

An Evaluation of Enriched Boric Acid in European PWRs



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Technical Report

An Evaluation of Enriched Boric Acid in European PWRs

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EPRI Project Manager
H. Ocken

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Principal Investigator
K. Garbett

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REPORT SUMMARY

Utilities introduced enriched boric acid (EBA) in a number of Siemens-designed PWRs when the plants converted operation from uranium dioxide to mixed oxide fuel. This report describes why and how the plants changed to EBA, and the operational consequences associated with the conversion. It also compares operational experiences in plants now operating on EBA and discusses possible implications for U.S. PWRs. EBA is a possible solution to some of the challenges faced by U.S. PWRs that continue to burn uranium dioxide fuel under increasingly demanding conditions.

Background

Previous EPRI studies (NP 6485 and TR 109992) that evaluated the costs and benefits associated with EBA use at U.S. PWRs focused on potential radiation exposure savings. Due to the high costs of implementing EBA and the fact that nuclear plant personnel exposures are at historically low levels, no U.S. PWR has implemented EBA. However, a number of Siemens PWRs now use mixed oxide (MOX) fuel to improve fuel economy. Issues associated with core physics and burning MOX fuel make EBA far more attractive under such circumstances. At these plants, staff implemented operation with ~ 30% 10B boric acid, rather than the 19.8% present in natural boric acid. This transition necessitated a number of changes in plant systems and operating procedures.

Objectives

To describe the successful application of EBA in Siemens PWRs, including the changeover and its impact on power operations. To describe the similarities and differences in the design of Siemens and U.S. PWRs and the effect on the potential conversion to EBA at U.S. PWRs

Approach

The principal investigator reviewed experiences in the use of EBA in Siemens PWRs. They also held extensive discussions with key personnel at those plants that implemented EBA.

Results

Six PWRs in Germany and one in Switzerland converted to operation with 27 – 30% 10B boric acid to permit the plant to burn fuel more highly enriched in 235U or MOX fuel. The main cost saving associated with the use of EBA is improved fuel economy, including a reduction in the number of new fuel assemblies required. The changes plant managers carried out had no impact on plant safety at any time, and minimal impact on plant operations. All borated systems converted to the same 10B:11B isotopic ratio. Most Siemens PWRs converted to EBA using a “drain and fill” compensation method, in which part of the boric acid is discharged to waste and

replaced by 96 weight percent 10B boric acid. The change to EBA had no significant impact on either reactivity or chemistry control during normal operation. Monitoring of the 10B:11B ratio is routine. The most significant ongoing cost of EBA operation is the loss of EBA during the fuel cycle.

Plant managers could implement the same conversion method in a U.S. PWR if they used a similar 10B enrichment level. However, conversion of the refueling water storage tank (RWST) would violate the Tech. Spec. limit during draining. It would therefore require a temporary alleviation permitted by the NRC. The EPRI EBA assessments showed that boric acid losses at U.S. PWRs are high. If utilities implement EBA, a significant reduction in these losses is necessary to reduce ongoing EBA replacement costs during normal operation to the low levels found in European PWRs.

EPRI Perspective

This report establishes that utilities can achieve conversion to operation with EBA with little difficulty. Duke Energy is planning to convert to MOX fuel at its Catawba and McGuire PWRs in 2007. Plant staff are now undertaking evaluations similar to those described in this report. They do not expect any significant challenge to implementing the conversion at these two plants.

The main challenge to EBA conversion is demonstrating its cost effectiveness in PWRs continuing to burn uranium dioxide fuel. Investigators expect that the higher pH values achieved with EBA will reduce corrosion product release from primary system component surfaces and subsequent crud buildup on the reactor core. Operation at higher pH levels should reduce the potential for the axial offset anomaly (AOA), avoidance of which will be a continuing challenge as PWRs seek to operate at higher power levels. Computational models suggest this will indeed be the case, and EPRI is organizing an experimental program to confirm these predictions.

Key Words

Radiation buildup
PWRs
Water chemistry
Mixed Oxide Fuel

ABSTRACT

Plant managers introduced Enriched Boric Acid (EBA) in a number of Siemens-designed PWRs when the plants converted from uranium dioxide to mixed oxide fuel to improve fuel economy. The main cost saving associated with the use of EBA is improved fuel economy, including a reduction in the number of new fuel assemblies required. However, due to the high costs of implementing EBA and the fact that nuclear plant personnel exposures are at historically low levels, no U.S. PWR has implemented EBA. This report describes the successful application of EBA in Siemens PWRs, including the changeover and its impact on power operations. It also describes the similarities and differences in the design of Siemens and U.S. PWRs and the effect on the potential conversion to EBA at U.S. PWRs

The main challenge to EBA conversion is demonstrating its cost effectiveness in PWRs continuing to burn uranium dioxide fuel. Investigators expect that the higher pH values achieved with EBA will reduce corrosion product release from primary system component surfaces and subsequent crud buildup on the reactor core. Operation at higher pH levels should reduce the potential for the axial offset anomaly (AOA), avoidance of which will be a continuing challenge as PWRs seek to operate at higher power levels.

SUMMARY

Boric acid is used in all civil PWRs as a chemical shim to control excess reactivity in the fuel assemblies during a fuel cycle. Although natural boric acid is normally used, only the ^{10}B isotope is involved in reactivity control, via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction which produces the alkali $^7\text{LiOH}$. In natural boric acid the ^{10}B isotope is normally present at 19.8% atom percent, which leaves scope for operating with enriched ^{10}B boric acid (EBA) to increase the boron reactivity worth and to reduce to 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 deposits which are implicated in the development of an Axial Offset Anomaly (AOA). The second is to increase shutdown margins and chemical shim control when part-mixed oxide (MOX) cores or more highly enriched fuel is loaded. The latter option is the basis of the use of EBA in Siemens PWRs.

Most of the recent Siemens PWRs have converted to operate with enriched boric acid (EBA) at an enrichment of 27-30 atom % ^{10}B . This report describes why the change to EBA was made, how it was carried out and what were the operational consequences. It also compares the experience in Siemens PWRs with the earlier assessments made for U.S. PWRs and discusses possible implications for U.S. PWRs. The conclusions reached are:

- (1) EBA can be used to give either improved pH control to reduce radiation exposure, fuel clad corrosion and, possibly, Axial Offset Anomalies (AOA), or to enable operation with more highly ^{235}U enriched or MOX fuel.
- (2) The main cost saving associated with the use of EBA in Siemens PWRs is the improved fuel economy, including the lower “back end” costs of storage and final disposal that result from the loading of more highly enriched ^{235}U and MOX fuel. Both contribute to the reduced numbers of new fuel assemblies required. Reduced radiation exposure is a minor factor. This is in contrast with the earlier U.S. PWR evaluations where improved radiation exposure was predicted to be the main benefit.
- (3) Seven of the most recent Siemens PWRs have been converted to operate with 27-30 atom % ^{10}B boric acid. These are Grafenrheinfeld (1997, 31%), Grohnde (1997, 27%), Gösgen (1997, 28%), Brokdorf (1998, 28%), Philippsburg 2 (1998, 29%), Emsland (2000, 28%) and Isar 2 (2000, 30%). Neckarwestheim 2 is planning to change to 27-28% EBA in 2002.

- (4) Siemens PWRs are all single unit stations, mainly with uprated cores of 3765-3950 MWth for the 4-loop stations converted to operate with EBA. Gösgen is a 3-loop 3002 MWth station.
- (5) While many details of Siemens PWR designs are similar to those in Westinghouse PWRs, there are some differences that influence the change to EBA. These include slightly smaller Spent Fuel Pools located in the containment building and four independent Residual Heat Removal and Emergency Core-Cooling trains, which include four Flood Tanks. The latter replace the single Refuelling Water Storage Tank present in Westinghouse PWRs. No Siemens PWR has a Boron Thermal Regeneration System or deborating resin beds.
- (6) Siemens PWRs operate on a 12-month fuel cycle, which includes ~10 months full power operation, one-month stretch-out operation and a short refuelling shutdown. All operate to the VGB high pH water chemistry, which is the equivalent of the EPRI “Modified Chemistry”. Stations converted to operate with EBA load more highly ²³⁵U enriched fuel and, except for Emsland, MOX fuel. None, however, has suffered from AOA.
- (7) Siemens PWRs recover essentially all the boric acid let down from the primary circuit and run all ion-exchange mixed-bed filters to exhaustion. The recovered boric acid contains both silica and some lithium, but this has no reported detrimental effect on operations.
- (8) The change to EBA in Siemens PWRs is carried out by methods designed to give sufficient extra ¹⁰B reactivity worth, while minimising waste boric acid discharges.
- (9) In Siemens PWRs the change is carried out so that there is no impact on plant safety at any time and with minimal impact on plant operations, and all borated water systems must be converted to the same ¹⁰B:¹¹B isotopic ratio.
- (10) In Siemens PWRs, with the exception of the primary circuit and the Coolant Volume and Chemistry Control System, all borated water systems are converted to EBA during the final months of normal operation. The primary circuit and Coolant Volume and Chemistry Control Systems are converted to EBA as they are borated during the shutdown.
- (11) Most Siemens PWRs have converted to EBA by a “drain and fill” “compensation method”, in which part of the boric acid is discharged to waste and is replaced by 96 weight % ¹⁰B boric acid.
- (12) 96 weight % ¹⁰B boric acid is used to convert the 7000 ppm B boric acid solution in the Boric Acid Tanks to 30 atom % ¹⁰B, as this produces the minimum amount of natural boric acid waste. Systems containing 2200 ppm B boric acid can be converted to 30 atom % ¹⁰B with minimum waste boric acid production by adding 7000 ppm B 30 atom % ¹⁰B boric acid diluted to a 31.4% “blend” with demineralised water. For a 2900 ppm B solution the equivalent dilution would be 41.5%.

- (13) Gösgen converted to EBA by an “addition method”, in which the addition of 96 weight % ¹⁰B boric acid also increased the total boric acid inventory.
- (14) Most Siemens PWRs discharge the waste natural boric acid after processing it through mixed-bed ion-exchange resin beds.
- (15) The change to EBA is reported to have no significant impact on either reactivity or chemistry control during normal operation. In addition, there are either no significant or only minimal effects on the operation of any other borated water circuit. In Siemens PWRs experience shows that it is only necessary to measure the ¹⁰B:¹¹B isotopic ratio at monthly, or even three-monthly intervals and that boron control can be achieved using the normal methods of analysis.
- (16) No significant changes in primary circuit radiation fields have yet been observed in Siemens PWRs, but this is not an unexpected result because the plants that have converted to EBA operate at only slightly higher pH levels than previously.
- (17) The most important ongoing cost of EBA operation in Siemens PWRs is the loss of EBA during the fuel cycle. Efficient recovery of EBA by the boron recycle evaporator is essential, as is the minimisation of EBA losses on anion resins by operating the mixed-bed filters to exhaustion.
- (18) U.S. PWR evaluations are based on a mixture of “feed and bleed” and “drain and fill” methods of conversion to EBA, which would mainly be carried out during the shutdown. Generally, higher EBA enrichments than those used in Siemens PWRs are proposed in order to permit operation at higher pH. While the most recent assessment considers the potential saving if AOA were to be prevented, it is not yet certain that EBA will prevent AOA. The resolution of this question will require experimental study and verification.
- (19) Comparison with U.S. PWR assessments shows that the Siemens method could be used in U.S. PWRs if a similar enrichment level is used, but that conversion of the Refuelling Water Storage Tank by a “drain and fill” method would violate the minimum Tech. Spec. limit during draining, and could only be used if a temporary alleviation was permitted by NRC. If higher enrichments were needed, then a “fill and bleed” method similar to that proposed by Westinghouse would have to be followed.
- (20) The U.S. assessments show that boric acid losses in U.S. PWRs are high. If EBA operation was adopted, these losses would need to be reduced significantly to reduce the ongoing EBA replacement costs during normal operation to the level found in Siemens PWRs.
- (21) U.S. PWR evaluations are based on a mixture of “feed and bleed” and “drain and fill” methods of conversion to EBA, which would mainly be carried out during the shutdown. Generally, higher EBA enrichments than those used in Siemens PWRs are proposed in

order to achieve the required radiation exposure savings. The most recent assessment considers the potential saving if AOA were to be prevented; however, the prevention of AOA is rather speculative.

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1

INTRODUCTION AND PROJECT OBJECTIVES

1.1 Introduction

Boric acid is used in all civil PWRs as a chemical shim to control excess reactivity in the fuel assemblies during a fuel cycle. Although natural boric acid is normally used, only the ^{10}B isotope is involved in reactivity control, via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction which produces the alkali $^7\text{LiOH}$. In natural boric acid the ^{10}B isotope is normally present at 19.8% atom percent, which leaves scope for operating with enriched ^{10}B boric acid (EBA) to increase the boron reactivity worth and to reduce to total amount of boric acid required at all stages of the cycle (1-1, 1-2).

EBA can be used in two ways. The first is to permit operation at higher pH throughout a fuel cycle (1-3), either for radiation field control, or to mitigate against the formation of fuel crud deposits which are implicated in the development of an Axial Offset Anomaly (AOA). The second is to increase shutdown margins and chemical shim control (1-4) when part-mixed oxide (MOX) cores or more highly enriched fuel is loaded. These two options are summarised below.

1.1.1 Improved pH Control

In a normal 12-month fuel cycle using ^{235}U enriched fuel, the natural boric acid concentration required to suppress the excess reactivity at the start of the cycle (beginning of cycle, BOC) is about 1000 ppm B (~0.6% boric acid). After an initial fall as xenon poison grows-in, the boric acid concentration is reduced at ~3 ppm B per day throughout the cycle to compensate for fuel burn-up, until, normally, it reaches 0 ppm B at the end of the cycle (EOC). In practice, close to EOC there may be insufficient reactivity remaining to sustain 100% power operation even at 0 ppm B and, in this case, power slowly decreases. This stretch-out period is a normal feature of many fuel cycles and is the normal method of EOC operation in Siemens PWR fuel cycles.

^{235}U fuel enrichments are generally higher in extended fuel cycles and burnable poisons are often present in the feed fuel. Boric acid concentrations at BOC are greater and can be up to 1800 ppm B for an 18-month cycle and 2400 ppm B for a 24-month cycle. With burnable poisons present, the concentration in the early part of the cycle is lower, but generally it still remains high for the first few months of the cycle (e.g. 1200 to 1400 ppm B for 18-month cycles).

Primary coolant pH control in PWRs was originally designed to minimise radiation fields, while at the same time minimising Zircaloy-4 fuel clad corrosion and crud deposition on the fuel. Early studies showed that crud deposition occurred at low pH and in U.S. PWRs a “pH_{Tave}6.9 Co-ordinated Water Chemistry” regime was specified to minimise radiation fields, Zircaloy-4 fuel

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clad corrosion and deposition on the fuel (1-5). This specification was based on magnetite solubility and selected Zircaloy-4 clad corrosion data, and boron and lithium concentrations were reduced in parallel to maintain a constant pH throughout the cycle. $\text{pH}_{\text{Tave}}6.9$ was achievable even at the maximum BOC boric acid concentration in a 12-month cycle. Later, based on nickel ferrite solubility data, it was realised that the optimum pH for minimising radiation fields was higher, and it is currently thought to be in the range $\text{pH}_{\text{Tave}}7.2-7.4$. The revised specification is known as the “Modified Chemistry” regime, but, because the upper lithium concentration is limited to 2.2 ± 0.15 ppm Li to avoid increased Zircaloy-4 corrosion, the higher pH cannot be achieved at BOC. Instead, pH rises in the first part of the cycle from $\text{pH}_{\text{Tave}}6.9$ to 7.2 or 7.4, before the boron and lithium concentrations are co-ordinated at the higher pH.

In an extended fuel cycle the boric acid concentrations for the first few months of the cycle are such that even $\text{pH}_{\text{Tave}}6.9$ cannot be achieved without increasing the lithium concentration above the maximum value of 2.35 ppm Li. As this would increase the risk of fuel crud deposition significantly, an increase in the maximum lithium concentration to 3.5 ppm Li at BOC is normally allowed. With this modification, a co-ordinated $\text{pH}_{\text{Tave}}6.9$ regime can be used from about 1900 ppm B, whilst in a “Modified Chemistry” regime the pH is first co-ordinated at $\text{pH}_{\text{Tave}}6.9$ from about 1900 to 1200 ppm B, before the pH is allowed to rise at constant 2.2 ppm lithium to the upper co-ordination pH (1-5). However, since the mid-1990s it has been recognised that even these variants of the primary water chemistry regimes may not be sufficient to limit fuel crud deposition when high duty cores are loaded and sub-cooled nucleate boiling levels increase. Plants with these high duty cores have suffered from Axial Offset Anomalies (AOA), and an increase in pH is now recommended in the early part of the fuel cycle to limit this possibility (1-5).

Although U.S. PWRs use T_{ave} to define the co-ordination pH, most European operators define the primary coolant pH at 300°C. German stations follow this approach, and all Siemens PWRs use $\text{pH}_{300^\circ\text{C}}$. In addition, Siemens Fuel Division imposes a maximum lithium concentration limit of 2.0 ppm for more recent PWRs (2.2 ppm in older Siemens PWRs, exceptionally 2.5 ppm at Ringhals 2 in Sweden), which limits the scope for extended fuel cycle operation. Currently, all Siemens follow the “VGB High pH Water Chemistry” regime. This is the equivalent of the U.S. “Modified Chemistry” regime, but with a final co-ordination pH set at $\text{pH}_{300^\circ\text{C}}7.4$, and with the reduced upper lithium limit (1-6). As with U.S. PWRs, the pH in the early part of the cycle starts at about $\text{pH}_{300^\circ\text{C}}6.9-7.0$, but since Siemens PWRs only use 12-month fuel cycles lower pHs do not occur.

The problems associated with operation at low pH in the early part of a fuel cycle can be solved by operating with enriched boric acid, rather than natural boric acid. For example, 30% EBA would allow operation at a co-ordinated pH of $\text{pH}_{\text{Tave}}7.1$ throughout an 18 month cycle, whilst 50% EBA would allow operation at $\text{pH}_{\text{Tave}}7.3$. These considerations form the basis of the earlier studies carried out on the use of EBA in U.S., Korean and Japanese PWRs (1-7 to 1-15), and although Siemens PWRs do not use EBA primarily to improve pH control it is an additional benefit that should result from its use.

1.1.2 Mixed Oxide and Higher ^{235}U Enriched Fuel Operation

As an alternative to normal ^{235}U enriched fuel, mixed oxide (MOX) fuel containing both uranium and plutonium oxide can be loaded into PWR cores. Using MOX fuel produced from reprocessed spent fuel increases the overall ^{235}U utilisation that can be achieved and, therefore, reduces fuel costs, but is offset by reprocessing and licensing costs. In European PWRs reprocessing spent fuel once to produce MOX fuel has been shown to be economic, and a large number of German, Swiss, French and Belgian PWRs now operate with MOX fuel.

