud on heat transfer surfaces. This means specifically on fuel element surfaces. The fuel crud deposits in the PWRs are normally consisting of a single, more adherent layer with a thickness of 10-350 mg·dm⁻² (0.8-29 µm, generally in the lower range), and an estimated density of 1200 kg·m⁻³ and hence rather porous, despite being adherent, [Hazelton, 1987]. The crud thickness in the mid-core positions is typically less (4-6 mg·dm⁻² or 0.3-0.5 µm) than at the top (50-65 mg·dm⁻² or 4-5 µm), [Hazelton, 1987]. It has been reported from earlier operation that 30–78% of the fuel crud metal content consisted of iron and 8-57% of nickel in an extensive review of PWR and BWR crud deposits, [Hazelton, 1987]. A more modern average composition of the fuel crud has been reported by [Polley & Pick, 1986] as shown in Table 4-1.
Table 4-1: Fuel crud elemental compositions in Westinghouse plants per 1986 (10 plants during 1–3 cycles), after [Polley & Pick, 1986].

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>68±7 %</td>
<td>57–80%</td>
</tr>
<tr>
<td>Ni</td>
<td>29±6 %</td>
<td>19–38%</td>
</tr>
<tr>
<td>Cr</td>
<td>3±2 %</td>
<td>1–6%</td>
</tr>
<tr>
<td>Co</td>
<td>0.2±0.2 %</td>
<td>0.03–0.5%</td>
</tr>
</tbody>
</table>

An example of axial crud distribution has been reported also for the PWR KWO (Obriegheim), which is the first commercial German PWR plant that had considerably corrosion and crud deposits after its first cycle of operation in 1971, [Riess; 1976]. The reason was that the hydrogen pressure was insufficient and that no lithium was injected during that period. The absence of lithium and hydrogen was justified with the operating experience in a heavy water cooled and moderated plant in Germany, the MZFR (Mehrzweck-Forschungs-Reaktor in Karlsruhe). The total amount of crud was considerably higher in the hotter top part of the core than in the lower part, as seen in Figure 4-1. It is also interesting to note that the nickel concentration is much higher in the top with a nickel-to-iron ratio above 0.5, being then at risk to produce AOA (Axial Offset Anomaly), which actually was observed. The excessive crud input is not typical for modern PWRs, but the case is of interest in the analysis of the AOA phenomenon today.

Figure 4-1: The fuel crud deposits in the PWR Obrigheim. The maximum deposits was ~8mg cm⁻², which is extremely high for a PWR, after [Riess, 1976] Figure 3-1.
5 Current coolant chemistry guidelines and practices (Rolf Riess)

5.1 Introduction

The primary coolant in the RCS serves as a moderator and is a medium for transporting heat from the core to the steam generators. Hence, it must not endanger plant operation by the corrosion of materials and consequences thereof. The task of water chemistry can be divided into the following main points:

- Metal release rates of the structural materials should be minimal.
- The occurrence of localized forms of corrosion should be counteracted.
- The transport and deposition of corrosion products must be influenced in such a manner, that induced radioactivity of the primary coolant system is kept low.
- The deposition of corrosion products on heat transfer surfaces, particularly on fuel assemblies, should be prevented as far as possible.
- Radiolytic formation of oxygen should be mitigated.

In certain instances, situations may be encountered where chemistry conditions that are optimum for achieving one goal can lead to a decreased level of achievement relative to other goals. As a result of such considerations, the water chemistry specifications must define parameters to achieve a balance among the five goals, recognizing that highest priority is designed to materials and fuel integrity goals. Although the other goals are in the second line of priority, like radiation build-up, they cannot be ignored and became with the time of growing attention.

The water chemistry conditions applied to the RCS materials must fulfil the above mentioned chemistry requirements. Thus the primary coolant of PWRs, which contains boric acid (900–1800 ppm B at Beginning of Cycle (BOC) as a neutron absorber is chemically conditioned by the addition of isotopically pure Lithium -hydroxide (>99% Li-7) (2–6 ppm Li at BOC) as a non-volatile alkalizing agent and by the addition of hydrogen. In recent years, the injection of Zn has been qualified as a tool to mitigate activity build-up and to delay crack initiation and reduce the crack propagation in RCS materials.

The quality requirements are fixed in the Coolant Specification by the various vendors, utilities and institutions. As examples, the Primary Coolant Specifications of EPRI, VGB, EdF, and those for VVER–units are discussed in more detail. However, before starting this discussion, it should be recognized that specific operational modes have to be considered, which are not covered by specifications valid for steady state operation. Such modes are shown in Table 5-1:

Table 5-1: Operational status modes.