The presence of plutonium has a number of consequential effects, which are mainly due to its higher absorption cross section for thermal neutrons compared with ^{235}U . Greater thermal neutron absorption increases the average overall energy of the neutron spectrum in reactors using MOX fuel (1-4, 1-16), referred to as “hardening the neutron spectrum”. This, in turn, reduces the absorption cross sections of the materials used in the control rods and of the ^{10}B present in the boric acid, and the control rods and the chemical shim become less effective. At the same time MOX fuel has a larger Doppler coefficient (a more negative fuel temperature coefficient) and a larger (more negative) moderator temperature coefficient, which means that a greater shutdown margin is required to absorb the increase in reactivity on cool down to cold shutdown conditions.

In existing PWRs fuelled with normal ^{235}U enriched fuel, plutonium is produced during the fuel cycle and some of this is burned as fuel. In an equilibrium fuel cycle, approximately one third of the energy generated comes from plutonium fission and reactor control systems are designed to function with some plutonium present (1-4). In practice the design margins are such that cores containing up to one third MOX fuel can be loaded and controlled during power operation; cores containing ~30% MOX fuel gives zero net plutonium production and, therefore, maximise utilisation of the original ^{235}U content of the fuel. However, at cold shutdown, the control rods will not accommodate the increase in the shutdown margin required with MOX fuel and the natural boric acid concentration must be increased by about 40% to ensure safe shutdown. Since an increase of this magnitude is not readily accommodated in existing PWR designs due to boric acid solubility and trace heating limitations, the increased shutdown margin is most conveniently achieved by increasing the ^{10}B isotopic ratio in the boric acid by loading EBA.

In recent years there have also been proposals to operate with 100% MOX cores (1-4, 1-17). A change to 100% MOX fuel cannot be made without making additional changes to the control rods, since the worth of the standard silver-indium-cadmium control rods will be reduced to about 80% in a 100% MOX core. Consequently, either the number of standard control rods must be increased, or their worth increased by using enriched boron carbide as the absorber, or a mixture of both standard silver-indium-cadmium and enriched boron carbide control rods must be loaded. In addition to the reduced control rod worth, the effectiveness of natural boric acid will also be reduced, in this case to about 33% of its effectiveness in a normal core. To cater for this change the only option will be to use EBA, at an enrichment that is probably >60%.

Fuel assemblies containing mixed oxides (MOX) have been loaded in a number of German, Swiss, Belgian and French PWRs since the 1980s. In Germany test assemblies were first used in the experimental Kahl boiling water reactor in 1966 and commercial PWR trials started at Obrigheim in 1980. Since the mid-1980s many of the German PWRs have operated with MOX

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fuel present, although generally only a limited number were present at any time (4-20 assemblies) and there was no need to alter the normal operating conditions. Based on this experience, most German PWRs are now licensed to operate with part-MOX cores. In 2000 (1-16, 1-18) the following German stations were licensed to load MOX fuel:

Obrigheim (28 assemblies, 26% of the core, 3.8% by weight plutonium isotopes, MOX first loaded 1972),

Biblis A and B (42 assemblies, 42%, equivalent of 3.5% ^{235}U , licences applied for ca. 1994, but not granted by 2000),

Neckarwestheim 1 (16 assemblies, 9%, 3.04% Pu, 1982),

Unterweser (48 assemblies, 25%, 3.28% Pu, 1984),

Grafenrheinfeld (64 assemblies, 33%, 3.07% Pu, 1985),

Grohnde (64 assemblies, 33%, 3.2% Pu, 1988),

Philippsburg 2 (72 assemblies, 37%, 3.5% Pu, 1988),

Brokdorf (dependent on self-generated plutonium, equivalent of 4.0% ^{235}U , 1988),

Isar 2 (96 assemblies, 50%, equivalent of 4.0% ^{235}U , 1998),

Emsland (48 assemblies, 25%, 3.8% Pu, no MOX fuel loaded to date), and

Neckarwestheim 2 (72 assemblies, 37%, 3.8% Pu, 1998).

In addition, by 2000 the Swiss PWRs Gösgen (MOX first loaded 1997), Beznau 1 (1978) and 2 (1984) were also licensed to load MOX fuel, as were the Belgian PWRs Doel 3 and Tihange 2 (both 1995) and twenty of the French 900 MWe PWRs (St Laurent B1 and B2 (1987 and 1988), Gravelines 1 to 4 (1997, 1998, 1989 and 1989), Dampiere 1 to 4 (1990, 1993, 1998 and 1998), Blayais 1 and 2 (1997 and 1994), Tricastin 1 to 4 (1997, 1996, 1996 and 1997) and Chinon B1 to B4 (1999, 1999, 1999 and 1998)). Eventually it is expected that twenty-eight of the thirty-four 900 MWe PWRs will be licensed to load MOX fuel (1-19, which discusses the “back end” MOX options in detail for French PWRs). The first six French 900 MWe and the 1300 MWe and 1450 MWe PWRs were not designed to operate with MOX fuel.

Although, to date, the licensed number of assemblies have not been loaded at any Siemens PWR due to manufacturing supply limitations, by 2000 several had loaded up to 50 MOX fuel assemblies per reactor (e.g. Philippsburg 2 with 51 MOX assemblies and Gösgen with 48 MOX assemblies in-core in 1998). As yet no U.S. PWR has loaded MOX fuel, but Duke Power plan to load MOX fuel at McGuire 1 and 2 and Catawba 1 and 2 in 2007 under a 1999 Department of Energy contract to dispose of excess weapons grade plutonium.

In parallel with the use of MOX fuel, most recent German PWRs have uprated and have increased the ^{235}U enrichment in the fuel (1-20, 1-21). Details of the individual station uprates are summarised in Section 2, but generally they are between 2.25% and 5%. With time, most can be expected to uprate by up to 5%. Originally the maximum fuel enrichment used in Siemens PWRs was ~3.4-3.6% ^{235}U , but since about 1996 it has been increased to ~4.0-4.5% ^{235}U (1-20). Most of these higher enrichment fuel assemblies contain gadolinium oxide burnable poison in

the fuel pellets and the stated intention is to use such fuel for four or even five 12-month cycles (e.g. some fuel at Gösgen has already been used for five cycles). At the same time there has been a move towards “low-leakage” cores and Siemens PWR cores generally have high peaking factors.

Both the higher initial enrichments, and their use for more cycles, reduce the overall numbers of fuel assemblies used, with consequent economies in the costs of new fuel (1-19 to 1-22) and long-term spent fuel storage. However, the higher enrichments reduce the shutdown margins and favour a change to EBA. This was the situation at Grafenrheinfeld, where the loading of 4.4% ^{235}U enriched fuel in the standard 12-month cycle was sufficient in itself to warrant the change to EBA to give the additional shutdown margin required (1-23). This is also the case at Emsland, which is the only Siemens PWR operating with EBA that has not currently loaded MOX fuel (all the remaining PWRs, including Grafenrheinfeld, load both more highly enriched fuel and MOX fuel). However, changing to EBA is not the only solution. For example, Neckarwestheim 1 and 2 moved to a two year-three shutdown fuel cycle in 1998/99 (1-20, 1-24, 1-25). At Neckarwestheim 2 there were two short 6-month cycles in 1998, with two 7-day refuelling shutdowns, followed by a single shutdown in 1999; there were two further 7-day shutdowns in 2000. In the first of the 1998 shutdowns, eight new assemblies were loaded and the remainder reshuffled; in the second, 48 new assemblies were loaded and the remainder reshuffled. A saving of eight new fuel assemblies was reported. The new approach has enabled the station to load 4.4% ^{235}U enriched assemblies and MOX fuel assemblies (32 MOX assemblies in 2001) without having to change to EBA. The only penalty was an increase in the cold shutdown boron concentration to 2400 ppm B.

It should be noted here that, currently, Siemens PWRs have not moved to 18-month cycles, since the short shutdowns regularly achieved (15-30 days) do not require longer cycles to improve the economics. A further factor is that the 12-month cycles match the annual power demands in Europe, which are low in summer. However, in future, longer cycles could be an option and have been considered (1-20).

Because of the twin factors of loading MOX fuel and ^{235}U fuel of higher enrichment, seven of the most recent Siemens PWRs have converted to operate with ~30 atom % EBA. These are Grafenrheinfeld (1997, 31%), Grohnde (1997, 27%), Gösgen (1997, 28%), Brokdorf (1998, 28%), Philippsburg 2 (1998, 29%), Emsland (2000, 28%) and Isar 2 (2000, 30%). Neckarwestheim 2 is planning to change to 27-28% EBA in 2002. The background to, and methodology for, these changes form the basis of this report.

1.2 Project Objectives

The principal objectives of this study were to describe the successful application of EBA in Siemens PWRs and to compare the experiences in these stations with the theoretical studies carried out thus far for U.S. PWRs.

For this, the main requirement was to understand the detailed differences that exist between Siemens PWRs and typical U.S. PWRs, and then to review the way that the changeover to EBA was made at Siemens PWRs and how the change has affected power operations. Next,

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comparisons were made with theoretical studies of EBA operation in U.S. PWRs, the differences discussed and, finally, conclusions reached on how the Siemens approach can be applied in U.S. PWRs.

To meet these objectives, Section 2 gives a general history of the development of the standard Siemens PWR design and describes all the water circuits that are implicated in the changeover to EBA; comparisons with Westinghouse PWR designs are made where appropriate. Section 2 also summarises the fuel cycle for Siemens PWRs, the primary coolant chemistry and the recent power up-rate history for the PWRs that have moved to EBA operation.

Section 3 reviews the published papers on the use of EBA in Siemens PWRs. More importantly, it summarises detailed data provided by one of the Siemens PWRs on the how the changeover would be managed and the cost implications. These data are presented here in generic form, since the time scales quoted are all relative to a planned date for the start of a refuelling shutdown. Although comments are given on the implications for each of the water circuits considered, the underlying safety assessment studies were not available. However, clearly they were not a significant factor in making the change to EBA.

Section 4 compares the actual application in Siemens PWRs with U.S. assessments, making reference, as necessary, to aspects of the different approaches where design differences and Tech. Spec. requirements between plant designs and regulatory approaches may have a significant impact on a change to EBA. For these comparisons, EBA costs are compared on the common basis of the current price of enriched boric acid of \$2.25 per gram of contained ^{10}B (not including duty, taxes or shipping charges) (1-26).

The different cost-benefit basis used for Siemens and U.S. PWRs, the different methods of changing to EBA and the impact on normal operations are discussed in Section 5 and, finally, overall conclusions are reached in Section 6.

1.3 References

- 1-1 V Goehlich, "Enriched Boric Acid Products", Water Chemistry of Nuclear Reactor Systems 6, BNES, Vol 1, 187, 1992.
- 1-2 V Goehlich and J Florinski, "Enriched Boric Acid for Pressurised Water Reactors", Chemistry in Water Reactors: Operating Experience and New Developments, SFEN, Vol 1, 128, 1994.
- 1-3 N Henzel, "Alternative Water Chemistry for the Primary Loop of PWR Plants", Influence of Water Chemistry on Fuel Clad Behaviour, Proc. Technical Committee Meeting, Řež, October 1993, IAEA-TECDOC-927, 421, 1997
- 1-4 J Nedderman, "100% MOX Cores? Nearly No Problem", Nuclear Engineering International, Fuel Review 1996: MOX Fuel, 28, 1996.

- 1-5 “PWR Primary Water Chemistry Guidelines”, Revision 4, Volume 1, EPRI Report TR-105714-V1R4, 1999.
- 1-6 R Roofthoof, M C Thiry, A Cascia, K Garbett, M Halin, E F Lillo, K-H Walter and M Zmitko, “Primary Circuit Chemistry of Western PWR and VVER Power Plants”, Unipede Report, 02004Ren9653, 1996.
- 1-7 J A Battaglia and J Roesmer, “Utilisation of Enriched Boric Acid in Pressurised Water Reactor Plant”, Proceedings of the EPRI Seminar on PWR Primary Water Chemistry and Radiation Field Control, Paper 34, 1988.
- 1-8 W B Rodill, “Enriched Boron Study Surry Power Station Units 1 and 2”, Proceedings of the EPRI Seminar on PWR Primary Water Chemistry and Radiation Field Control, Paper 35, 1988.
- 1-9 J A Battaglia, L A Lamati, R M Waters, C A Bergmann, J M von Hollen and S M Ditommaso, “Enriched Boric Acid for PWR Application, Cost Evaluation Study for a Twin-Unit PWR”, EPRI Report EPRI NP-6458, 1989.
- 1-10 Westinghouse Electric Corporation, “Final Report Cost Evaluation Study for the Application of Enriched Boric Acid in Millstone Nuclear Power Station Unit 3 for Northeast Utilities Service Company”, Westinghouse Report WP0606-1, 1991.
- 1-11 J Sejvar, C A Bergmann, W J Leech, J D Perock and R J Jacko, “Re-evaluation of the Benefits of Implementing Enriched Boric Acid”, EPRI Report TR-109992, 1998.
- 1-12 E G Lin, C G Lee, Y N Suh and G S Jun, “Technical Review of B-10 Enriched Boric Acid for Control Role in Pressurised Light Water Reactor”, J. Korean Nucl. Soc, Vol. 27(4), 591, 1995.
- 1-13 E K Kim, B S Choi, Y S Ko, Y D Hong, C K Lee, H L Chang, K S Chun and S N Kim, “Study on Chemical and Volume Control System Design Improvement of Pressurised Water Reactor to Use the Enriched Boric Acid”, KAERI Report, KAERI/RR-1591/95, 1995.
- 1-14 T Ichimura, J Sevjar and H Takiguchi, “Evaluation of Dose Reduction Initiatives for Tsuruga Units 3 & 4”, 10th Pacific Basin Nuclear Conference, Kobe, Japan, October, 1996.
- 1-15 H Ocken, P Frattini and C J Wood, “Prospects for Enriched Boric Acid in U.S. PWRs”, Water Chemistry of Nuclear Reactor Systems 8, BNES, Vol 1, 49, 2000.
- 1-16 German-American Academic Council and National Academy of Sciences, “U.S.-German Co-operation in Elimination of Excess Weapons Plutonium, Appendix B, WPU Disposition Using MOX”, National Academy Press, 1995.

Introduction and Project Objectives

- 1-17 Combustion Engineering Inc., “Analysis of Existing ABB-CE Light Water Reactors for the Disposal of Weapons-Grade Plutonium”, DOE Plutonium Disposal Study, DOE Report DOE/SF/19682-3, 1994.
- 1-18 German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety “Nuclear Safety in Germany”, Report under the Convention on Nuclear Safety, September 1998.
- 1-19 J-M Charpin, B Dessus and R Pellat, “Economic Forecast Study of the Nuclear Power Option”, Report to the Prime Minister, French Government Report, July 2000.
- 1-20 M Beer, R Güldner and E Weber, “Fuel Cycle Optimization for Pressurized Water Reactors”, Siemens AG Report, Power Generation Group, 1999 (Top Operation '99, Berlin Oct 24-26, 1999, atw – Internationale Zeitschrift für Kernenergie, 44 (12), 733, 1999).
- 1-21 F Burtak and P Urban, “High-Burnup Fuel Assemblies Reduce Fuel Cycle Costs”, atw – Internationale Zeitschrift für Kernenergie, 45 (8/9), 549, 2000.
- 1-22 J M Hall, Eagle-Pitcher Technologies, LLC, Personal Communication to H Ocken, May 2001.
- 1-23 K-G Seifert and J Florinski, “Operation with Enriched Boric Acid in the Nuclear Power Plant Grafenrheinfeld”, 1998 JAIF Int. Conf. on Water Chemistry in Nuclear Power Plants, Kashiwazaki City, Japan, 516, 1998.
- 1-24 VBG, “Operating Experience with Nuclear Power Plants in 1998”, VGB PowerTech, 5/99, 13-21, 1999.
- 1-25 VBG, “Operating Experience with Nuclear Power Plants in 1999”, VGB PowerTech, 5/2000, 24-25, 2000.
- 1-26 J M Hall, Eagle-Pitcher Technologies, LLC, Personal Communication, June 2001.

2

SIEMENS PWR CHARACTERISTICS

The German vendor Siemens AG, which operated mainly under the name Kraftwerk Union AG (KWU), designed, built and commissioned 16 Pressurised Water Reactors between 1964 and 1989. Of these, 13 are in Germany and one each in the Netherlands, Switzerland and Spain. The dates when these stations first achieved criticality, and their original and current outputs are summarised in Table 2-1.

2.1 Design Development

The first three stations, Obrigheim, Stade and Borssele, were first generation units in which the standard Siemens overall design concept was developed. Obrigheim is a 2-loop station with a primary circuit based on a Westinghouse design. It originally had Inconel 600 tubed steam generators, but these were replaced by Incoloy 800 tubed steam generators in 1983. However, even at this early stage, the overall design concept differed significantly from U.S. PWR practice in that Obrigheim had a double containment structure, with an inner cylindrical steel vessel containing both the primary circuit and the Spent Fuel Pool and an outer reinforced concrete structure. The inner containment was also designed for routine man access, as it is in all later stations. Stade was a 4-loop station, which installed Incoloy 800 tubed steam generators for the first time. At Stade the outer containment annulus housed the Flood Tanks (borated water storage tanks used to supply refuelling water and the Emergency Core-Cooling Systems, which are the equivalent of the Refuelling Water Storage Tank, RWST, in Westinghouse PWRs), the Primary Coolant Storage Tanks (equivalent to the Boron Recycle Letdown Tanks and the Reactor Make-up Water Tank), safety injection pumps and the gas decay tanks, some of which features became standard in all later designs. The inner containment housed the primary circuit, Spent Fuel Pool and the Accumulators. Borssele (Netherlands) was again a 2-loop station, which had similar features to Stade. All three stations had containment spray systems, but while Obrigheim and Stade were built with Gaseous Radwaste gas decay tanks, as are found in most U.S. PWRs, Borssele was the first Siemens PWR fitted with a carbon bed delay system. Stade has since also had a carbon bed delay system installed.