<table>
<thead>
<tr>
<th></th>
<th>EPRI</th>
<th>VGB</th>
<th>EdF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold shut-down</td>
<td>&lt;250 °F</td>
<td>&lt;120°C</td>
<td>&lt;120°C</td>
</tr>
<tr>
<td>Start-up</td>
<td>&gt;250 °F</td>
<td>&gt;120°C But not critical</td>
<td>&gt;120°C But not critical</td>
</tr>
<tr>
<td>Power operation</td>
<td>Reactor critical</td>
<td>Reactor critical</td>
<td>Reactor critical</td>
</tr>
</tbody>
</table>

Moreover it seems appropriate to describe the definitions of the terms used in this report.
Typical Values

Typical values are values, which can be achieved during undisturbed steady-state plant operation. They are plant specific. Slight deviations from the typical value will have no consequences regarding system integrity (VGB).

Limit Values

Limit values are values that must be respected by the plant operators under any circumstances. Deviations include the possibility of materials corrosion and the consequences thereof. Immediate corrective measures are required.

Control Values

Control values are those parameters, which determine the entire situation of water chemistry regarding an optimum plant operation and thereby ensuring the absence of corrosion in the systems. They are selected because of their decisive importance and their exact measurability with state of the art analytical methods. For control parameters Action Levels are defined.

Diagnostic Values

Diagnostic values are values, which supplement the entire picture of the applied water chemistry. Because diagnostic values are connected directly or indirectly with control values, they will enable to identify the root cause of deviations.

Action Levels

Action levels are values, which are defined for remedial actions to be taken when parameters are confirmed to be outside the control values. In such cases, efforts should be made to bring the values within the appropriate limit within a certain time window. Such time limits can be taken from Table 5-2.

Table 5-2: Overview on definitions and time windows.

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Definitions/Consequences EPRI</th>
<th>Definitions/Consequences VGB</th>
<th>Definitions/Consequences EdF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical value</td>
<td>NV</td>
<td>No specification</td>
<td>Values resulting from undisturbed operation</td>
</tr>
<tr>
<td>Action Level 1</td>
<td>AL 1</td>
<td>7 days without power reduction</td>
<td>28 days without power reduction</td>
</tr>
<tr>
<td>Action Level 2</td>
<td>AL 2</td>
<td>24 hrs</td>
<td>7 days</td>
</tr>
<tr>
<td>Action Level 3</td>
<td>AL 3</td>
<td>Immediate shut-down with temp. &lt;250 °F</td>
<td>12 hrs before shut-down</td>
</tr>
</tbody>
</table>

ANT International, 2012
6 Future coolant chemistry programs

6.1 PWR plants (Rolf Riess)

6.1.1 EPRI programs

The ANT International position regarding the future of the Primary side coolant chemistry has been explained in great detail in Volume I of this report; a summary is given in Section 7 of this report. The main topics were: “Elevated pH, zinc chemistry and hydrogen control”. In essence, the results of this evaluation are the following:

- **Elevated pH**: There is internationally a clear trend to higher pH-values (7.2 to 7.4 at 300°C).
- **Hydrogen**: The optimization efforts are not going in the same direction, e.g. US trend is to increase the hydrogen values >50 cc/kg whereas the Japanese nuclear community tends to adjust H₂ at values ≤10 cc/kg. The European plants see no need for immediate changes that may be of limited benefit and may jeopardize other issues, due to the lack of feedback.
- **Zinc**: There is a consensus to inject Zinc in order to benefit from the positive effect to mitigate crack initiation and to reduce plant dose rates.

The future of the PWR coolant chemistry is e.g. described by [Fruzzetti & Perkins, 2008], at the NPC 2008 Conference. They illustrated for example the effects of water chemistry on Plant operation (Figure 6-1 by using a BWR as reference). According to EPRI, the Primary coolant optimizations will be focused on:

- Zinc injection
- Hydrogen optimization and
- pH optimization

In the area of Zinc injection, the number of plants applying this technology is steadily increasing as can be seen in Figure 6-2.

In Figure 6-3, Fruzzetti and Perkins are providing an overview, which Development programs are in progress.

The second area for chemistry optimization is Hydrogen. The scenario for this item can be taken from Figure 6-4.

When comparing the ANT International and the EPRI position, a consensus is obvious regarding pH-values and Zinc is, whereas the hydrogen concentration remains a subject for discussions.

However, there remains one item to be evaluated, which is the use of Enriched Boric Acid (EBA). This subject will be discussed later in Section 8.
Figure 6-1: Effects of water chemistry on plant operations, [Fruzzetti & Perkins, 2008].

Figure 6-2: Zinc application, [Fruzzetti & Perkins, 2008].
7 Recommendations for plant specific applications
(Suat Odar)

Before summarizing the recommendations for plant specific Water Chemistry applications it is useful to describe the basis for these recommendations briefly, which were given in Volume I, Section 5 in more detail.

7.1 Basis for the ANT recommendations

7.1.1 Coolant dissolved hydrogen concentration

7.1.1.1 Influence on material compatibility (PWSCC)

Recently, especially in the USA, PWR industry is considering to increase the Dissolved Hydrogen concentration as a measure to mitigate PWSCC. Regarding this issue, it should be considered that other material characteristics and parameters such as heat, annealing procedures, stresses and/or temperature have much more impact on PWSCC susceptibility rather than environmental chemistry conditions. However, water chemistry parameters, especially the coolant dissolved hydrogen concentration, have a quite important influence on PWSCC initiation and Crack Growth Rate (CGR). Whereas, the PWSCC CGR can be mitigated by both increasing and decreasing the dissolved hydrogen concentration to above or below the corrosion potential of Ni/NiO phase boundary, crack initiation can be mitigated only by decreasing the dissolved hydrogen concentration to very low levels (refer to Volume I Section 5). An increase in dissolved hydrogen concentration has none or negative influence on crack initiation. Based on this knowledge, intensive discussions on strategies with respect to dissolved hydrogen concentration are going on worldwide in the PWR industry. Several organizations, especially US PWR operators and EPRI are favouring the increase in dissolved hydrogen concentrations above the upper historical limit of 50 cc/kg recommended by Water Chemistry Guidelines based on the assumption that the cracks that cannot be detected by None Destructive Examinations (NDEs) are already existing. The objective of this approach is to slow down the propagation rate of existing cracks. Even though, the Ni/NiO phase boundary and with it the peak in CGR changes with temperature (see Figure 7-1 a and b), an increase in dissolved hydrogen concentrations provides for the entire PWR operating temperature range, from core inlet to pressuriser temperature of 290 to 345°C, a beneficial effect on PWSCC CGR. The higher the temperature and the bigger is the difference in initial and target dissolved hydrogen concentration, and the higher is the improvement factor (see Figure 7-1 c). However, this is a wrong approach if crack initiation needs to be mitigated.
Figure 7-1: Dissolved hydrogen influence on PWSCC CGR in Ni base alloys at different temperatures (a + b) and factor of improvements for CGR in Alloy 182 by the change of dissolved hydrogen concentration from 25 cc/kg to higher or lower concentrations [Andresen & Hickling, 2007].

In contrast to this approach, other organizations, Swedish and Japanese PWR industry, are favouring the decrease of dissolved hydrogen concentration to the level of 5-8 cc/kg [Molander et al, 2007a] and [Molander et al, 2007b], [Molander et al, 2008], [Molander et al, 2009a] and [Molander et al, 2009b], with the objective to mitigate the crack initiation. By decreasing the dissolved hydrogen to these concentration levels, PWSCC mitigation can be achieved, not only in the crack initiation but also in CGR at areas with temperatures above 330°C (pressuriser with 345°C). However, at areas with temperatures lower than 330°C, in core inlet and outlet, low dissolved hydrogen concentrations might result in an increase of CGR (see Figure 7-1c). This increase in CGR at core outlet (325°C) is much bigger than at core inlet (290°C), where it might be insignificant due to the small height of the CGR peak (see Figure 7-1a and b).

In addition to the effect of dissolved hydrogen concentration on PWSCC CGR and crack initiation, the further “cons and pros” of both approaches can be summarized as follows:
8 Enriched Boric Acid (EBA) (Rolf Riess)

[Nordmann, 2008] concluded that in case an operating plant wants to switch to the use of EBA, this undertaking may be questionable due to technical difficulties and the cost to be expected. Therefore, he recommended that new plants should directly be designed with the EBA option. In this section only the technical part of the transition to EBA is discussed as it was performed by Siemens designed units.