The next five stations, Biblis A, Biblis B, Unterweser, Neckarwestheim 1 and Gösgen (Switzerland) were second generation units. Biblis A was essentially the prototype of the standard 4-loop 1300 MWe design, although it was only designed to produce 1200 MWe. However, both Biblis B and Unterweser were designed as 1300 MWe units. All three were very similar and had the standard 1300 MWe reactor core used in all later 4-loop designs. This had an active length of 3.9 m (12.8 ft) and an effective diameter of 3.6 m (11.8 ft). As at Stade, the Flood Tanks and safety injection pumps were housed in the outer annulus of the concrete containment vessel, while the spherical inner steel containment vessel contained the primary

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circuit, Accumulators and the Spent Fuel Pool. Biblis A and B were still fitted with containment spray systems, but this feature was omitted from Unterweser, Neckarwestheim 1 and all later stations. All five had Gaseous Radwaste carbon bed delay systems, rather than gas decay tanks (as were all later Siemens PWRs) and all had the Boric Acid Tanks, Primary Coolant Storage Tanks, Liquid Radwaste Tanks and other elements of the Coolant Volume and Chemical Control Systems installed in the reactor auxiliary building.

At the 4-loop units, four 50% duty combined Emergency Core-Cooling and Residual Heat Removal trains were installed (one per loop), each consisting of a high pressure safety injection pump, two Accumulators and a low pressure safety injection pump (2-1). The pumps were connected to the Flood Tanks. At Biblis A the four trains were interconnected, but the four trains were separate and independent in all later units (from Biblis B onwards). The Coolant Volume and Chemical Control System also incorporated a degasser that could be used to remove fission product gases. The degasser and the Primary Coolant Storage Tanks were connected to a low pressure nitrogen purge system, which both nitrogen blanketed the vessels and removed any fission product gases. The latter were recirculated through the Gaseous Radwaste carbon bed delay system before they were discharged from the plant stack.

Neckarwestheim 1 and Gösgen were 3-loop units with smaller cores (2.985 m x 3.24 m at Neckarwestheim and 3.58 x 3.24 m at Gösgen), but in other respects had equivalent features to Biblis A and B and Unterweser, although only three Emergency Core-Cooling trains were fitted.

The next five third generation stations were the four standard 4-loop 1300 MWe units Grafenrheinfeld, Grohnde, Philippsburg 2 and Brokdorf and the 3-loop 1000 MWe station Trillo (Spain). The 4-loop units were essentially identical to Unterweser, but incorporated a number of improvements. The primary circuits of all these units, starting with Grafenrheinfeld, were fitted with a nitrogen pressurised Volume Control Tank and added hydrogen via a hydrogen injection system fitted to the charging pump suction line – a feature introduced to reduce the risk of hydrogen fires following the Three Mile Island 2 accident. Improved primary and auxiliary circuit plant drain systems (to recover coolant leaks and, therefore, to reduce non-recoverable boric acid losses) and an Extra (or emergency) Boration System were also installed. Of equal importance, Philippsburg 2 and Brokdorf were the first units to have reduced primary circuit high cobalt hard facing Stellite™ inventories, although the reductions in these units were not as great as in the later “Konvoi” stations. Reducing the exposed area of high cobalt alloys has led to a major reduction in primary circuit radiation fields and radiation exposure. Trillo had a smaller core than the 4-loop stations (3.4 m x 3.47 m), but was otherwise equivalent in design. Although it was commissioned after the other third generation stations, there was no reduction in the primary circuit Stellite™ inventory at Trillo.

The final three units were the fourth generation 4-loop “Konvoi” stations, Isar 2, Emsland and Neckarwestheim 2. Again they were essentially identical to the earlier standard 1300 MWe stations, but had a larger containment and auxiliary building allowing for better shielding and maintenance environments. Extra (emergency) Boration Systems were again installed. In these stations most of the Stellites™ and other high cobalt hard facing alloys were removed from the primary circuit and all have operated with very low primary circuit doserates and low personnel doses.

2.2 Fuel Assemblies, Core Power and Primary Circuit Chemistry

All Siemens PWRs normally operate on 12-month fuel cycles, which usually consists of ~10 months full power operation (300 ± 30 efpy), one to two months stretch-out operation and a one month refuelling and maintenance shutdown. Originally, the fuel was only designed for three fuel cycle burn-ups ($33000 \text{ MWd tonne U}^{-1}$), but since the mid-1990s enrichments have been increased to ~4.5% ^{235}U , allowing the fuel to be used for four or even five cycles. Burn-ups are now $40000\text{-}50000 \text{ MWd tonne U}^{-1}$, and even higher burn-ups, up to $80000 \text{ MWd tonne U}^{-1}$, are being considered (2-2, 2-3). These high enrichment fuel assemblies normally incorporate up to 5-7% gadolinium oxide as a burnable poison in the fuel pellets of some fuel rods. The number of new fuel assemblies loaded for each cycle has always been variable, ranging from 44 to 72 assemblies for the 4-loop plants. From the late 1980s to the early 1990s most 4-loop stations loaded between 48 and 56 new fuel assemblies for each 12-month cycle. In 1998/99 this number had been reduced to 44 to 52 new fuel assemblies. For the higher enrichments and burn-ups now used, there is a saving of about 10% in the numbers of new fuel assemblies loaded each cycle, relative to the position in the early 1990s (2-2).

Fuel assemblies containing mixed oxides (MOX) were tested in a number of units since the early 1990s, and most German PWRs are now licensed to operate with part-MOX cores (see Section 1). In addition, the Swiss PWR Gösigen is also licensed to load MOX fuel. By 2000 several of the reactors had loaded up to 50 MOX fuel assemblies per cycle, requiring the change to enriched boric acid operation.

The standard 1300 MWe 4-loop stations were originally designed with core powers of 3733 MWth at Biblis B and Unterweser and 3765 MWth in later units; since then essentially all have been uprated (Table 2-1). Initially the core power was increased to 3850 MWth in the “Konvoi” stations by using the design reserves in the turboalternators. Later, similar changes were made at other stations as the LP turbine rotors were replaced allowing output to be increased. More recently the core power of most of the 1300 MWe and “Konvoi” stations have been, or are being, increased further to between 3900 and 3965 MWth, a step which significantly increases T_{hot} and, hence, the average primary circuit temperature. At Isar 2 the increase from 3850 to 3950 MWth increased T_{ave} from 308.5°C to 310.6°C , while at Neckarwestheim 2 the increase from 3850 MWth to 3965 MWth will increase T_{ave} from 308.5°C to 311°C .

From about 1982 all Siemens PWRs have operated to either the “VGB High pH Water Chemistry” regime, or to the “ $\text{pH}_{300^{\circ}\text{C}}6.9$ Co-ordinated Water Chemistry” regime. The high pH chemistry is effectively identical to the EPRI “Modified Chemistry” regime, but with the final co-ordination band controlled at $\text{pH}_{300^{\circ}\text{C}}7.4$ and the upper lithium limit restricted to 2.0/2.2 ppm Li. From first start-up Grafenrheinfeld, Unterweser and Brokdorf operated to the “ $\text{pH}_{300^{\circ}\text{C}}6.9$ co-ordinated chemistry” regime, but these three stations now also operate to the high pH chemistry. As noted above, the Siemens Fuels Division does not allow operation above a limit of 2.0 ppm lithium for later PWRs and 2.2 ppm lithium for older PWRs. Further details of the water chemistry used in Siemens PWRs is given in References 2-4 and 2-5.

In Siemens PWRs two additional aspects are important with respect to operation with EBA. The first is the method of operating the mixed-bed ion-exchange filters, and the second is the recovery of essentially all boric acid letdown from the primary circuit. Both are essential aspects in the minimising EBA losses during the cycle.

As described below (Section 2.3.1), the Coolant Purification System is similar to those in Westinghouse PWRs, but there are two slightly larger mixed-bed filters (demineralisers) and the cation resin bed is omitted (2-4). The increased size ($2 \times 2.0 \text{ m}^3$ of 1.5:1 cation:anion resin in the 4-loop Siemens PWRs, compared with $2 \times 0.85 \text{ m}^3$ of 2:1 cation:anion resin plus a 0.85 m^3 cation bed in a Westinghouse PWR) is a consequence of the higher design purification flow rates in Siemens PWRs. One of the mixed beds (the operational bed) is operated in the Li^+ /borate form and is in operation at all times. The other bed (the lithium removal bed) is operated in the H^+ /borate form and is operated intermittently to remove lithium from the coolant. During refuelling the lithium removal bed is fully lithiated in-situ to become the operational bed for the next cycle. The old operational bed is used for coolant clean-up during the shutdown and is then discharged to radwaste. A new H^+ / OH^- bed is loaded, borated in-situ, and this becomes the new lithium removal bed for the next cycle. In this method of operation the resin charges in two demineralisers alternate between the Li^+ /borate and H^+ /borate forms and both are operated to exhaustion (activity break-through). The Spent Fuel Pool Purification System mixed-bed filter is identical to the Coolant Purification System mixed-bed filters and is similarly operated to exhaustion. This method of operation minimises EBA losses associated with replacing the mixed-bed filters.

No Siemens PWR is fitted with a Boron Thermal Regeneration System (BTRS) or with separate deborating anion beds for boron control at EOC.

Because Siemens PWRs are designed to recover essentially all boric acid letdown from the primary circuit, the later third and fourth generation stations were fitted with uprated plant drain systems to recover any coolant leaks and, therefore, to minimise any non-recoverable losses. Compared with the earlier second generation PWRs, non-recoverable losses in the later stations are very low, a feature that is a significant factor in the successful use of EBA.

Because essentially all the boric acid is recovered, the 7000 ppm B boric acid stored in the Boric Acid Tanks normally contains significant amounts of lithium and silica. Since lithium is not specifically removed in the early stages of a shutdown, sufficient lithium is added during boration to raise the primary coolant lithium concentration by 1-1.5 ppm. No detrimental consequences of this addition (e.g. the production of particulate corrosion products) are reported in Siemens PWRs (2-5). Because the mixed-bed filter in the Coolant Treatment System (i.e. BRS) does not remove silica, it concentrates in the boric acid in the Boric Acid Tanks. At start-up, with the coolant at 2200 ppm B, the silica concentration in the primary circuit can reach 2-3 ppm SiO_2 , although the concentration is reduced when the coolant is diluted to achieve criticality. Again, no detrimental effects from these higher silica concentrations have been reported, even though Siemens PWRs operate with highly rated fuel.

2.3 Systems Affected by the Change to Enriched Boric Acid

The change to enriched boric acid in Siemens PWRs potentially affects the following borated water systems,

- (i) Primary Circuit, YA or JE (Reactor Coolant System, RCS)
- (ii) Coolant Purification and Volume Control Systems, TC or KB (equivalent to the Chemical and Volume Control System, CVCS)
- (iii) Residual Heat Removal and Emergency Core-Cooling Systems, TH or JN (equivalent to the Residual Heat Removal System, Accumulators and Refuelling Water Storage Tank, RWST)
- (iv) Extra Boration System, TW or JDH (Emergency Boration System)
- (v) Spent Fuel Pool System, TG or FA, and
- (vi) Radioactive Liquid Waste System, TR or KP (Liquid Radwaste System),

where the system identification letters listed are those used in the earlier and later Siemens PWRs, respectively. Equivalent system names used in Westinghouse PWRs are given in parentheses. Philippsburg 2 and the “Konvoi” stations use the second later set of identification letters, as defined in the Standard Identification System for Power Plants (KKS – Kraftwerk-Kennzeichensystem (2-6)). A more complete set is given in Appendix B.

Unlike Westinghouse PWRs, there are no external boric acid and water tanks at Siemens PWRs. Instead, the equivalents of the Refuelling Water Storage Tank (the Flood Tanks) and Reactor Make-up Water Storage Tank (one or more of the Primary Coolant Storage Tanks) are installed in the outer containment annulus and the auxiliary building, respectively (see Section 2.1). Further, all Siemens PWRs are designed as independent units, and none use common borated water facilities as is found in a number of twin U.S. PWR stations.

The layout of these systems in the containment of a “Konvoi” station is shown in Figure 2-1, whilst schematic layouts of the water circuits are shown in Figures 2-2 to 2-5. The arrangement in earlier stations is similar, and the systems are described below.

2.3.1 Primary Circuit

The Primary Circuit (Figure 2-2) is basically identical to that in a Westinghouse PWR and consists of a reactor pressure vessel (RPV) and 2, 3 or 4 loops, each of which contains a hot leg, a vertical steam generator (SG), an intermediate (crossover) leg, a main coolant pump (RCP) and a cold leg. The pressuriser is connected to the hot leg of one of the loops via a surge line, and a spray line is taken from the cold leg of the same loop. An auxiliary spray line is taken from the cold leg of a second loop. The design operating conditions for the stations are summarised in Table 2-2.

The compositions of the main alloys used in the circuits are given in Table 2-3 and surface areas in Table 2-4 (2-2). The reactor pressure vessel, pressuriser, main coolant pump bowls, loop

pipework and steam generator channel heads are made from low alloy steels (type 22 NiMoCr 3 7, 20 MnMoNi 5 5, type 18 NiMoCr 3 7 or equivalents). These are weld clad internally with the niobium stabilised stainless steel 1.4550 (X10 CrNiNb 18 9, equivalent to 347 SS). The steam generator divider plates at later stations are also made from 1.4550 stainless steel. Reactor internals and coolant purification and residual heat removal systems pipework are also preferably made from 1.4550 stainless steel, although some vessels, such as the Volume Control Tank (VCT), are made from 1.4541 (X10 CrNiTi 18 9, equivalent to 321 SS), 1.4550 or 1.4571 (X6 CrNiMoTi 17 12 2, equivalent to 316Ti SS) stainless steel. The main coolant pump shafts are made from forged 1.4313 ferritic stainless steel (X3 CrNiMo 13 4), the impellers from cast 1.4313 steel and the diffusers from 1.4550 stainless steel. Small quantities of other alloys, e.g. 1.4006 SS and Inconel X750, are used as components in the core internals, fuel assemblies and control rod drive mechanisms. In the earlier stations, graphite containing 30 % antimony was used in the main bearings and seal rings of the main coolant pumps. This gave rise to a significant contribution to radiation fields from ^{124}Sb . In all Siemens PWRs (with the exception of the original Inconel 600 tubed SGs at Obrigheim) the steam generators are tubed in Incoloy 800. Inconel 82 (NiCr 20 Nb) is mainly used to plate the underside of the low alloy steel steam generator tubesheets.

Fuel assemblies of all Siemens PWRs have Zircaloy-4 clad, Zircaloy-4 guide tubes and 1.4550 top and bottom nozzles. More recently, Duplex clad fuel has been loaded, while earlier fuel had 1.4550 or 1.4541 SS guide tubes and nozzles. In early fuel the spacer grids were made from Inconel 718, plated with nickel to facilitate brazing. PWRs now load fuel assemblies having Zircaloy-4 spacer grids, but usually with top and bottom spacer grids still made from nickel-plated Inconel 718. In addition to these main constructional materials, small amounts of high cobalt containing materials, StellitesTM and similar alloys, are used on wear surfaces in the primary circuit and CVCS. Estimated surface areas of the various alloys present in the primary circuit are dependent on the number of primary coolant loops and the use of Inconel or Zircaloy gridded fuel. All recent Siemens PWRs have the same type of steam generator.

2.3.2 Coolant Purification and Volume Control Systems

Changes in chemical composition and volume are carried out using the Primary Coolant Purification System (Figure 2-2, equivalent to the Chemical and Volume Control System, CVCS, and Boron Recycle System, BRS, in Westinghouse PWRs). The overall system consists of a number of sub-systems: the Level and Volume Control System, the Coolant Storage System, the Boric Acid and Demineralised Water Control System, the Chemical Control System, the Coolant Purification System, the Coolant Treatment System and the Coolant Degasification System. Associated with the system is the main coolant pump Seal Water Supply System. With the exception of the letdown section of the Level and Volume Control System, all components are located in the auxiliary building.

In the Level and Volume Control System, letdown is taken from the intermediate leg of one of the loops and is cooled progressively in a regenerative heat exchanger (“Konvoi” stations have two regenerative heat exchangers) and in two parallel non-regenerative heat exchangers. The pressure is then reduced by HP pressure reducing control valves to about 2 to 4 bar (as opposed to letdown orifices in Westinghouse PWRs). All these components are located in the

containment. The flow rate is normally controlled at between 18 and 36 m³ h⁻¹ (79.25/158.5 U.S. gpm, 5/10 kg s⁻¹, dependent on the station), while the maximum rate varies between 72 and 90 m³ h⁻¹ (317/396 U.S. gpm, 20 to 25 kg s⁻¹, max. 0.10 to 0.125 % of the primary coolant flow). Beyond the containment the letdown can be purified by passage through an ion-exchange resin bed and a reactor coolant filter and then, if required, routed to a thermal-vacuum degasser (i. e., a deaerator) operating at 50°C, -0.87 bar g, which is normally bypassed.

In early stations the letdown is then routed via a spray head into the gas space of the Volume Control Tank (VCT) and the charging flow is taken from the base of the VCT. In later stations (Grafenrheinfeld, Grohnde, Philippsburg 2, Brokdorf, Trillo) the VCT is mainly bypassed and operates with a much reduced throughput, receiving only the main coolant pump No. 1 seal leak-off flows and charging pump mini-flow returns (Fig. 2-3). In the “Konvoi” stations the seal water leak-off is routed to the coolant drains system and the VCT operates on a dead leg, receiving only the charging pump mini-flow returns. The charging flow is pumped by one or more charging pumps, which raise the pressure to about 180 bar, back to the cold legs of all of the loops of the primary circuit via the regenerative heat exchanger(s).

Part of the charging flow is diverted and filtered to provide a seal water injection flow to the No. 1 seals of the main coolant pumps. In earlier stations the main coolant pump seal leak-off return flows were routed to the letdown line downstream of the HP pressure reducing valves. At all later plants the main coolant pump seal leak-off flows are routed to the VCT water space.

Whilst basically similar, details of the Coolant Purification System differ from plant to plant. The main difference is the number and type of ion-exchange resin beds and reactor coolant filters installed. In later stations, the standard provision is two parallel mixed-bed ion-exchange filters (one in the saturated Li⁺/borate form (operational mixed-bed) and one in the H⁺/borate form (lithium removal bed)) followed by one or usually two cartridge type reactor coolant filters in parallel (originally intended to trap resin fines, but now used to remove fine particulate). At the early PWR Stade, an additional cation ion-exchange bed is installed upstream of the mixed-beds and at Obrigheim there are upstream reactor coolant filters. Radionuclides are mainly removed by the mixed-bed filters, either during normal operation or at shutdown (see Section 2.2), except for noble gases, which are removed using the degasser and discharged via the Gaseous Radwaste System. All except the earliest stations have a Gaseous Radwaste off-gas system operating at reduced nitrogen pressure, in which the off-gases are recirculated through a series of carbon delay beds and are vented only occasionally to the stack. For PWRs with hydrogen overpressurised VCTs, the VCT is not normally vented.