8.1 Introduction

Boric acid is used in all PWRs as a chemical shim to control excess reactivity in the fuel assembly during a fuel cycle. Although natural boric acid is normally used, only the B-10 isotope is involved in reactivity control via the B-10 (n,α) Li-7 reaction which produces the alkali Li-7 OH, in addition to what is added. In natural boric acid the B-10 isotope is normally present at about 19.8 atom % (the exact percentage may vary from one to another ore), which leaves scope for operating with enriched B-10 boric acid (EBA) to increase the boron reactivity worth and to reduce the total amount of boric acid required at all stages of the cycle.

EBA can be used in two ways. The first is to permit operation at higher pH throughout a fuel cycle, either for radiation field control, or to mitigate against the formation of fuel crud deposit which are implicated e.g. in the development of an axial offset anomaly (AOA). The second is to increase shutdown margins and chemical shim control when part – mixed oxides – (MOX) cores or more highly enriched fuel is loaded. The latter option is the basis of the use of EBA in Siemens PWRs.

The majority of Siemens PWRs have converted to operation with enriched boric acid (EBA) at an enrichment of 27–30 atom% B-10. This report describes why the change to EBA was made, how it was carried and what where the operational consequences.

In a recent paper [Wiedenmann & Nordmann, 2012], the reasons for using EBA is explained by the new situation. The economics of operating PWRs demand increased fuel economy which in turn places increasing demands on the primary coolant chemistry. Higher energy production can be achieved by using increased enrichment of the nuclear fuel, higher fuel burn up and longer fuel cycles, which in turn requires increased amounts of neutron poison to maintain reactivity control. In addition, greater amounts of chemical shim are required when utilizing alternative, high-reactivity fuels such as mixed uranium/plutonium oxide (MOX) fuels. If the boric acid is enriched in the 10B isotope, then the maximum amount of chemical shim can be increased without exceeding the chemistry limits set by the acidity of boric acid or the concentration limit of lithium (PWR) or potassium (VVER). With sufficient isotopic enrichment, it therefore becomes possible to operate the entire PWR fuel cycle with constant pH \(_{300^\circ C}\) at the favored value of 7.2-7.4.

The use of Enriched Boric Acid (with ~40% 10B instead of ~20% in natural boron) decreases the required amount of Boric acid and thus of lithium by a factor of two. This provides many advantages in enhancing operational safety and life time of several components, as well as facilitating dose rate reduction programs in PWRs and VVER Nuclear Power Plants. When lowering the total boron concentration in the primary coolant, it is possible to minimize:

- dose rates during maintenance activities - optimal pH\(_T\) from the beginning of the fuel cycle (BOC) can mitigate corrosion products that become activated;
- the risk of corrosion of various materials of the Reactor Coolant System - allowing a lower lithium (or potassium) concentration mainly at BOC; the sensitive materials are fuel cladding (zirconium alloy), stainless steels (AISI 304 type), nickel-based Alloy 600;
- the risk of Axial Offset Anomalies - resulting from precipitation of boron compounds on the fuel cladding;
- the need for design modification to support either larger volume or higher boric acid concentration of safety tanks.
Finally, EBA may also be added in units operating with natural boron. As B-10 becomes depleted, a small quantity of EBA (rather than larger quantities of natural boron) can be added to adjust the B-10 proportion within the specified tolerances. In this manner, EBA may be applied to decrease the amount of waste discharged into the environment.

If the benefits of EBA deserve economic and technical evaluation in operating plants (which are more difficult and costly to transition), then it seems clear that any new plant should consider a design with the EBA option.

8.2 Background

The standard water chemistry specification for the primary coolant of Siemens/KWU designed PWRs at full power has been the following: (see also Section 5).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>≤ 2.0 mg Li-7/kg*</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2 to 4 mg H₂/kg</td>
</tr>
<tr>
<td>Oxygen</td>
<td>&lt; 0.005 mg O₂/kg</td>
</tr>
<tr>
<td>Chloride</td>
<td>&lt; 0.2 mg Cl/kg</td>
</tr>
</tbody>
</table>

*) depending on the boron concentration.

However, the plant operational performance has been challenged by economic pressure, which can be characterized by:

- Advanced fuel concept
- Load following operation
- Plant life extension.

As mentioned above in Section 8.1, the advanced fuel concept can be described by higher U-235 enrichment and/or MOX and may be aimed at higher burn-up, longer cycles, and increased rod power. Such fuel concepts are comprising higher fissionable material content. That means, the concept requires more reactivity control, achievable in part by fuel rods, containing burn-out absorbers like gadolinium oxide, but to a large extent by more dissolved boron in the primary coolant.