Chemical control of boric acid is normally carried out either by adding “blended” boric acid or water to the VCT inlet (when not bypassed), or by adding concentrated boric acid to the charging pump suction line. The two Boric Acid Tanks, the Boric Acid Batching Tank and the six Primary Coolant Storage Tanks are located in the auxiliary building. In “Konvoi” stations the Batching Tank has a capacity of 10 m³ and the two 7000 ppm B (4% boric acid) Boric Acid Tanks a capacity of 206 m³; the Boric Acid Tanks in pre-“Konvoi” stations hold 180 m³ boric acid. One Primary Coolant Storage Tank is always connected to the divert valve upstream of the VCT to collect boric acid letdown from the RCS. A second tank always contains demineralised (“deionat”) water for RCS dilution, or for mixing with 4% boric acid to produce boric acid

“blend” for RCS make-up. The remaining tanks are used as required during power operation, shutdown or start-up either to collect primary coolant, store primary coolant ready to supply the boron recycle evaporator, to collect distillate produced by the boron recycle evaporator, or to receive fresh demineralised water. The Boric Acid Tanks and the Primary Coolant Storage Tanks are connected to the off-gas system and are maintained under a reduced pressure inert nitrogen atmosphere.

Lithium addition is carried out using a chemical addition vessel and lithium removal by using the mixed-bed in the H^+ /borate form, unlike Westinghouse PWRs which use a cation bed. Other chemicals, hydrazine or hydrogen peroxide are also added using the chemical addition vessel.

In the earlier PWRs (Obrigheim, Stade, Borssele, Biblis A and B, Neckarwestheim 1, Unterweser and Gösgen) hydrogen is added via the gas space of the Volume Control Tank (VCT) as in Westinghouse PWRs. However, to minimise the risks of hydrogen explosions in tanks, all stations built since 1980 (Grafenrheinfeld, Grohnde, Philippsburg 2, Brokdorf, Trillo, Emsland, Isar 2 and Neckarwestheim 2) have hydrogen added via an injection system, followed by a de-training vessel, both located in the charging pump suction line, Figure 2-3 (2-6). A small flow of primary coolant ($\sim 0.3 \text{ kg sec}^{-1}$ at Neckarwestheim 2) is taken from downstream of the charging pumps and passes via the hydrogen injector to the charging pump suction line. The hydrogen concentration is controlled by adjusting the hydrogen gas pressure (8-10 bar) in the line connected to the injector, which controls the rate of hydrogen addition. In these later stations a nitrogen atmosphere of between 2 and 4 bar (absolute, normal pressure 2.3-2.7 bar) is maintained in the VCT to provide the required charging pump suction pressure. The VCT nitrogen purge is also connected to the off-gas system and is routed to the carbon bed delay system. Because the tanks are nitrogen blanketed and, in later stations, the VCT is pressurised with nitrogen, nitrogen is also normally present at 6-8 mg kg^{-1} (ppm) in the primary coolant, as is $\sim 1 \text{ mg kg}^{-1}$ ammonia formed by radiolysis in the core.

Boric acid letdown from the primary circuit can either be recovered for re-use or processed as liquid radwaste. The Coolant Treatment System is the equivalent of the Boron Recycle System (BRS) in Westinghouse PWRs and contains an inlet mixed-bed ion-exchange filter, a boron recycle evaporator and a degasser. As noted above, boric acid for recovery by evaporation is collected in one of the Primary Coolant Storage Tanks, distillate is collected in a second, whilst concentrated boric acid is returned to the Boric Acid Tanks. In Siemens stations, essentially all the boric acid is recovered.

2.3.3 Residual Heat Removal and Emergency Core Cooling Systems

Siemens PWRs have a combined Residual Heat Removal and Emergency Core-Cooling System. As noted above, four trains are installed in 4-loop stations (three in 3-loop stations), which are interconnected at Biblis A, but are separated at Biblis B and all later stations (2-1). The overall system as fitted in the “Konvoi” stations is shown in Figure 2.4. As noted above, the Flood Tanks and safety injection pumps are located in the outer containment annulus, while the Accumulators are located in the inner containment.

The four separate trains in the later 4-loop stations each have a high pressure injection pump (HPSIP), two Accumulators (one each connected to the hot and cold legs) and a low pressure injection pump (LPIP). The low- and high-pressure pumps of each train are connected to the Flood Tanks (borated water storage tanks, collectively equivalent to the RWSR) via suction lines. In “Konvoi” stations each train has a single Flood Tank (472 m³, >2200 ppm B; 2400 ppm B at Neckarwestheim 2 with 4.4% ²³⁵U and MOX fuel), which is part of the outer annulus structure; in earlier stations each train has two separate stainless steel Flood Tanks (2 x 194 m³). Another suction line, which is isolated during normal operation, links the containment sump to the LPIP. The HPSIP can also be switched to liquid in the containment sump, and under these conditions the LPIP acts as a booster pump. The discharge lines branch inside the containment into two branches, the hot- and cold-leg injection lines. The high-pressure injection sub-system is normally connected to the hot side via a self-actuated three-way valve, which switches the emergency core cooling flow from the hot leg to the cold leg in the event of a break in the hot-leg injection line.

In the 4-loop stations each of the eight Accumulators holds 34 m³ boric acid (>2200 ppm B; 2400 ppm B at Neckarwestheim 2), set to inject at a primary circuit pressure of <25 bar. As in Westinghouse PWRs, no action is required for the first 30 minutes of a LOCA (loss of coolant accident) and the HPSIP work at a zero-flow charging head of 110 bar, while each LPIP will produce a flow rate of ~330 kg s⁻¹.

2.3.4 Extra Boration System

The later stations have an Extra Boration System (emergency boration system) consisting of four small trains, each associated with one of the Emergency Core-Cooling trains (Figure 2-2). Each train has a small storage tank (17 m³ in “Konvoi” stations, 8 m³ in pre-“Konvoi” stations) containing 7000 ppm B. In shutdowns involving an ATWS (Anticipated Transient Without Scram), or when the Volume Control System is not available, the contents of the tanks are pumped into the primary circuit, normally via cold legs, but, if necessary, via the Pressuriser sprays. The injection lines can also be connected to the Flood Tanks to provide an additional core-cooling injection route.

2.3.5 Spent Fuel Pool Systems

The Spent Fuel Pool Cooling and Purification System consists of two sub-systems, the Spent Fuel Pool Cooling System and the Spent Fuel Pool Purification System (Figure 2-2). In “Konvoi” stations the purification system contains two pumps in parallel, a single mixed-bed ion-exchange resin, followed by two particulate filters in parallel; earlier stations are similar.

The reactor refuelling pool is normally filled via overhead sprays from the Flood Tanks. These are normally routed via the Spent Fuel Pool Purification System mixed-bed filter. The latter can also be used to purify the contents of the Flood Tanks.

2.3.6 Radioactive Liquid Waste System

The Radioactive Liquid Waste System in the 4-loop stations normally consists of five liquid radwaste storage tanks ($5 \times 70 \text{ m}^3$ in “Konvoi” stations), two liquid radwaste evaporators, one mixed-bed ion exchange filter and three control tanks ($3 \times 70 \text{ m}^3$ in “Konvoi” stations). Some stations do not include the mixed-bed filter. A schematic diagram of the system is shown in Figure 2-5. Similar plant is installed in the other Siemens PWRs.

In use, two of the Liquid Radwaste Tanks are used to collect more active liquid radwaste ($3.7 - 3.7 \times 10^3 \text{ Bq cm}^{-2}$), which is processed by one of the two evaporators. The other tanks are used for low level liquid waste ($<3.7 \text{ Bq cm}^{-2}$), as is the second evaporator. If necessary, chemical solutions can be added to any of the five Liquid Radwaste Tanks to adjust the pH.

Distillate from both evaporators is routed to the three control tanks from which it is discharged. If necessary, the contents can be recirculated through the mixed-bed ion exchange resin bed before discharge. Concentrate from the evaporators is routed to storage tanks (four 34 m^3 tanks in “Konvoi” stations), from which it is sent for encapsulation as solid radwaste.

2.4 References

- 2-1 H L Schnurer and H G Seipel, “The Safety Concept of Nuclear Power Plants in the Federal Republic of Germany” Nuclear Safety, Vol 24 (6), 743, 1983.
- 2-2 M Beer, R Güldner and E Weber, “Fuel Cycle Optimization for Pressurized Water Reactors”, Siemens AG Report, Power Generation Group, 1999 (Top Operation '99, Berlin Oct 24-26, 1999, atw – Internationale Zeitschrift für Kernenergie, 12, 733, 1999).
- 2-3 F Burtak and P Urban, “High-Burnup Fuel Assemblies Reduce Fuel Cycle Costs”, atw – Internationale Zeitschrift für Kernenergie, 8/9, 549, 2000.
- 2-4 R Roofthoof, M C Thiry, A Cascia, K Garbett, M Halin, E F Lillo, K-H Walter and M Zmitko, “Primary Circuit Chemistry of Western PWR and VVER Power Plants”, Unipede Report, 02004Ren9653, 1996.
- 2-5 A A Strasser, H J Schröder and K D Sheppard, “ Primary Water Chemistry, Fuel Rod Corrosion, and Crud Deposition in PWRs, A Comparison of European and U.S. Plant Performance”, EPRI Report EPRI TR-107255, 1996.
- 2-6 Kraftwerk Union AG, “Kraftwerk-Kennzeichensystem, Identification System for Power Plants”, 1986.
- 2-7 K Streit, W Rühle and G Enkler, “Operational Performance at the German Pre-Konvoi Philippsburg 2 NPP”, 1998 JAIF Int. Conf. on Water Chemistry in Nuclear Power Plants, Kashiwazaki City, Japan, 73, 1998.

**Table 2-1
Station Outputs and Core Upgrading for Siemens PWRs**

Station	First Critical	As Built		December 2000		Core Power uprate (%)
		MWth	MWe (gross)	MWth	MWe (gross)	
Obrigheim	September 1968	1050	340	1050	357	
Stade	January 1972	1892	662	1892	672	-
Borssele	June 1973	1365	477	1365	481	-
Biblis A	July 1974	3517	1204	3517	1225	-
Biblis B	March 1976	3733	1300	3733	1300	-
Neckarwestheim 1	May 1976	2495	855	2497	840 (j)	-
Unterweser	October 1979	3733	1300	3900 (a)	1410	4.47
Gösgen	January 1979	2806	970	3002 (b)	1020	6.99
Grafenrheinfeld	December 1981	3765	1300	3765 (c)	1345	-
Grohnde	September 1984	3765	1360	3900 (d)	1430	3.59
Philippsburg 2	December 1984	3765	1349	3950 (e)	1458	4.91
Brokdorf	October 1986	3765	1383	3765 (f)	1440	-
Isar 2	January 1988	3765	1370	3950 (g)	1475	4.91
Emsland	April 1988	3765	1314	3900 (h)	1400	3.59
Trillo	May 1988	3010	1041	3010	1066	-
Neckarwestheim 2	December 1988	3765	1316	3850 (i)	1365	2.26

(a) from 9/2000; (b) 2900 MWth from 1985; to 3002 MWth from 7/1993 (c) uprating planned; (d) 3850 MWth from 2/1990 to 12/1999; (e) 3803 MWth from 11/1991, 3850 MWth from 8/1992 to 10/2000; (f) application to increase to 3850 MWth (2.26%) rejected 1998; (g) 3850 MWth from 3/1991 to 11/1998, uprate in two stages completed 1/2000; (h) 3790 MWth from 2/1990 to 6/1991; 3850 from 8/2000 (i) 3850 MWth from 5/1991, will uprate to 3965 MWth in 2001; (j) after condenser retubing.

Table 2-2
Design Operating Conditions for Siemens PWRs

Station	Pressure (bar)	Temperature (°C)		
		T _{hot}	T _{cold}	T _{Ave}
Obrigheim	148	310	283	296.5
Stade	154	312	284	298
Borssele	155	317.5	292.5	305
Biblis A	155	313	283	298
Biblis B	155	319	288	303.5
Neckarwestheim 1	158	319.5	290.5	305
Unterweser	155	323	290	306.5
Gösgen	158	326.5	293.5	310
Grafenrheinfeld	158	326	291	308.5
Grohnde	158	326	291	308.5
Philippsburg 2	158	326	291	308.5
Brokdorf	158	326	291	308.5
Isar 2	158	326	291	308.5
Emsland	158	326	291	308.5
Trillo	158	326	293	309.5
Neckarwestheim 2	158	326	291	308.5

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Table 2-3

Compositions of Important Alloys in Contact with the Primary Coolant in Siemens PWR Primary Circuits

Alloy	Composition (Percent by Weight)								
	C	Si	Ni	Cr	Fe	Mn	Co	Others	Zr
1.4550 (a)	≤0.04	≤1	9/12	17/19	bal.	≤2	<0.2	Nb≥10xC (≤0.65)	-
1.4541 (a)	≤0.06	≤1	9/12	17/19	bal.	≤2	<0.2	Ti≥5xC (≤0.55)	-
Inconel 82 (b)	≤0.1	≤0.5	≥67	18/22	≤3	2.5/3.5	≤0.2	Nb=2/3, Cu≤0.5 Ti=0.75	-
Incoloy 800 (a)	≤0.03	0.3/0.7	32/35	20/23	bal.	0.4/1	<0.1	Ti≤0.6, Cu≤0.75 Al=0.15/0.45 Ti/C≥12 Ti/C+N≥8	-
Inconel 718	≤0.08	≤0.35	50/55	17/21	bal.	≤0.35	≤1/0.1	Cu≤0.3 Mo=2.8/3.3 Ti=0.65/1.15 Nb+Ta=4.75/5.5	-
Inconel X750	≤0.08	≤0.5	≥70	14/17	5/9	≤1	≤1	Ti=2.5/2.75 Nb=0.7/1.2 Al=0.4/1	-
Nickel Braze (c)	-	-	77	13	-	-	<0.1	P=10	-
Zircaloy-4 (d)	≤0.027	≤0.012	≤0.007	0.07/0.13	0.18/0.24	≤0.005	0.002	Sn=1.2-1.7 Fe+Cr=0.28/0.37	bal.
Stellite 6™ (e)	0.9/1.4	≤1.5	≤3	26/32	≤3	≤1	Bal.	W=3.6/6, Mo ≤1.5	-

- (a) Siemens specification.
- (b) Tubesheet clad; ASME quotes Co ≤0.15% when specified
- (c) Nickel braze for Inconel 718 grids (PWRs).
- (d) ASTM Standard
- (e) Other varieties of Stellites™ -type hard facing alloys also used.

Table 2-4
Surface Areas of Different Alloys in Siemens PWRs

Alloy	Component	Surface Area (m ²)					
		3-Loop		4-Loop			
		Neckar I	Gösgen	Standard 1300 MWe	Philipps-burg 2	Brokdorf	Konvoi
Stainless Steel	Core Internals	592	623	1126	1050	1126	1047
	RPV & Pressuriser Clad, Main Loop Pipework SG Channel Head Clad			719	670	670	672
	Main Coolant Pump Clad, 1.4313 Impeller, Diffuser	620 total	700 total	145	145	145	145
	Control Rod Drives	108	118	204	204	204	204
	Control Rod & Thimble Plugs	174.3	197.4	226	226	226	226
	Control Rod Guide Assemblies	294.8	355.2	340	340	340	340
	Fuel Assembly Nozzles, etc	146 (g)	146 (g)	321 (g)	321 (g)	321 (g)	357 (g)
	Fuel Assembly Guide Tubes/Plugs	998 (a)	1120 (a)	1404 (a)	1404(a)	1404 (a)	1404 (a)
	Auxiliary Systems	-	-	506	506	506	506
	Incoloy 800	SG Tubing	11655	15460	18155	21759	21659
Inconel 82	SG Tubesheet Clad	-	-	26.5	26.5	26.5	26.5
Inconel 718	Fuel Grids	660 (a)	754 (a)	727 (a)	727 (a)	727 (a)	727 (a)
	Control Rods	-	-	226	226	226	226
Inconel X750	Control Rod Drives, etc	36	36	17	17	17	17
Ni Braze	Fuel Grids	-	-	63 (a)	63 (a)	63 (a)	63 (a)
Zircaloy-4	Fuel Clad	-	-	9307	9307	9307	9307
Stellites™	Control Rod Drive Assemblies	0.77	0.83	1.46(f)	1.46(f)	1.46(f)	1.46(f)
	Reactor Pressure Vessel	1.19 (e)	1.28 (e)	1.62	0.06	0.06	0.06
	Main Coolant Pumps	0.87 (b)	1.72 (c)	2.92 (c)	1.2 (b)	0 (c)	0/0.3 (d)
	Auxiliary System Valves	?	?	5.8-6.5	1.10	1.2	0.71

- (a) Mainly replaced by Zircaloy-4 spacer grids and guide tubes. (b) Andritz pumps.
(c) KSB pumps, at Philippsburg area reduced to 0.2 m² on replacing RCP shafts.
(d) Isar 2 and Emsland Stellite™ free KSB pumps, Neckar II Andritz pumps (0.3 m²).
(e) Neckar I - Cobal 7™ and Stellite 6™; Gösgen - Castadur N 9080™ and Stellite 6™.
(f) Haynes 25™ (1.34 m², 49 % Co), Acrit Co-40™ (0.12 m², 67 % Co).
(g) Dependent on fuel elements.

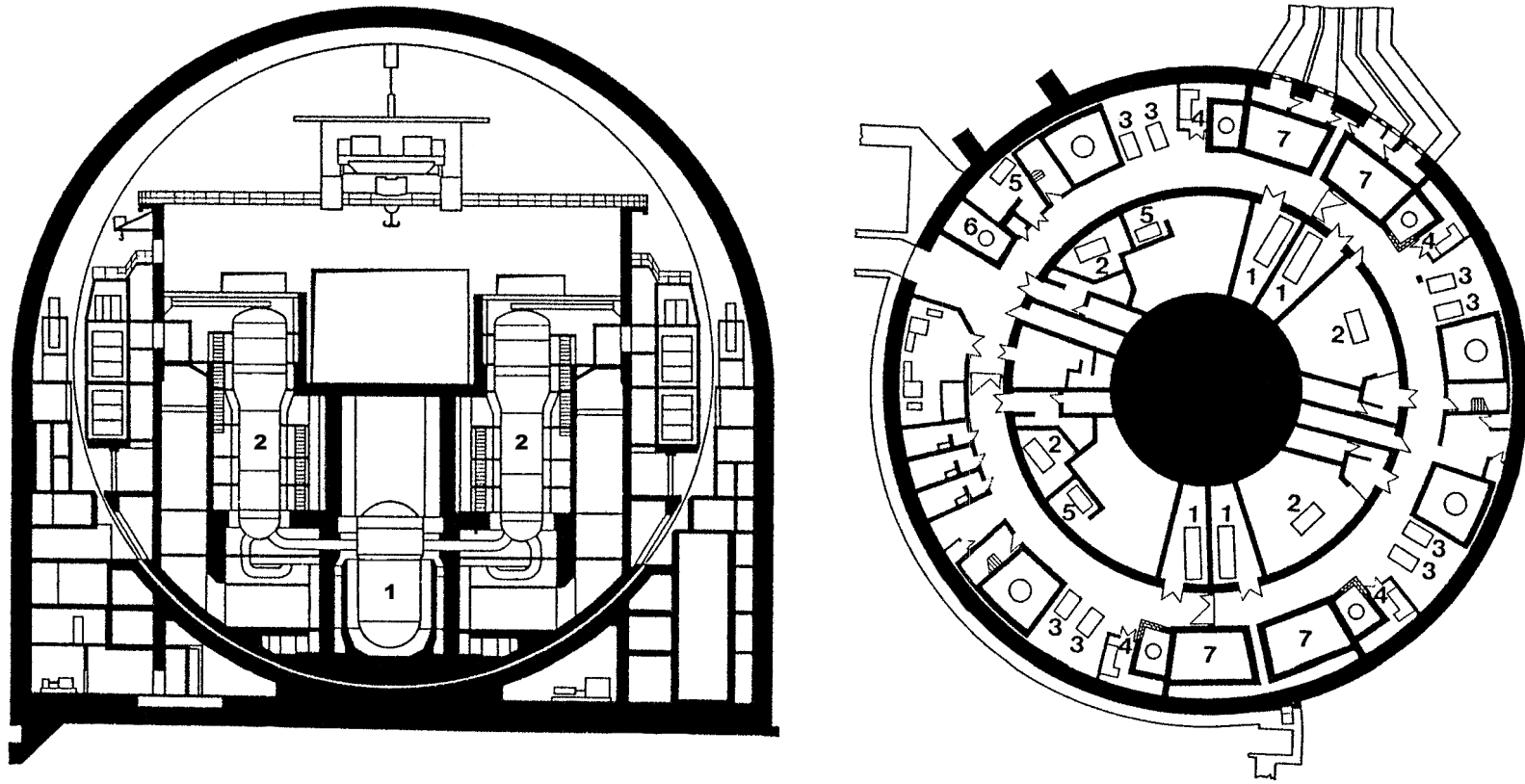


Figure 2-1
Layout of a "Konvoi" PWR Reactor

Left-Cross Section of the Reactor Building (1 - Reactor Pressure Vessel, 2 - Steam Generator)
Right-Outer Annulus at the 6m level (1 - Safety Injection Pump, 2 - Residual Heat Removal Pump
3 - Nuclear Component Cooling Pump, 4 - Extra Boration Pump, 5 - Spent Fuel Pool Cooling Pump
6 - Fuel Cool Heat Exchanger, 7 - Flood Tank)

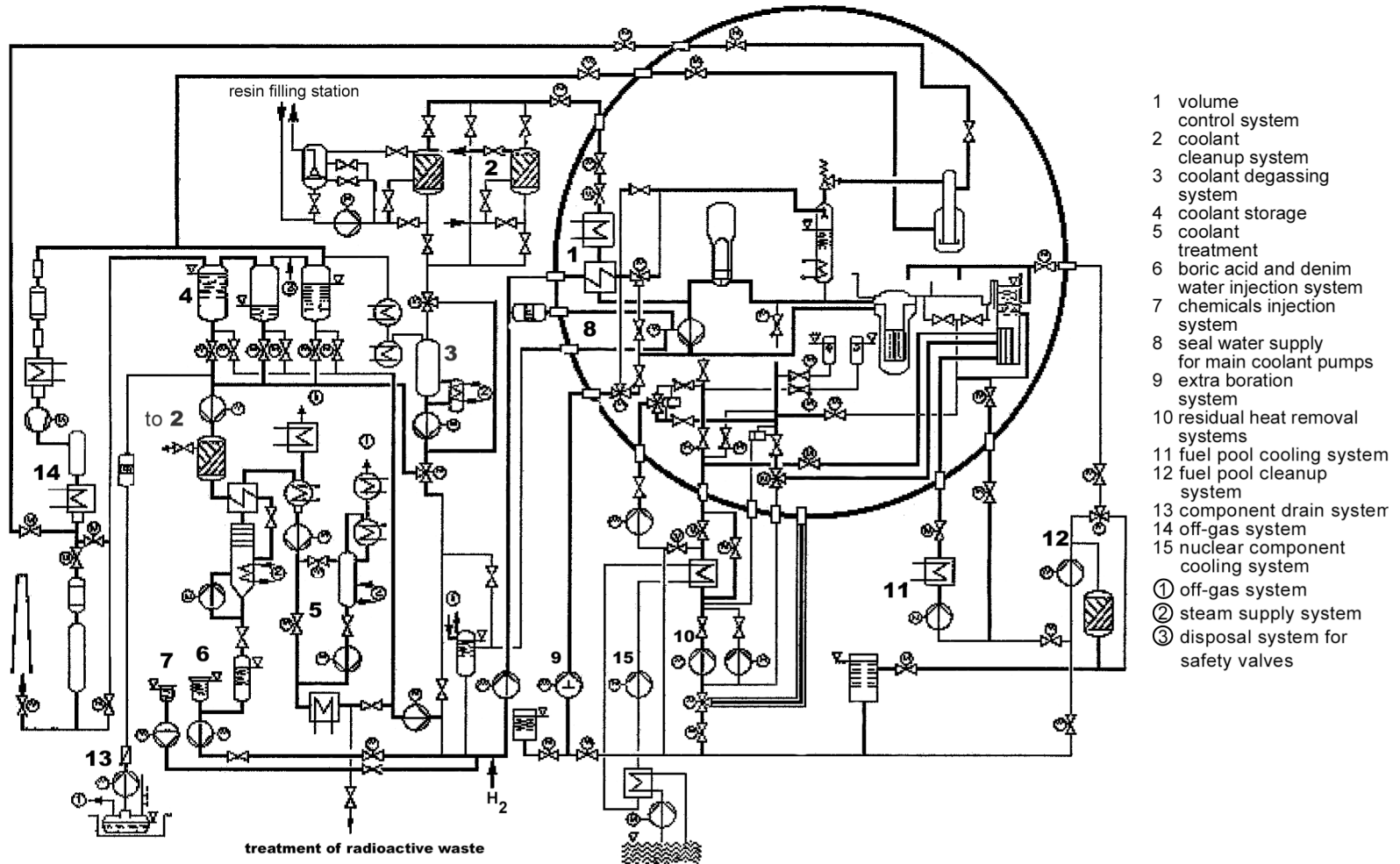


Figure 2-2
 Schematic Flow Diagram of the Primary and Nuclear Auxiliary Systems in a Siemens 1300 MWe PWR (2-4, 2-7)

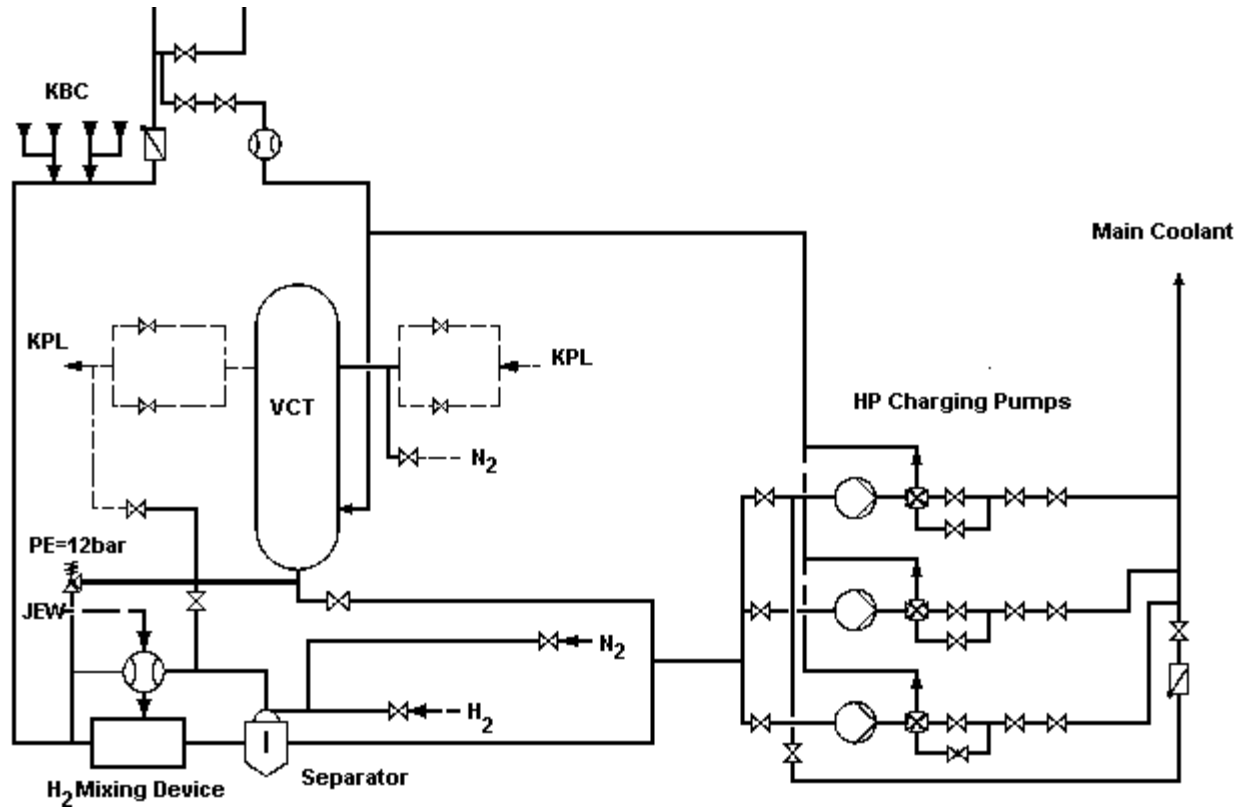


Figure 2-3
Schematic Flow Diagram of the Hydrogen Injection System in the CVCS of a Siemens 1300 MWe PWR (2-7)

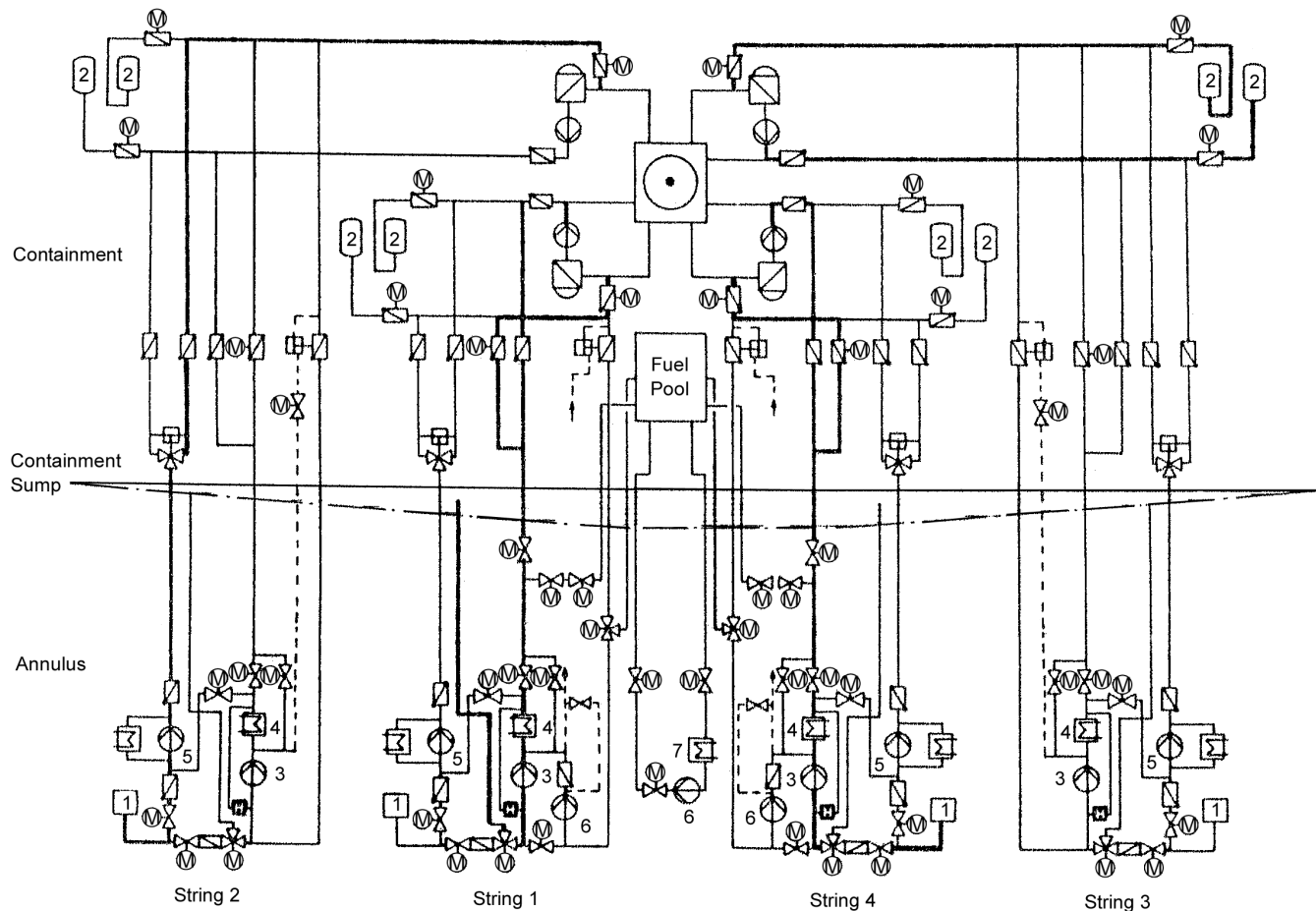


Figure 2-4
Schematic Flow Diagram of the Residual Heat Removal and Emergency Core-Cooling System in Siemens 1300 MWe PWRs

Each train is shown in bold in one of its possible operation modes; 1 – sump recirculation mode, 2 – high pressure safety injection, 3 – accumulator injection, 4 – low pressure injection. (1 – Flood Tank, 2 – Accumulator, 3 – Residual Heat Removal Pump (Low Pressure Injection Pump), 4 – Residual Heat Exchanger, 5 – High Pressure Safety Injection Pump, 6 – Spent Fuel Pool Cooling Pump, 7 – Spent Fuel Pool Heat Exchanger.)(2-1)

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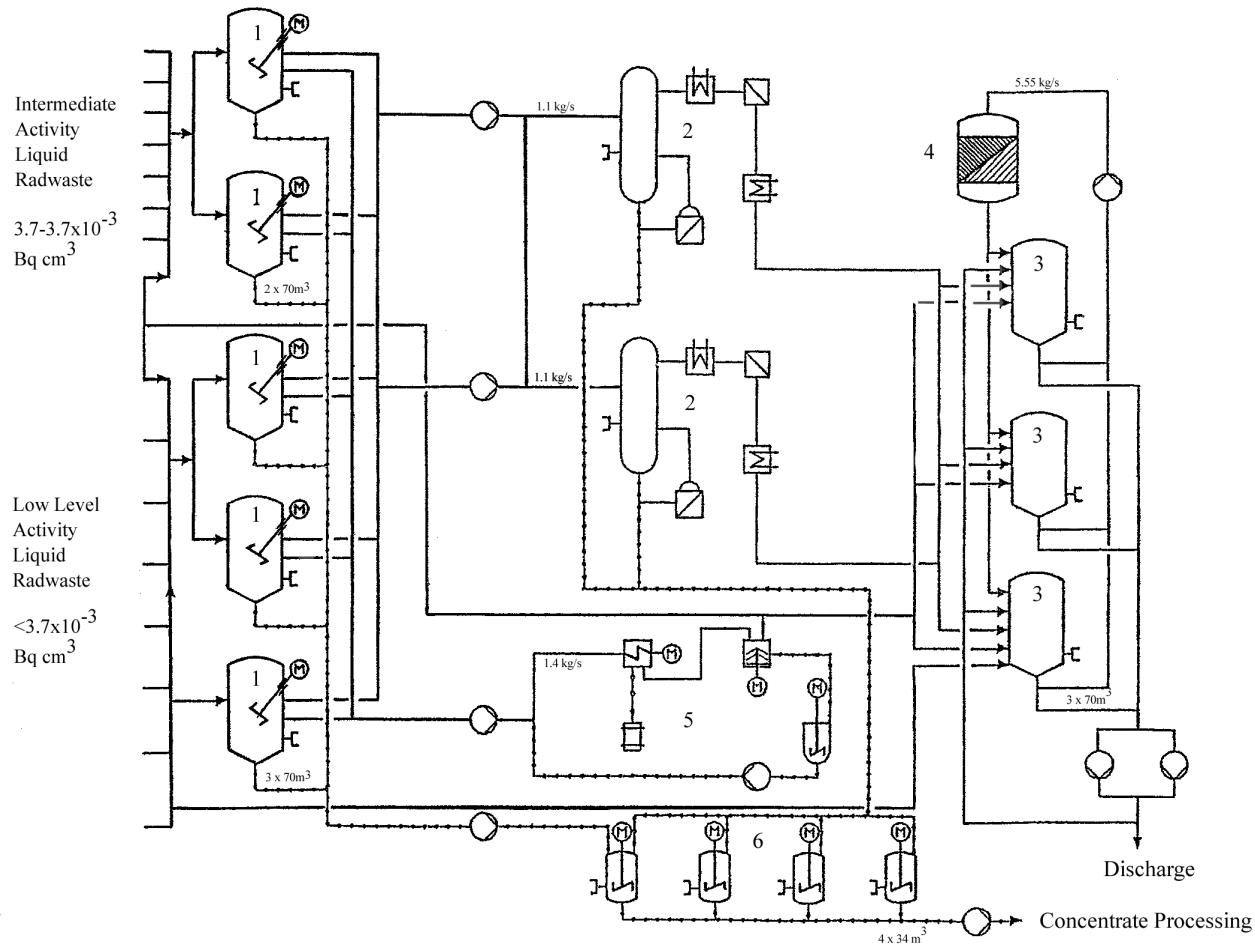


Figure 2-5
Liquid Radwaste System in a Siemens "Konvoi" PWR.