Further aims were to yield a more negative temperature coefficient of reactivity for MOX fuel due to reduce boron effectiveness and to produce higher surface heat flux and larger void fraction, in particular in the hot channels. The resulting problem for chemical engineering was the requirement of a higher boron inventory. The options to resolve these problems were:

- Increased borate systems volume limited by existing storage tank capacity and pump characteristics.
- Increased boron concentration in storage tanks limited by solubility at ambient temperature, thus requiring safety relevant heating systems in tanks containing >7000 ppm B.

In summary, the enrichment of fuel and the use of MOX still require sub criticality, which can only be guaranteed by the increase of the B-10 concentration. The resulting problem for water chemistry is a lower pH at BOC, which is detrimental to activity transport and dose rate build-up. In addition, a higher alkalizing agent concentration is required to maintain an adequate pH. Both, low pH- and high LiOH-concentrations are undesirable. As a consequence, a new chemistry approach has been recommended to solve the problem in the following way:
9 Purification and filtration of coolant (Suat Odar)

The purification of the reactor coolant is performed by demineralises in the Chemical and Volume Control System (CVCS) of all PWR plants. VVER plants have two Coolant Purification Systems and they are differently designed for VVER-440 and VVER-1000. In case of VVER-440, these two systems are the high pressure Primary Circuit Purification System (SVO-1) and low pressure and low temperature Letdown Clean-up System (SVO-2), which both are using demineralises for the coolant purification. Together, the Primary Circuit Purification (SVO-1) and the Letdown Clean-up Systems (SVO-2) are the equivalent of the CVCS in PWR plants. VVER-1000 plants have also two different purification systems. The one is the Letdown Clean-up System (SVO-2) the same as used in VVER-440 plants. However, the other one Primary Circuit Purification System (SVO-1) does not use demineralises; it consists of High Temperature Mechanical Filters. These systems are explained in more detail in the following.

9.1 Chemical and volume control system

CVCS is a Coolant Letdown Circuit that recycles about 10% of the reactor coolant volume per hour. It is designed to fulfil the following objectives at PWR and VVER plants:

- Supply the RCS with make-up water,
- Control temporary changes of reactor coolant volume due to changes in operating conditions (e.g. temperature),
- Provide purification of the reactor coolant to remove impurities, corrosion and fission products,
- Control boric acid concentration in reactor coolant,
- Maintain hydrogen and other chemicals concentrations (e.g. PWR: LiOH; VVER: NH₃) in the reactor coolant,
- Provide degasification of the reactor coolant (all Siemens-KWU designed PWRs),
- Provide seal injection water for the Reactor Coolant Pumps (RCP).

In order to fulfil all these objectives, CVCS is designed to have different subsystems. Although the basic design is very similar in PWR and VVER plants, they differ significantly from each other in some details. Even, in the case of PWR plants, CVCS design might differ remarkably depending on the plant designer. In the following sections, those differences are explained.

9.1.1 PWR plants

CVCS is a Coolant Letdown Circuit with different equipment, such as Coolers, Heaters, Pressure Reducers, Volume Control Tank (VCT), HP- Changing Pumps and several Sub-Systems that are connected to this Letdown Circuit. It takes about 10% of the reactor coolant volume per hour and after its treatment (purification, degasification, hydrogenation and control of the boric acid concentration) feeds it back to RCS. The following Sub-systems are considered to fulfil numerous objectives:

- Coolant purification demineralises,
- Thermal deborating demineralises (not in every PWRs),
- Coolant Degasification System (in all Siemens-KWU designed PWRs but not in most of other PWRs designed by Westinghouse, Framatome, CE, B&W, etc.),
- Chemical Injection Systems,
- Hydrogen Injection System (as separate system in the new Siemens designed PWRs),
- Reactor Make-up Water Storage Tanks/System,
- Boric Acid Recycling System and Borated Coolant Storage Tanks.

Depending on the plant designer, the CVCS of different PWR plants may differ significantly in detail. Typical CVCS flow diagrams for Westinghouse, Framatome, B&W and Siemens-KWU designed PWR plants are given in Figure 9-1, Figure 9-2, Figure 9-3 and Figure 9-4 respectively.

Figure 9-1: Typical CVCS design of a PWR designed by Westinghouse, [Unipede, 1996].
10 Chemical injection systems (Suat Odar)

Chemical injection systems used in PWR and VVER plants have similar design. However, due to different coolant chemistry applied in PWR and VVER plants, the type and number of chemicals to be injected are different, except for boric acid, which is used in both reactor types for excess reactivity control. In the following, the chemical injection systems at PWR and VVER plants are explained.