(1 – Liquid Radwaste Storage Tanks (2 High & 3 Low Activity), 2 – Evaporators (1 High & 1 Low Activity), 3 – Control Tanks, 4 – Mixed-Bed Filter, 5 – Chemical Treatment/Centrifuge Plant, 6 – Concentrate Storage Tanks

3

CHANGE TO ENRICHED BORIC ACID IN SIEMENS PWRs

The change to enriched boric acid (EBA) in Siemens PWRs has been completed successfully in most of the later stations (3-1 to 3-5). The principle reasons for the change have been outlined in Section 1, but are mainly the result of the decision to load MOX fuel and higher ^{235}U enriched fuel to give improved fuel economy. These changes result in increased rod powers, higher burn-ups and, possibly, longer fuel cycles, all requiring a higher boron reactivity worth to give the necessary reactivity control, especially for MOX fuel under cold shutdown conditions. Although the extra reactivity control could be achieved simply by increasing the volume and/or the concentration of natural boric acid, the scope for this is limited (finite storage tank capacities, finite boric acid solubility) and the more satisfactory approach is to change to EBA. Changing to EBA also gives the additional benefit of improving the primary coolant pH control, enabling the stations to operate at $\text{pH}_{300^\circ\text{C}} 7.2$ to 7.4 throughout a 12-month fuel cycle without increasing the lithium concentration above 2.0 ppm. Improved pH control should also give the secondary benefit of improved radiation field control, by virtue of the reduced corrosion product activity transport and deposition in the primary circuit. A final significant factor in the current use of EBA is that the cost of the 96 weight % ^{10}B boric acid supplied by Eagle-Pitcher that is used to increase the ^{10}B enrichment has fallen by 2.5 times since 1985 (in real terms) and currently is $\sim \$2.25 \text{ g}^{-1}$ of contained ^{10}B ($\sim \$0.37$ per gram as boric acid), or $\$2.16 \text{ g}^{-1}$ for 96 weight % ^{10}B . However, the actual cost, including shipping to Europe, for Siemens PWRs was somewhat lower, but still $> \$2 \text{ g}^{-1} \text{ }^{10}\text{B}$ (3-6).

3.1 General Principles

The following general principles have been applied to the change to EBA in all Siemens PWRs (3-1 to 3-3),

- (a) There should be no impact on plant safety at any time.
- (b) Plant operations should be impaired as little as possible.
- (c) There should be no extension of the plant outage for refuelling and maintenance.
- (d) An identical $^{10}\text{B}:^{11}\text{B}$ ratio should be produced in all systems.
- (e) The ^{10}B concentration should always be within the specified tolerance limits.
- (f) The change should be completed before loading the higher burn-up or higher power density fuel assemblies.
- (g) There should be minimum waste (liquid discharges and radwaste) production and minimum overall use of the costly 96 weight % ^{10}B boric acid.

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These are applied as follows (3-1 to 3-5, 3-7, 3-8),

- (1) For safety and operational reasons, it is mandatory that all systems containing boric acid (boron) must be changed to the same isotopic ratio. Partial changeovers, or variable $^{10}\text{B}:^{11}\text{B}$ ratios are not permissible because of the risk of a boron dilution accident.
- (2) There is no change in materials' compatibility, since the change does not alter the composition of the boric acid, merely its isotopic ratio. All safety systems remain at the same, or very similar, boric acid concentration.
- (3) The small increase in the primary coolant pH as a result of the lower overall boric acid concentration has a negligible effect on materials' properties and, probably, a beneficial effect on corrosion product behaviour. Alternatively, the same or, possibly, even a higher pH is achievable at BOC at a lower lithium concentration, thus reducing the risks from fuel clad corrosion and reducing radiation fields.
- (4) The change to EBA gives more reactivity control, without increasing the total volumes of boric acid solution stored in the various storage tanks in the plant.
- (5) By utilising the in-built redundancy conferred by the provision of a Residual Heat Removal and Emergency Core-Cooling train for each loop (i.e. four trains in a 4-loop plant and three trains in a 3-loop plant), is it possible to change each train to EBA in turn during normal operation, without compromising plant safety function margins.
- (6) The Spent Fuel Pool can similarly be changed to EBA during normal operation.
- (7) By overdosing the available parts of the Residual Heat Removal and Emergency Core-Cooling Systems, pipework sections that are isolated during normal operation can be changed to EBA when the systems are used during the subsequent shutdown. All parts of the system are then brought to the correct final isotopic ratio.
- (8) The Boric Acid Tanks are changed to EBA during stretch-out operation, when they can be isolated from the primary circuit.
- (9) The Boric Acid Batching Tank is used to prepare the 7000 ppm B 96 weight % ^{10}B boric acid solution used for the changes. Preparation of the 96% ^{10}B boric acid is only carried out when boron concentrations in the coolant are sufficiently low that further preparation of natural boric acid is not required (i.e. close to stretch-out operation).
- (10) The primary circuit and Coolant Purification and Volume Control Systems (i.e. the RCS and CVCS) are only changed when the circuits are borated during the shutdown for refuelling, using the contents of the Boric Acid Tanks, which have already been changed to 96 weight % ^{10}B boric acid.
- (11) The refuelling cavity is filled from the Flood Tanks (the equivalent of the RWST in Westinghouse PWRs), which have already been changed to ^{10}B boric acid.
- (12) 30% atom % (28.05 weight %) ^{10}B boric acid was selected as the optimum boric acid enrichment. In addition to it being sufficient to give the necessary additional boron reactivity worth, it produces minimum boric acid waste during the changeover.

- (13) If there is no change in total boron concentration, at 96 weight % ^{10}B boric acid the amount of EBA added to a tank is equal to the amount of natural boric acid that must be discharged to waste when it is converted to 30 atom % ^{10}B boric acid. Waste is, therefore, minimised (see Appendix A).
- (14) When a 7000 ppm 30 atom % (28.05 weight %) ^{10}B boric acid solution is added to a tank containing 2200 ppm B natural boric acid, minimum boric acid waste is produced if it is added as a 31% “blend” with demineralised water. (see Appendix B – strictly the optimum dilution is 31.4%; there are different optimum dilutions for other tank concentrations, e.g. 28.5% for 2000 ppm B and 41.5% for 2900 ppm B).

Two basic methods have been used in Siemens PWRs. The first is the so-called “compensation method”, the second is the “addition method”; these two options are summarised below,

- (i) In the “compensation method” part of the existing boric acid inventory in all the borated water systems is replaced by 96 weight % boric acid, but the replaced boric acid must either be discharged as waste water or reprocessed as liquid radwaste.
- (ii) In the “addition method” the total boron inventory in each borated water system (i.e. the boric acid concentration) is increased, which has the advantage that no waste is produced.

The “compensation method” has been used in the majority of cases and is used when discharge of waste water to the river (or estuary) is possible, (i. e., when the cost of full radwaste processing can be avoided). This approach minimises costs and the only radwaste produced is the liquid radwaste system mixed-bed ion-exchange resin used for the purification of the discharged boric acid (and then the additional discharge only contributes to the total usage of this bed).

The “addition method” has been used when any waste generation had to be avoided and when the boric acid tanks had sufficient spare capacity. It was used at Gösgen, which increased its ^{10}B isotopic ratio in stages, firstly to 21 atom % in 1996 and then to 28 atom % in 1997 (3-2); make-up to convert the various tanks was 31% 96 weight % ^{10}B boric acid (3-6), see above. Gösgen loaded 8 MOX assemblies in 1997, 28 in 1998 and 48 in 1999 (3-9) and currently is operating at a shutdown boric acid concentration of 2500 ppm B (3-7).

In both methods, the final ^{10}B : ^{11}B ratios were similar, although the actual target ratios at each individual station depended on the core design and were slightly different for each plant, and thorough mixing of the replaced or added 96% ^{10}B boric acid was both essential and mandatory.

In all cases, the actual ^{10}B concentrations achieved were slightly in excess of the licensed values, e.g. Grafenrheinfeld 31% (license >30 %), Gösgen 28.5% (28%), Brokdorf 27.5 % (>26%), Philippsburg 2 29.5% (>29%) and Isar 2 >30% (>30%).

3.2 Method of Changeover to EBA

The “compensation method” is a “drain and fill” method that was first used at Grafenrheinfeld (3-1); it was also used at Philippsburg 2 (3-8, 3-10) and will also be used at Neckarwestheim 2

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(3-7). Tables 3-1 and 3-2 gives the calculated changes in boric acid inventory for Grafenrheinfeld and for a “Konvoi” station, noting that Grafenrheinfeld changed to 30 atom % ^{10}B boric acid (28.05 weight %), while the data for the “Konvoi” station are for 27 atom % ^{10}B boric acid.

Note that the calculations for Grafenrheinfeld include the Residual Heat Removal System pipework, whereas those for the “Konvoi” station do not, although they do include an additional 50 m^3 unspecified waste boric acid discharge. Instead, in the “Konvoi” station it is assumed that the sections of the RHRS pipework will be brought to the correct isotopic ratio when the system is recirculated using the routine weekly surveillance test procedure. Any isolated pipework sections are covered by using a slightly higher tank dosing level of 27.5 atom % ^{10}B . In the “Konvoi” plant the initial concentration in the Spent Fuel Pool, Flood Tanks, etc. was initially 2400 ppm B, and the calculations and procedures allow for the extra addition of demineralised water to reduce the concentration to the original cold shutdown value.

In both cases 7000 ppm total B containing 96 weight % ^{10}B as boric acid was used as the ^{10}B concentrate. At Grafenrheinfeld the boric acid was added as a “blend” diluted to 31% ^{10}B boric acid with demineralised water, so that the boric acid was diluted to 2170 ppm total B, 96 weight % ^{10}B boric acid. This method was also used at Gösigen. In contrast, in the “Konvoi” station, where the overall boron concentration will be diluted from 2400 to 2200 ppm B, the 7000 ppm B ^{10}B boric acid solution is added first and is followed by an addition of demineralised water. Because of the dilution, the addition of 96 weight % ^{10}B boric acid is equivalent to it being added as a 25% “blend”, rather than the 31% “blend” used at Grafenrheinfeld. Appendix B gives the method of calculating the optimum dilutions to minimise waste boric acid discharges.

Table 3-3 gives the Eagle-Picher specification for 96 weight % ^{10}B boric acid.

In all the Siemens assessments natural boric acid is assumed to contain 19.8 atom % ^{10}B , equivalent to 18.34 weight % ^{10}B . Slightly different values are used in U.S. assessments and indeed the relative percentage of ^{10}B in natural boric acid varies, depending on its origin. For natural boric acid the molecular weight is normally taken as 61.83 and for boron it is 10.81. For 96 weight % ^{10}B boric acid the molecular weight is 61.07 and for boron it is 10.05.

3.2.1 Grafenrheinfeld and Other Siemens PWRs

At Grafenrheinfeld (3-1) the mass balance reproduced in Table 3-1 indicated that 6576 kg of 96 weight % ^{10}B boric acid (1082 kg 96 weight % ^{10}B , cost ~\$2.34m at $\$2.16\text{ g}^{-1}$) would have to be added to the borated water systems to bring them up to 30 atom % ^{10}B and that 432 m^3 of existing natural boric acid would have to be discharged to waste. The two main issues raised were, firstly, the method of changeover and, secondly, the method of disposing of the waste boric acid.

The changeover method selected was to change each of the four Residual Heat Removal/Emergency Core-Cooling trains (TH 10, 20, 30 and 40) and Extra Boration System trains (TW 10, 20, 30 and 40) in sequence during the three-month period before the shutdown at the end of the 15th cycle in May 1997. The change itself began in February 1997 and specifically

included the Flood Tanks and the Extra Boration System tanks of all four trains, the Spent Fuel Pool and the Boric Acid Tanks. It did not include the Residual Heat Removal System pipework, heat exchangers, etc. or the primary circuit, all of which were converted to 30 atom % ^{10}B as the primary circuit was borated during the shutdown. Neither did it include the Accumulators, which were converted during the shutdown. Although details of the exact sequence followed are not available, it is believed to be generally similar to that proposed for the "Konvoi" station, (Section 3.2.2) and to that used at Philippsburg 2 (3-8, 3-10), except that at both the "Konvoi" station and Philippsburg 2 the Accumulators will be/were changed during normal operation before shutdown.

Measurement and control of the isotopic ^{10}B : ^{11}B ratio was achieved using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) method developed by Eagle-Picher, while the 96 weight % ^{10}B boric acid was supplied to Grafenrheinfeld in 40 kg drums. The changeover method adopted was reported (3-1) to give a reproducible ^{10}B enrichment in all borated water systems. During the shutdown the primary circuit and Residual Heat Removal Systems were reported to be brought homogeneously up to 2200 ppm B containing 30 atom % ^{10}B five hours after the shutdown started.

Although no specific details have been given of the times taken to change the Residual Heat Removal/Emergency Boration System trains at Grafenrheinfeld before the shutdown, the general experience at the stations converted to EBA is reported (3-2, 3-4) to be,

- (1) No special replacements or mixing actions need be taken for pipework with a diameter <50 mm diameter in systems having a constant boric acid concentration (i. e., 2200 or 7000 ppm B, due to the mixing that occurs naturally as the solutions circulate).
- (2) Systems connected to the primary circuit with a variable boric acid concentration can be changed during circuit shutdown and cool down, avoiding any need for special mixing actions.
- (3) After adding 96 weight % ^{10}B boric acid to the Flood Tanks, the contents can be homogeneously mixed in 8-10 hours using the Residual Heat Removal System pumps and high pressure safety injection pumps.
- (4) The Spent Fuel Pool can be mixed in about 30 hours using the Spent Fuel Pool Purification System pump.
- (5) The contents of the primary circuit and the reactor cavity (refuelling pool) can be mixed using the Residual Heat Removal System pumps.

In all cases, a homogeneous mixture was deemed to have been achieved when the ^{10}B and total boron concentrations in two subsequent samples only changed within the tolerances of the analytical methods (ICP-MS and auto-titration, respectively).

Discharge of contaminated boric acid was identified as one of the problems and costs associated with the change to EBA. At Grafenrheinfeld 432 m³ of waste natural boric acid containing 1.04 x 10⁹ Bq active isotopes had to be processed. Two routes were available (3-1):

- (1) Evaporating the boric acid using the liquid radwaste evaporator to produce 28 m³ of boric acid concentrate containing 33000 ppm B, which could then be encapsulated. The cost of

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this option was estimated to be \$1.23m, including long-term storage. In addition, there was a high risk that the evaporator column would become encrusted.

- (2) Decontaminating the boric acid by ion exchange using the liquid radwaste system ion exchange resin bed, before discharging it to the local river (River Main) after dilution.

Based on site tests, which showed that essentially all ^{60}Co , ^{58}Co and ^{124}Sb activity (the main radionuclides present) in the boric acid would be removed by ion exchange, decontamination was selected as the discharge route. Agreement was reached with the local authorities for the discharge on condition that (a) the boric acid concentration in the discharge to the local river would be <1 ppm B (the German limit for drinking water) and (b) the total activity released would be <1 % of the permitted annual discharge. The actual results achieved are summarised in Figure 3-2 and show that both targets were met (~ 0.55 ppm B, 0.029 % of the annual discharge (limit 5.55×10^{10} Bq)), and that the only isotope not removed by ion exchange was the minor radionuclide $^{123\text{m}}\text{Te}$.

Similar results were obtained at Philippsburg 2 (3-8, 3-10), although here the discharge limits into the River Rhine were <1 ppm B and $<4 \times 10^5$ Bq. At Philippsburg 2 the saving from decontaminating the waste was estimated at \sim \$1m.

Although the overall cost at Grafenrheinfeld was not reported, the overall cost for Philippsburg 2 was \sim DM6m (\sim \$3m) (3-8), of which \sim \$2.3m would have been for the 96 weight % ^{10}B boric acid.

3.2.2 “Konvoi” Station

For the “Konvoi” station (Neckarwestheim 2) changing to 27 atom % ^{10}B , the mass balance given in Table 3-2 shows that 5577 kg 96 weight % ^{10}B boric acid (914.33 kg ^{10}B) must be added to the borated water systems, and that 675.2 m³ of natural boric acid must be discharged to waste. The estimated cost of the boric acid at $\$2.16 \text{ g}^{-1}$ 96 weight % ^{10}B is \$1.97m; other costs (e.g., waste processing and operational costs) are not available (3-7). Discharge is to the local river, after processing by ion exchange and dilution, and will have to meet similar limits to those imposed at Grafenrheinfeld.

In the “Konvoi” station the basic approach used is similar to that at Grafenrheinfeld, but with minor changes to improve the process and to minimise wastes. Again, the first stage is the sequential change of the four Flood Tanks (collectively equivalent to the RWST) and Residual Heat Removal/Emergency Core-Cooling trains, but including in this case the associated Accumulators. Next is the change of the Spent Fuel Pool and the four Extra (emergency) Boration System tanks. The Boric Acid Tanks are changed during stretch-out operation and, finally, the primary circuit and isolated sections of pipework are changed as the circuit is borated during the shutdown using ^{10}B boric acid from the Boric Acid Tanks. For all steps, 96 weight % ^{10}B boric acid is prepared in the normal Boric Acid Batching (mixing) Tank at a strength of 7000 ppm B. A simplified timeline for a changeover is given in Table 3-4 and further details are summarised below (3-7).

In the outline given below, the four primary circuit loops are designated JEC 10, 20, 30 and 40, and the associated Residual Heat Removal/ Emergency Core-Cooling System trains JNA 10, 20, 30 and 40, the Flood Tanks (RWST) JNK 10, 20, 30 and 40, the Accumulators JNG 11/12, 21/22, 31/32 and 41/42 and the Extra (emergency) Boration System trains JDH 10, 20, 30 and 40. The 96 weight % ^{10}B boric acid is prepared in the Boric Acid Batching (mixing) Tank KCB10. The stages are as follows.

Train 10 - Flood tank (JNK10), Accumulators (JNG11 and 12) and Residual Heat Removal Train (JNA10)

- (1) Purify the contents of the Flood Tank by recirculating them through the Spent Fuel Pool mixed-bed filter.
- (2) The calculated amount of waste natural boric acid (including that for the Accumulators) is discharged to the Liquid Radwaste Tanks designated for the change via the Spent Fuel Pool mixed-bed filter.
- (3) The Accumulator pressures are reduced to 6 bar and a small amount of boric acid (equivalent to the boric acid waste from the two Accumulators) is transferred from one of the Accumulators to the Flood Tank. The remaining Accumulator contents are emptied into the Flood Tanks of trains 30 and 40 using a temporary hose and pipework and the Accumulators are de-pressurised.
- (4) The Flood Tank is brought to 2200 ppm B 27.5 atom % ^{10}B boric acid by adding the calculated volumes of 7000 ppm B 96 weight % ^{10}B boric acid from the Boric Acid Batching Tank and demineralised water to the Flood Tank, and the contents recirculated until they are homogenous.
- (5) The Accumulators are refilled from the Flood Tank using the safety injection pump.
- (6) The volume transferred to the Accumulators is replaced with boric acid from the Flood Tanks of trains 30 and 40 and the Flood Tank again brought to 2200 ppm B 27.5 atom % ^{10}B boric acid by adding 7000 ppm B 96 weight % ^{10}B boric acid and demineralised water. The contents are recirculated until they are homogenous.
- (7) The Residual Heat Removal System pipework (excluding isolated sections) are brought to 27.5 atom % ^{10}B by recirculation using the weekly surveillance test procedure.