10.1 PWR plants

In PWR plants, boric acid as chemical shim, lithium-hydroxide as alkalizing agent and hydrogen gas to suppress the water radiolysis, are injected to control the coolant chemistry. In all PWR plants that are although designed from different plant designers, the chemical injection systems have very similar design. They all are part of the CVCS-Complex and injecting the chemicals into the low-pressure letdown line upstream HP-Charging Pumps. Figure 10-1 schematically shows these chemical injection systems in the case of Siemens-KWU designed PWR plants as an example. In the following sections, a brief description of these chemical injections systems is given.

Figure 10-1: Chemical injection systems and hydrogen addition in a Siemens-KWU designed PWR.
10.1.1 Boric acid injection system

The objective of the Boric Acid Injection System is to prepare the boric acid solution of about 4\% by wt (7000 mg/kg), provide the first filling of the RCS and safety injection systems with boric acid of necessary concentration and to inject the necessary amount of boric acid into RCS during the plant shutdown operations. In general, the Boric Acid Injection System consists mainly of a Batching tank with a stirrer to prepare boric acid solution, Boric Acid Storage tanks and injection pumps. Figure 10-2 shows the typical Boric Acid Injection System implemented in Siemens-KWU designed PWR plants as an example.

In Siemens-KWU designed PWR, plants boric acid is recovered from letdown coolant by evaporators in the Boron Recovery System. Letdown coolant is evaporated up to 4\% boric acid (7000 mg/kg boron) concentration, then the concentrate is diverted automatically into Boric Acid Storage Tanks. The content of this Boric Acid Storage Tank is designed more than sufficiently to increase the coolant boron concentration at the end of fuel cycle from ~0 mg/kg to ≥ 2200 mg/kg for the refuelling outage. The Boric Acid Batching tank is used for the preparation of boric acid solution only to compensate some operational losses.

During power operation, Boric acid / Make-up water injection are automatically performed and controlled by Core Reactivity Control System, which adjusts the amount and the ratio of boric acid to make-up water injection according to the core reactivity demand. This avoids unnecessary control rod movements.
11 Coolant monitoring concept (Suat Odar)

Adequate water chemistry control program is indispensable for operational performance of the plant systems and components to avoid any significant corrosion, radiation field problems. The basis for the water chemistry control is the result of sampling analyses, which are gained by using the sampling and monitoring system. Since the seventies, based on achieved field experience, several guidelines were published to describe how the sampling systems should be designed to get representative samples. Accordingly, these guidelines were used to design the sampling systems for the new nuclear power plants (PWRs, BWRs and VVERs). In addition, continuous implementation of the new field experiences allows improvements of the sampling systems. Furthermore, monitoring techniques and equipment were continuously improved in order to more adequately meet the water chemistry guideline requirements, and yield more cost effective results for utilities.

Comprehensive discussions about how to gain representative samples and the detailed description of the current sampling system designs used in different type of PWR and VVER plants in European countries and in North America are out of the scope of this report. All these items have been covered in LCC4 Annual Report (AR) Section 3. Therefore, here in Section 10 of this report, only the important aspects of the representative sampling and the current sampling systems including the analytical equipment used in currently operating PWR and VVER plants are briefly described. For details, the reader is kindly asked to refer to the LCC4 AR Section 3.

11.1 Representative sampling

The sampling systems in nuclear power plants have to fulfil all requirements necessary for representative sampling, not only concerning dissolved species or gases, but also for suspended solids (corrosion products, crud). For this, special features must be considered in the design of the sampling system hardware and sampling procedures. Experiences with power plants in the past have shown that in many cases the analytic results of the samples were not representative. This was usually recognized by achieving unrealistic or inexplicable sampling results. If the detected error is small and reasonably constant in the sampling system, the results can still be used for trend analysis since a baseline can be established. On the contrary, if the error is inconsistent, the data produced are useless and may even mislead the plant operators in their corrective decisions. Field experiences with power plants confirm that many factors can affect the representativeness of the sampling results. Therefore, the sampling system and measuring chain should be considered as a whole for a proper monitoring / analytical determination of chemistry parameters. Based on field experiences, the potential error sources for sampling are:

1) Location of the sampling point,
2) Sampling nozzle,
3) Sampling line design (isometric), sampling transport,
4) Sampling equipment design,
5) Materials selection of sampling system,
6) Sampling equipment operation,
7) Sampling procedures and treatment.
The effect of all these error sources on the representativeness of the sampling was discussed in detail in LCC4 AR. Therefore, this will not be repeated in this section. On the other side, the sampling systems already exist at operating power plants and a change/modification of their design (items 1-5 as possible error sources) will usually not be considered. However, there are still several aspects that need to be considered to get representative samples, which will be discussed in the following sections. These are the influence of “Long Hot Sampling Lines” and “Sampling Flow Rates” on the representativeness of the sampling. Another aspect is to decide if “Isokinetic Sampling Line” is needed for the Coolant Sampling System.

11.1.1 Isokinetic sampling process

The need for Isokinetic sampling Process may rise only for sampling of corrosion products, if any! Particles in a fluid, that changes its direction, tend to keep their direction due to their inertia and therefore diverting from the fluid lines. This phenomenon is more noticeable for larger and heavier particles, or for particles having higher density difference with the fluid medium. Therefore, this effect is more pronounced for instance in the case of heavy, big particles in air than for light and small particles in water.

Isokinetic sampling technique has equal collection efficiency for all particles present in the sampled fluid, regardless of the fluid velocity and orientation of the sampling nozzle in the fluid stream. This ability requires the fluid entering the sampling nozzle to have the same velocity vector (speed and direction) as the main stream. In other words, in an isokinetic sampling process, all phases in the fluid stream are entering the opening of the sampling nozzle with a velocity vector \( V \) equal to the velocity vector \( W \) of the fluid in the stream being sampled. If this condition is not fulfilled, there would be perturbation of the flow profile (i.e. change of direction), so that particles with different density than the fluid and consequently different inertia tend to drift away from the fluid streaming line. This will result in a non-representative sampling of the suspended matter, (see Figure 11-1), [Lister et al, 2007].

![Figure 11-1: Schematic illustration of a sampling of a fluid stream with suspended particulates.](image-url)
12 Summary, conclusions and recommendations of volume II (Rolf Riess, Suat Odar and Francis Nordmann)

This section consists of conclusive summary regarding the information given in the previous sections. It summarizes also the recommendations for water chemistry strategies as discussed in the individual sections. The chronology as described in Section 2 and the description of the properties of water (Section 3.1) are considered to be a useful background information and they do not require specific recommendations.

12.1 Fundamentals of the water chemistry (Section 3)

Water chemistry has the objective to suppress the water radiolysis, to protect the integrity of RCS materials, to avoid heavy deposits on fuel assemblies and their consequent results regarding enhanced fuel cladding corrosion, AOA and increase in out-of-core RCS radiation fields. In order to fulfill these objectives, hydrogen for the suppression of the radiolysis and lithium hydroxide to control the alkalinity (pHT) is added with success to reactor coolant since 1960s up to now. Since 1990s several plants started to inject zinc into reactor coolant either to mitigate PWSCC or to reduce radiation fields to lower levels also with success.

Worldwide, the PWR plants have been operating with coolant Dissolved Hydrogen (DH) concentration in the range of 25-50 cc/kg (2.2 to 4.5 mg/kg). On the one hand, this concentration range is a historical value applied without any adverse effects, on the other hand due to operational conveniences, this DH concentration range is adequately provided by hydrogen partial pressure in the Volume Control Tank of the CVCS, which is needed as pre-pressure upstream HD Charging pumps for reliable pump operation. Therefore, no one wanted to change it until the beginning of 2000s (that will be explained later). Actually the Critical Hydrogen Concentration (CHC) for counteracting radiolysis is far below this operational range. The in-pile loop measurements and theoretical radiolysis model calculations reveal that the CHC is in the range of ~1 cc/kg. However, all PWR plant measurements indicate that CHC is in the range of ~4-5 cc/kg. This field information should not be ignored if some intention exists for a PWR plant to reduce the coolant DH concentration with the objective to mitigate PWSCC (see later).