Train 20 - Flood tank (JNK20), Accumulators (JNG21 and 22) and Residual Heat Removal Train (JNA20)

These are changed to 27.5 atom % ^{10}B in an identical way to train 10.

Train 40 - Flood tank (JNK40), Accumulators (JNG41 and 42) and Residual Heat Removal Train (JNA40)

The change of this train is similar to trains 10 and 20, but reduces the amount of waste discharged by using some boric acid from the Spent Fuel Pool.

- (1) Purify the contents of the Flood Tank by recirculating it through the Spent Fuel Pool mixed-bed filter.

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- (2) The calculated amount of waste natural boric acid (including that for the Accumulators and the extra to be added from the Spent Fuel Pool) is discharged to the Liquid Radwaste Tanks designated for the change via the Spent Fuel Pool mixed-bed filter.
- (3) The Accumulator pressures are reduced to 6 bar. Accumulator JNG41 is emptied into the Flood Tank of train 30 (JNK30). The second Accumulator (JNG42) is also emptied, in part into the Flood Tank of train 30 and in part into the Flood Tank of train 40 (JNK40). In both cases temporary hoses and pipework are used. The Accumulators are then depressurised.
- (4) The Flood Tank is brought to 2200 ppm B 27.5 atom % ^{10}B boric acid by adding the calculated volumes of 7000 ppm B 96 weight % ^{10}B boric acid from the Boric Acid Batching Tank and demineralised water to the Flood Tank, and the contents recirculated until they are homogenous.
- (5) The Accumulators are refilled from the Flood Tank using the safety injection pump.
- (6) The volume transferred to the Accumulators is replaced by boric acid taken from the Flood Tank of train 30 and from the Spent Fuel Pool. The Flood Tank is again brought to 27.5 atom % ^{10}B boric acid by adding 7000 ppm B 96 weight % ^{10}B boric acid and demineralised water. The contents are recirculated until they are homogenous.
- (7) The Residual Heat Removal System pipework (excluding isolated sections) are brought to 27.5 atom % ^{10}B by recirculation using the weekly surveillance test procedure.

Train 30 - Flood tank (JNK30), Accumulators (JNG31 and 32) and Residual Heat Removal Train (JNA30)

These are changed to 27.5 atom % ^{10}B in a similar way to train 40.

Spent Fuel Pool (including the Transport Flask Pool) (FAB)

- (1) Purify the contents of the Spent Fuel Pool by recirculating them through the Spent Fuel Pool mixed-bed filter.
- (2) Boric acid is transferred to the Flood Tanks of trains 40 and 30 as part of the procedures given above. In both cases they are transferred via the Spent Fuel Pool mixed-bed filter and in each case the volume transferred is made up with demineralised water to reduce the concentration.
- (3) The remaining required volume of boric acid is discharged to the Liquid Radwaste Tanks designated for the changeover via the Spent Fuel Pool mixed-bed filter and demineralised water is added to reduce the concentration.
- (4) The Spent Fuel Pool is brought to 2200 ppm B 27.5 atom % ^{10}B boric acid by adding the calculated volume of 7000 ppm B 96 weight % ^{10}B boric acid from the Boric Acid Batching Tank. The contents are recirculated until they are homogenous using the Spent Fuel Pool Cooling System.

Extra (Emergency) Boration System Tanks JDH10-40

- (1) Drain the calculated amount of natural boric acid from each tank using a hose pipe and mobile pump, discharging the waste via the containment annulus building drains system to a Liquid Radwaste Tank.
- (2) Fill with the same volume of 7000 ppm B 96 weight % ^{10}B boric acid from the Boric Acid Batching Tank and recirculate until homogeneous.

Boric Acid Tanks KBC20 BB001 and BB002

- (1) Empty the Primary and Auxiliary Circuit Drains System Collection Tank to the Primary Coolant Storage System Tank designated to collect primary circuit letdown. Concentrate by evaporation and recover the letdown boric acid in the storage tanks to the Boric Acid Tanks.
- (2) Drain the calculated volume of boric acid from the Boric Acid Tanks using a hosepipe and mobile pump via the decontamination plant pipework to the Liquid Radwaste Storage Tanks.
- (3) Fill with the same volume of 7000 ppm B 96 weight % ^{10}B boric acid from the Boric Acid Batching Tank and recirculate until homogeneous.

Isolated Pipework Sections

During normal operation two sets of pipework section are isolated and cannot be changed to EBA. These are the pipe sections between the primary and secondary isolations to the primary circuit and the suction pipework between the primary circuit loops and the Residual Heat Removal System trains. Both are brought up to the required ^{10}B isotopic ratio during the shutdown when the Residual Heat Removal System is in use. The boric acid required for these sections is included in the concentrations of the systems already changed to EBA.

3.3 Direct Operational Consequences of the Change to EBA

Because of the approach used, the change to EBA only affects the operation of a limited number of systems. These are subsystems of the Coolant Purification and Volume Control System (the Boric Acid and Demineralised Water Control System, the Chemical Control System, the Coolant Purification System, Coolant Storage System and the Coolant Treatment System) and the Spent Fuel Pool Purification System.

3.3.1 Primary Circuit Boron Control

The change to EBA has a number of operational consequences, which are described below,

In Siemens PWRs boron concentration changes in the primary coolant to compensate for burn-up are carried out using the BODE-control system (Bor-Deionat control). This either adds 7000 ppm B boric acid, demineralised water, or a mixture of boric acid and demineralised water (“blend”) corresponding to the current boric acid concentration. In all instances the letdown from the primary circuit is diverted to one of the Primary Coolant Storage Tanks for recycling.

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In any cycle the actual boron concentration is directly linked to the core design and the boron reactivity worth of the boric acid. During 12-month cycles in Siemens PWRs using natural boric acid, the typical boron concentration at BOC for criticality is ~1000 ppm B and, after the initial reduction as xenon poison grows-in, the concentration reduces by ~3 ppm B d⁻¹ to compensate for burn-up. For 30 atomic % ¹⁰B boric acid these values are reduced to 660 ppm B and ~2 ppm B d⁻¹, respectively. In addition to any effect that these changes have on primary coolant pH, the reduced rate of change per day also reduces the daily amount of demineralised water that needs to be added. However, more importantly, it results in a much longer period at low boric acid concentration towards the end of the cycle (~30 %) and this, in turn, affects the addition of boric acid from the Boric Acid Tanks when “blend” is added. At low boric acid concentrations in Siemens PWRs, the boric acid addition rates fall below the minimum addition rate of the boric acid pumps and boric acid has to be added in a cyclic intermittent “pulse” type of operation. The change to EBA increases the length of time in the cycle when “pulse” boric acid pump operation has to be used.

Although the positions of control rods are not directly linked to the boric acid concentration, EBA has an indirect effect, since any increase in boric acid concentration will have a proportionately greater effect on the control rod positions with EBA, than with natural boric acid. In normal operation, the daily boric acid concentration change is specified so that it compensates for burn-up and essentially it has no effect on the control rod positions. However, when the rods have to be tested in routine surveillance tests, the additional affect of EBA on the rod positions has to be taken into account so that the Rod Insertion Limits (STAFAB in Siemens PWRs) are not exceeded. A similar consideration arises when the Extra Boration Systems are tested.

When demineralised water is added at start-up for the dilution to criticality, the change to EBA has no effect because the ratio between the shutdown and critical boron concentrations remains unchanged. However, the time taken to borate to shutdown concentrations is reduced, because of the higher boron reactivity worth of the 7000 ppm B solutions in the Boric Acid Tanks.

3.3.2 Borated Water and Other Systems

The change to EBA is reported to have no direct influence on the operation of the primary circuit (other than reactivity and pH control) or the letdown, charging and boric acid control functions of the Level and Volume Control System (CVCS) (3-7). In particular, the densities of natural and 96 weight % boric acid are not significantly different (1.0085 v. 1.0090 g cm⁻³ for 7000 ppm B at 30°C, respectively) and there is no physical effect on boric acid addition rates.

Of the auxiliary systems, there is no effect on the operation of the Reactor Refuelling Cavity (during refuelling), the Spent Fuel Pool, the Spent Fuel Pool Cooling and Purification Systems (other than resin replacement), the Residual Heat Removal and Emergency Core-Cooling System, the Extra (emergency) Boration System, the Primary and Auxiliary Circuit Drain Systems, the Containment and Auxiliary Building Drain Systems, the Liquid Radwaste System, or the Decontamination Plant. However, it is emphasised that leaks (e. g., sampling losses) from the systems are more costly than before due to the higher cost of EBA, compared with natural boric acid.

For other systems, there are some changes in the operation of the Boric Acid and Demineralised Water Control System, the Coolant and Spent Fuel Pool Purification Systems, the Coolant Degassification System, the Coolant Treatment System and the Coolant Storage System. Additionally, a number of non-borated water systems could be affected.

Boric Acid and Demineralised Water Control System

The direct operation of the Boric Acid Tanks and the Primary Coolant Storage Tank(s) containing demineralised water are not affected by the change to EBA. However, the operation of the Boric Acid Batching Tank is affected by virtue of the need to control the correct ^{10}B isotopic ratio of the EBA. This requires strict segregation and control of natural boric acid and 96 weight % ^{10}B boric acid storage, careful control during mixing and the avoidance of spillage of the costly 96 weight % ^{10}B boric acid. As with other systems, costs of sampling the tanks and leakage are proportionately higher.

Coolant and Spent Fuel Pool Purification Systems

The normal operation of the Coolant Purification System is not affected by the changeover to EBA. However, potentially there could be an effect when a new mixed-bed filter equilibrated at a different boron concentration is aligned, or when a resin bed is discharged to waste. The former is a well-known problem and is easily solved by re-equilibrating the bed fully before it is finally aligned. However, the effect on reactivity for each ppm B difference in concentration will be greater than before the change to EBA, and could create problems. The latter may occur initially if the rinsing operation contaminates the new mixed bed filter with some natural boric acid present in the resin transfer system, causing a small reduction the ^{10}B ratio in the primary coolant. However, any effect is small compared with natural ^{10}B burn-out during the cycle and is automatically compensated for by the normal reactivity control. Replacement of the cartridge filters fitted downstream of the mixed-bed filters will inevitably cause the irrecoverable loss of some EBA.

In the Spent Fuel Pool Purification System, the replacement of the mixed-bed filter and the resin catcher cartridge filter may similarly cause some loss of EBA. For the mixed-bed filter, flushing a new bed to the Primary Coolant Storage Tanks before it is aligned will avoid reactivity changes in the Spent Fuel Pool. Although losses of EBA could be reduced by flushing the mixed bed filter with demineralised water, this is not carried out as it releases activity back into the recovered boric acid.

Coolant Degassification System

Potentially, faulty operation of the CVCS degasser can deborate the coolant being treated. With EBA the effect of such faulty operation on reactivity control is greater. The addition of demineralised water has no effect, because of the unchanged distillate (deionat) volume in the evaporator sump. Most Westinghouse PWRs do not have CVCS degassers and would not be subject to this type of fault.

Coolant Treatment System

Change to Enriched Boric Acid in Siemens PWRs

Since Siemens PWRs recover essentially all boric acid, operation of the Coolant Treatment System (i. e., Boron Recycle System) evaporator and degasser are significant routes for ^{10}B losses from the system. In normal operation at higher boron concentrations, operation of the evaporator after the changeover to EBA is not significantly different. However, at lower boron concentrations, residual boron concentrations in the distillate are proportionately higher and there is, therefore, the potential for greater boron losses. Moreover, these conditions exist for a longer period in an EBA cycle than in a natural boric acid cycle. Even though the typical distillate concentration is ~ 0.3 ppm B with natural boric acid, a limit of <1 ppm B is applied after the change to EBA on economic grounds. There are no direct effects on the operation of the Coolant Treatment System degasser.

Coolant Storage System

Because of the smaller initial critical boron concentration at BOC with EBA (typically 600-700 v. 1000 ppm B), the start-up demineralised water demand is higher than in a natural boric acid cycle. For 27-30 % ^{10}B boric acid, more than three of the six Primary Coolant Purification Tanks must be filled with demineralised water (or recovered distillate) at start-up. The normal Siemens specification is that four tanks should contain demineralised water and, therefore, the actual requirement is unchanged.

Non-Borated Systems

A number of additional systems can be exposed to boric acid in exceptional circumstances. These are the Seal Water Supply System (supplying seal water to pumps in the various borated water systems), the Nuclear Component Cooling Water Systems, the Gaseous Radwaste System and the Steam Generator Blowdown System. There are no direct operational consequences on the operation of these systems from the change to EBA, however, any leaks (e. g., steam generator tube leaks) will be more costly.

3.3.3 Impact of EBA on Primary Coolant pH

For stations operating with natural boric acid, increasing the boron concentration (e.g. when changing to longer cycle lengths) inevitably results in a lower primary coolant pH, especially at BOC, which, in turn, is detrimental for activity transport and will cause radiation fields to rise. To counteract the fall in pH, the lithium concentration can be increased, but this is not allowable in Siemens PWRs because of the risk of increased Zircaloy-4 corrosion. These considerations indicate that both low pH and high lithium concentrations are undesirable, especially in Siemens PWRs where the upper lithium concentration is more restricted than in U.S. PWRs (see Section 1). The link between boron (boric acid) concentration and lithium concentration is shown in Figure 3-3.

Both problems can be solved by changing to EBA, which has several obvious water chemistry advantages (3-2, 3-3). Firstly, it enables a higher primary coolant pH to be achieved at BOC. Secondly, it enables the co-ordination pH to be reached earlier in the cycle. Finally, it permits operation at a higher pH, if necessary, during the co-ordinated pH phase of the cycle. These options are illustrated in Figure 3-4, which, for example, shows that while $\text{pH}_{300^\circ\text{C}} 7.4$ is achieved

at ~300 ppm B for all enrichments, this concentration is only reached after ~67% of the cycle with natural boric acid, compared with ~50% of the cycle with 30 atom % ^{10}B boric acid (taking the BOC concentration as 1000 ppm B for natural boron and 700 ppm B for 30 atom % ^{10}B boric acid).

3.4 Operational Results

After the change to EBA, station operators have reported few, if any, significant chemistry or operational control problems. The reported experience is summarised below.

pH Control

In terms of pH control, the most obvious effect has been the reduction in the boron concentration at the start of the fuel cycle and the consequent increase in $\text{pH}_{300^\circ\text{C}}$ during the initial part of the cycle. For example, at Grafenrheinfeld (3-1), the boron concentration at the start of its first EBA cycle (cycle 16) was reported to be ~600 ppm B, compared with ~1000 ppm B normally.

Comparable changes have been found at other stations. Figures 3-5 to 3-8 show boron, lithium and $\text{pH}_{300^\circ\text{C}}$ values for the final two cycles with natural boric acid (cycles 12 and 13) and the first two cycles with EBA (cycles 14 and 15) at Philippsburg 2 (3-8). With natural boric acid BOC boron concentrations were ~1080 and 1025 ppm B for cycles 12 and 13, respectively, and the BOC pHs were $\text{pH}_{300^\circ\text{C}}6.95-7.0$. In each cycle the co-ordination pH of $\text{pH}_{300^\circ\text{C}}7.4$ was reached when the boron concentration had fallen to ~300 ppm B, which was after about seven months operation. In contrast, after the change to EBA, the BOC boron concentrations were ~700 and 800 ppm B for cycles 14 and 15, respectively, and the BOC pHs were $\text{pH}_{300^\circ\text{C}}7.1-7.15$. In these cycles $\text{pH}_{300^\circ\text{C}}7.4$ was reached after about four and a half to five months operation, when the boron concentration had again fallen to ~300 ppm B.

Whilst the changes observed have been relatively small, due to the low EBA enrichment, they are still expected to have a long term impact on radiation fields, and to reduce both radiation fields and radiation exposure.

Chemistry Control

No significant changes to the normal chemistry control of the boric acid concentration have been required. After the change to EBA the normal chemistry control is performed as follows:

- (1) In Siemens PWRs, boric acid in the primary coolant is determined semi-continuously using a Metrohm on-line auto-titrator, normally at a frequency of once per hour, and the results are displayed in the control room. The analysis frequency is unaffected by the change to EBA. Further, since ^{10}B burn-up during an EBA cycle is identical to that during a natural boric acid cycle, and since ^{10}B burn-up does not significantly affect reactivity control via changes in boric acid concentration even when load always remains at 100% power, no change in the way the autotitrator is used is required (3-8).
- (2) The ^{10}B concentration in the primary coolant is normally measured at monthly in laboratory samples (although it has been suggested that quarterly measurements would be sufficient

Change to Enriched Boric Acid in Siemens PWRs

(3-8)). Generally, the isotopic ratio is measured by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) (3-11), but at one plant it is measured by a LAMBO (Laboratory Boron Concentration Measuring System) instrument. The latter is a laboratory neutron absorption instrument developed by Siemens. Although Siemens have developed a continuous on-line version of the neutron absorption instrument (COMBO – Continuous Boron Concentration Measuring System) (3-12) it has not been used. Experience shows that it is not necessary to measure the isotopic ratio at a higher frequency.

- (3) There are no significant changes to the analytical frequencies for other circuits.

Radionuclide Behaviour

No significant changes in radionuclide concentrations or primary circuit radiation fields have been observed. The observations are:

- (1) In the absence of fuel leaks, it has been suggested that an increase in tritium should occur due to the higher ^{10}B concentration via the $^{10}\text{B}(n,2\alpha)^3\text{H}$ reaction (3-1). However, since the ^{10}B concentrations in the coolant will be identical for both natural boric acid and EBA operation, no change in tritium production is expected and there has been no significant increase in the tritium concentration in the primary coolant.
- (2) So far there has been no change in primary coolant ^{60}Co concentrations or primary circuit radiation fields. Although such effects are predicted (see above), it is believed that they will only become apparent after several years' operation.

Impact on Plant Systems and Components

No adverse effects have been observed on any plant system or component exposed to EBA.

EBA Losses

It is the general experience that the avoidance of primary circuit leaks is the most important factor in minimising the ongoing costs of EBA operation (3-8).