In PWR plants, boric acid is used as chemical shim for the core reactivity control. Even though boric acid is a weak acid at PWR operating temperatures, it provides acidic conditions in the reactor coolant in absence of any alkali. Therefore, it is a necessity to add lithium hydroxide to reactor coolant to achieve alkaline conditions that is indispensable to minimize the RCS material corrosion and corrosion product release and transport to core for adequate radiation field control. Worldwide, till the end of 1990s, the operating coolant lithium concentration was in the range of 0.5 -2.2 mg/kg. Upper lithium concentration was limited mainly due to concerns regarding fuel -cladding corrosion. Some PWR plants (e.g. Ringhals units, Millstone-3) were operating with Beginning of Cycle (BOC) lithium concentration of 3.5 mg/kg; however, after several years of operation, this value was again decreased to 2.2 mg/kg due to concerns for PWSCC in nickel base Alloy 600MA SG tubes. Depending on how the lithium/pHT regime is applied, there exits several pHT control strategies, like “Coordinated Coolant Chemistry”, “Elevated Lithium chemistry”, “Modified Coolant Chemistry”, and “Coordinated Chemistry at Elevated pH”, in the order as they have been historically developed. Field experience gained in 1980s and 1990s confirmed that operating with elevated constant pHT close to 7.4, as long as possible, was favourable with respect to radiation field control. This was the basis for recent discussions in the PWR industry to elevate the BOC lithium concentration far above the traditional BOC concentration of 2.2 mg/kg.
Whenever the lithium concentration that is acceptable for any reason (restriction from fuel vendor, regulatory body, risk of some materials corrosion) is insufficient to get the appropriate $\text{pH}_7$ required to minimize Operational Radiation Exposure, a good option is to use Enriched Boric Acid (EBA) with an enrichment of about 30% B-10 instead of ~20% in natural boron. Such a reduction of boric acid concentration of a factor of 2 allows decreasing the lithium content to acceptable limits while reaching the optimum $\text{pH}_7$, even at BOC.

During the mid 1990s, some PWR plants started to inject zinc into reactor coolant with the objective either to mitigate PWSCC or to reduce radiation fields or for both reasons. Based on intensive qualification program performed by US and German PWR industry separately, it was confirmed that zinc injected into the reactor coolant is incorporated in the oxide layers on the RCS surfaces. This result in building of very stable oxide passive layers that protects the materials against general corrosion, mitigates the PWSCC, and reduces the corrosion product release. In addition, it was also found that zinc does not only replace the already incorporated radio-cobalt from the oxide layers but also seals the oxide layers by incorporation and thus inhibits the further incorporation of fresh radio-cobalts. Replacement from oxide layers and inhibition of further incorporation of radio-cobalt results in reduction of dose rates on RCS surfaces. Due to this replacement mechanism, introduction of zinc injection always results in enhanced release of corrosion products into reactor coolant, at least during the first two-three zinc cycles. Therefore, zinc injection should be applied cautiously at PWR plants with high duty cores with fuel surveillance programs in approval with fuel vendors. In the further cycles, this corrosion product release decreases due to reduction of the source term caused by better protective oxide layers. As of 2012, over 70 PWR units worldwide are applying zinc injection with success either to mitigate PWSCC or to reduce dose rates. During more than fifteen years of operation with zinc injection, no adverse effect on fuel performance was experienced. It was confirmed that zinc is a powerful tool to improve the passive oxide layers on RCS surfaces and to modify the fuel deposits to thinner and homogeneously distributed layers.

12.2 Plant experience and guidelines (Section 4, 5, 6)

Section 4 handles the behaviour of crud in the coolant and describes the impact of the corrosion products in case they are depositing e.g. on heat transfer surfaces. There are various locations in the RCS like the fuel surface where they may change the local chemistry or increase the thermal resistance. In most severe cases, the phenomenon of AOA was experienced and the necessary countermeasures were developed aiming at a minimization the crud content and at optimizing the RCS chemistry in order to avoid a significant deposition that may induce AOA.

However, during plant operation, all units had to comply with the water chemistry guidelines and there is essentially no big difference in the applicable guidelines in various countries like US, France, Germany and Japan. It is not only a technical problem to stay within these limits, it also involves legal aspects. Thus the fine tuning of coolant chemistry in PWRs remains a main task for plant chemists.

The trends in coolant chemistry however, are the increase of the lithium concentration from <2 or 2.2 ppm up to 3.5 ppm ($\mu$g/kg) or even higher. Regarding the hydrogen concentration, there are two directions which are either aiming at higher values of 60 to 80 cc $H_2$/kg or to the reduction of the $H_2$ concentration to lower concentrations compared to the historically existing values of 25-35 cc $H_2$/kg. (See Section 12.1).

The discussions of the specifications are including those for start-up and shutdown operation which is a summary of a STR related to the captioned subject.

A review of the future chemistry programs in various countries reveals that the major activities are located in the US and in France, whereby the French program is aiming at a detailed understanding of the corrosion processes at first plant start-up and during steady state operation.