In the majority of Siemens PWRs, all normal primary and auxiliary system leakage or letdown is recovered and recycled, and there is essentially no primary to secondary circuit leakage from damaged steam generator tubes. If discharges to the building drains systems are also minimised the majority of the losses, other than that due to ^{10}B burn-out, will be due to sampling, which are processed by the Liquid Radwaste System. ^{10}B burn-out is estimated to be ~ 10 kg ^{10}B per cycle (i.e. ~ 1 % of the initial inventory per cycle). When boric acid losses are minimised, it is found that the ^{10}B concentration in the primary circuit decreases by ~ 10 % per cycle, e.g. reducing ^{10}B from 28 % to 25 %, which is equivalent to ~ 13 kg ^{10}B per cycle. Note, however, that in practice any change due to burn-out becomes insignificant after refuelling, when the primary coolant mixes with the contents of the reactor refuelling cavity.

Most of the reduction in the ^{10}B enrichment is due to burn-out via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction, but the make-up requirement is clearly dependent on the magnitude of the losses from the borated water systems. It has been reported that the actual make-up requirements vary between 13 and 55

kg ^{10}B per cycle, with only 13 kg reported for Brokdorf and Gösgen (3-7), 50 kg at Grafenrheinfeld (3-9) and 55 kg at Philippsburg 2 (3-9). The replacement cost at Philippsburg 2 was quoted as ~\$100,000 per cycle. It should be noted that both Brokdorf and Gösgen operate with effectively no inadvertent boric acid losses during a cycle, and again that Siemens PWRs are fitted with plant drain systems to minimise non-recoverable boric acid losses.

3.5 References

- 3-1 K-G Seifert and J Florinski, "Operation with Enriched Boric Acid in the Nuclear Power Plant Grafenrheinfeld", 1998 JAIF Int. Conf. on Water Chemistry in Nuclear Power Plants, Kashiwazaki City, Japan, 516, 1998.
- 3-2 K Streit, W Rühle and G Enkler, "Operational Performance at the German Pre-Konvoi Philippsburg-2 NPP", 1998 JAIF Int. Conf. on Water Chemistry in Nuclear Power Plants, Kashiwazaki City, Japan, 73, 1998.
- 3-3 R Riess, N Henzel and T Marchl, "Use of B^{10} Enriched Boric Acid in Siemens PWRs", 4th Int. Seminar on Primary and Secondary Side Water Chemistry of Nuclear Power Plants, Balatonfüred, Hungary, September 1999.
- 3-4 U Staudt and T Marchl, "Field Experience with B-10-Enriched Boric Acid", Water Chemistry of Nuclear Reactor Systems 8, BNES, Vol 1, 45, 2000.
- 3-5 W Rühle, "Water Chemistry in BWR and PWR Nuclear Power Plants", Power Plant Chemistry, Vol 1, 5, 1999.
- 3-6 J M Hall and R Surmann, Eagle-Pitcher Technologies, Personal Communications, 2001.
- 3-7 K-H Walter, Personal Communication, 2001.
- 3-8 W Rühle, Personal Communication, 2001.
- 3-9 Hauptableitung für die Sicherheit der Kernanlagen (HSK, Swiss Nuclear Inspectorate), Annual Reports, 1995 to 1999.
- 3-10 R J Borland, "Trip Report for Visit to German PWRs to Discuss Implementation of Enriched Boric Acid", FirstEnergy Memorandum, July 1999.
- 3-11 M Bolz, W Hoffmann and W Rühle, "Bestimmung des Isotopenverhältnisses von $^{10}\text{B}/^{11}\text{B}$ ", VGB Konferenz Chemie in Kraftwerk, Essen, Paper N3, 1997.
- 3-12 K Nopitsch, H Bauer, F Schindhelm, K H Wiening and F J Stemmer, "Kontinuierliche Messung der Bor 10 -Konzentration in DWR-Kreisläufen", VGB Konferenz Chemie in Kraftwerk, Essen, Paper N2, 1997.

Change to Enriched Boric Acid in Siemens PWRs

Table 3-1
Calculated Mass Balance for the Changeover of Grafenrheinfeld to 30 atom % (28.05 weight %) ¹⁰B

System	Vessel	Initial Natural Boric Acid (18.34 weight %) Concentration (ppm B)	System Volume (m ³)		Additions Required (m ³)		Volume Discharged to Waste (m ³)	Amount Added (kg)	
			Maximum Volume	Usable Volume	96 weight % ¹⁰ B	Demineralised Water		As 96 weight % ¹⁰ B boric acid (a)	As 96 weight % ¹⁰ B (plus 4 weight % ¹¹ B)
Residual Heat Removal System	TH10	2200	388.0	339.5	15.1	33.4	48.5	650.2 (612.0)	107.0
	TH20	2200	388.0	339.5	15.1	33.4	48.5	650.2 (612.0)	107.0
	TH30	2200	388.0	339.5	15.1	33.4	48.5	650.2 (612.0)	107.0
	TH40	2200	388.0	339.5	15.1	33.4	48.5	650.2 (612.0)	107.0
	Total			1552.0	1358.0	60.4	133.6	194	2600.8 (2448.0)
	Pipework	2200	52.0	45.5	2.0	4.5	6.5	86.3 (81.2)	14.2
Accumulators	TH16	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH17	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH26	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH27	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH36	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH37	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH46	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	TH47	2200	34.0	29.8	1.3	2.9	4.2	55.9 (52.6)	9.2
	Total		272.0	238.4	10.4	23.2	33.6	447.2 (420.8)	73.6
Extra Boration System	TW10	7000	8.0	7.0	1.0	0	1.0	43.1 (40.6)	7.1
	TW20	7000	8.0	7.0	1.0	0	1.0	43.1 (40.6)	7.1
	TW30	7000	8.0	7.0	1.0	0	1.0	43.1 (40.6)	7.1
	TW40	7000	8.0	7.0	1.0	0	1.0	43.1 (40.6)	7.1
	Total			32.0	28.0	4.0	0	4.0	172.6 (162.4)
Spent Fuel Pool	-	2200	1373.0	1201.4	53.4	118.2	171.6	2300.0 (2165.0)	378.5
Boric Acid Tanks	-	7000	180.0	157.5	22.5	0	22.5	969.8 (912.3)	159.6
TOTAL			3461.0	3028.8	152.7	279.5	432.2	6576.1 (6189.9)	1082.2

Notes: (a) The values in parentheses are the original values given in Ref. 3-1. However, they were incorrectly scaled using the values for natural boric acid.

(b) Tanks TH10-40 are the Flood Tanks, TH16-47 are the Accumulators and TW10-40 are the Emergency Boration System Tanks (see Sections 2.3 and the Glossary). The four loops in all Siemens stations are designated 10, 20, 30 and 40.

Table 3-2
Calculated Mass Balance for the Changeover of a “Konvoi” Station to 27 atom % (25.16 weight %) ¹⁰B

System	Initial Value				Target Value					Changes		
	Volume (m ³)	Concentration (ppm B)	Initial ¹⁰ B (atom %)	Initial ¹⁰ B (weight %)	Volume (m ³)	Concentration (ppm B)	Target ¹⁰ B (atom %)	Target ¹⁰ B (weight %)	Equivalent natural ppm B	Waste Volume (m ³)	Mass ¹⁰ B added (kg)	Mass ¹⁰ B boric acid added (kg) (a)
Accumulators	272	2400	19.81	18.34	272	2200	27.50	25.64	3076	46.56	56.82	347
JNG10	68	2400	19.81	18.34	68	2200	27.50	25.64	3076	11.64	14.20	87
JNG20	68	2400	19.81	18.34	68	2200	27.50	25.64	3076	11.64	14.20	87
JNG30	68	2400	19.81	18.34	68	2200	27.50	25.64	3076	11.64	14.20	87
JNG40	68	2400	19.81	18.34	68	2200	27.50	25.64	3076	11.64	14.20	87
Flood Tanks	1889	2400	19.81	18.34	1889	2200	27.50	25.64	3076	323.25	394.60	2407
JNK10	472	2400	19.81	18.34	472	2200	27.50	25.64	3076	80.84	98.65	602
JNK20	472	2400	19.81	18.34	472	2200	27.50	25.64	3076	80.84	98.65	602
JNK30	472	2400	19.81	18.34	472	2200	27.50	25.64	3076	80.84	98.65	602
JNK40	472	2400	19.81	18.34	472	2200	27.50	25.64	3076	80.84	98.65	602
Spent Fuel Pool	1336	2400	19.81	18.34	1336	2200	27.50	25.64	3076	228.69	279.08	1702
Extra Boration System	68	7000	19.81	18.34	68	7000	27.50	25.64	9787	6.52	45.62	278
JDH10	17	7000	19.81	18.34	17	7000	27.50	25.64	9787	1.63	11.41	70
JDH20	17	7000	19.81	18.34	17	7000	27.50	25.64	9787	1.63	11.41	70
JDH30	17	7000	19.81	18.34	17	7000	27.50	25.64	9787	1.63	11.41	70
JDH40	17	7000	19.81	18.34	17	7000	27.50	25.64	9787	1.63	11.41	70
Boric Acid Tanks KCB20	206	7000	19.81	18.34	206	7000	27.50	25.64	9787	19.74	138.21	843
TOTAL	-	-	-	-	-	-	-	-	-	675.20 (b)	914.33	5577

Notes: (a) As 96 weight % ¹⁰B boric acid

(b) Includes 50.46 m³ unspecified waste.

(c) Tanks JNK10-40 are the Flood Tanks, JNG10-40 are the Accumulators and JDH10-40 are the Emergency Boration System Tanks (see Sections 2.3 and the Glossary). The four loops in all Siemens stations are designated 10, 20, 30 and 40.

Change to Enriched Boric Acid in Siemens PWRs

Table 3-3
 Specification for 96 weight % ¹⁰B Boric Acid

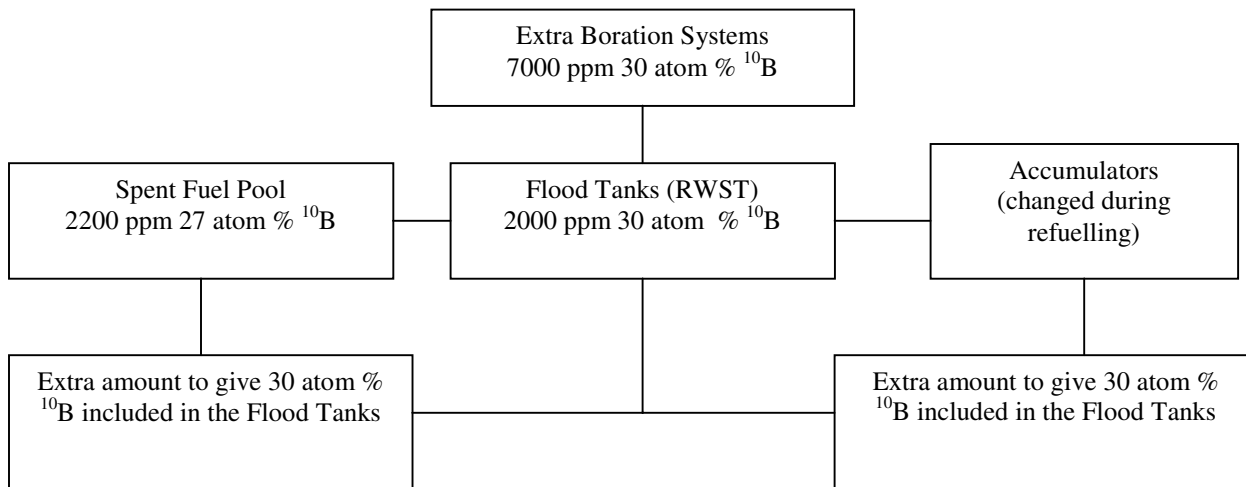
Parameter	Concentration
Isotopic Analysis	
Weight % ¹⁰ B	96 % minimum
Impurities	
Chloride	< 0.1 ppm
Fluoride	< 0.1 ppm
Phosphate	< 0.5 ppm
Sulphate	< 0.1 ppm
Silver	< 0.02 ppm
Calcium	< 1.0 ppm
Iron	< 1.0 ppm
Sodium	< 1.8 ppm
Heavy Metals (Pb)	< 0.7 ppm
Water Insolubles	< 10 ppm

Table 3-4
Timeline for the Change to EBA in a “Konvoi” Station

Item	Activity	Duration (days)	Days from Shutdown	
			Start	End
1	Planning of measures for the ¹⁰B changeover	56	-352	-296
	Calculation of specific amounts to be dosed into the tanks	19	-344	-325
	Preparation of the technical procedures for the changeover	19	-344	-325
	Preparing the alteration notifications	19	-344	-325
	Transmitting the alteration notifications to the safety authorities	0	-325	-325
	Preparation of the operating instructions for the ¹⁰ B changeover	41	-337	-296
	Ordering of the enriched boric acid	0	-344	-344
	Selection of the required measurement methods	30	-352	-322
	Ordering of the measurement instruments	0	-322	-322
	2	Plant Preparation	81	-147
Purification of the Spent Fuel Pool via the mixed bed filter		47	-147	-100
Installation of the auxiliary system for ¹⁰ B measurements		25	-140	-115
Commissioning of the ¹⁰ B measurement system		46	-112	-66
Check on the amounts in the Boric Acid Batching Tank (KCB10) and the Liquid Radwaste Tanks (KPK21/22/23)		11	-77	-66
¹⁰ B measurements ready		0	-66	-66
Changeover boric acid ready for use		0	-66	-66
3		¹⁰B changeover of RHRS loops, Flood Tanks & Accumulators	44	-63
	Spent Fuel Pool cooling via FAK20	33	-63	-30
	Changeover of RHRS train 10, flood tank JNK10, Accumulators JNG11/12	4	-63	-59
	Surveillance test on RHRS train 10	2	-59	-58
	Changeover of RHRS train 20, flood tank JNK20, Accumulators JNG21/22	4	-56	-52
	Surveillance test on RHRS train 20	2	-52	-50
	Changeover of RHRS train 40, flood tank JNK40, Accumulators JNG41/42	4	-49	-45
	Surveillance test on RHRS train 40	2	-45	-44
	Changeover of RHRS train 30, flood tank JNK30, Accumulators JNG31/32	4	-42	-38
	Surveillance test on RHRS train 30	2	-38	-36
4	¹⁰B changeover of Extra Boration System Tanks	2	-35	-34
5	¹⁰B changeover of Spent Fuel Pool, including the Transport Flask Pool	5	-35	-30
6	Mixing of Spent Fuel Pool cooling trains FAK 10/40	0.5	-30	-30
7	Start of stretch-out operation	0	-23	-23
8	¹⁰B changeover of Boric Acid Tanks KCB20	2	-21	-19
9	Start of refuelling shutdown	0	0	0

Change to Enriched Boric Acid in Siemens PWRs

A During Normal Operation (Loops 10-40)



B During the Refuelling Shutdown

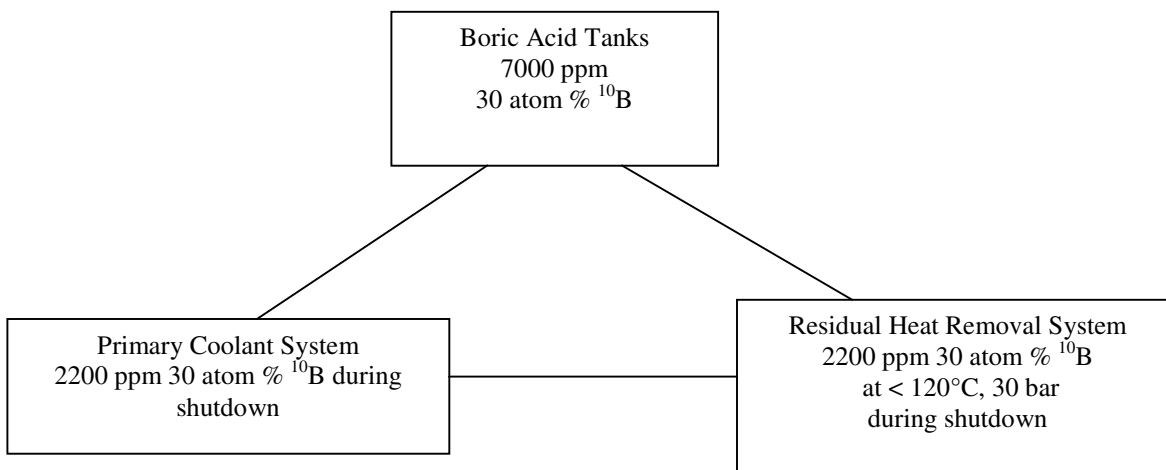
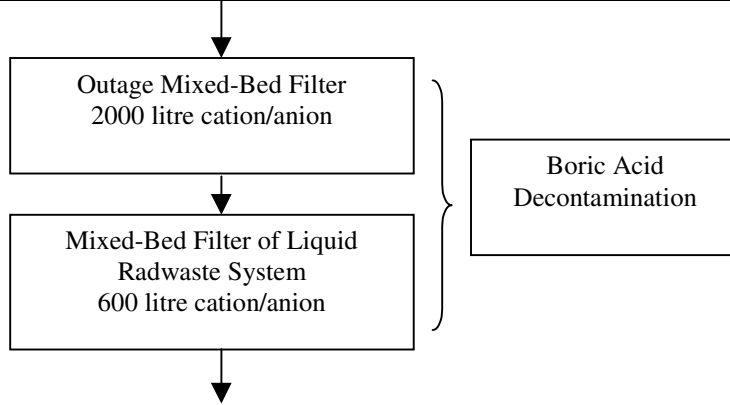


Figure 3-1
Schematic Outline of Change to EBA at Grafenrheinfeld (3-1)

Pre-cleaned using Spent Fuel Pool Purification System				
	Volume (m ³)	Boron Concentration (ppm)	Boric Acid (kg)	Activity (Bq m ⁻³)
Residual Heat Removal System TH 10-40	257.5	2200	3227.0	1.4 x 10 ⁶
Extra Boration System TW 10-40	4	7000	159.0	3.0 x 10 ⁵
Spent Fuel Pool	171	2200	2144.0	4.0 x 10 ⁶
<i>Total</i>	432	-	5530.0	-
Main nuclides	⁶⁰ Co, ⁵⁸ Co, ¹²⁴ Sb, ^{123m} Te		Absolute Activity 1.04 x 10 ⁹ Bq	



<i>KTA-1504 controls water discharge regulations</i>	Volume (m ³)	Boron Concentration (ppm)	Boric Acid (kg)	Activity (Bq)
Discharge (before dilution)	432	2200	5530	1.6 x 10 ⁷
Percentage of allowed annual discharge	0.029%			
Allowed annual discharge	5.55 x 10 ¹⁰ Bq			
Main Nuclides	^{123m} Te			
	Disposal Vessel – V = 70 m ³			

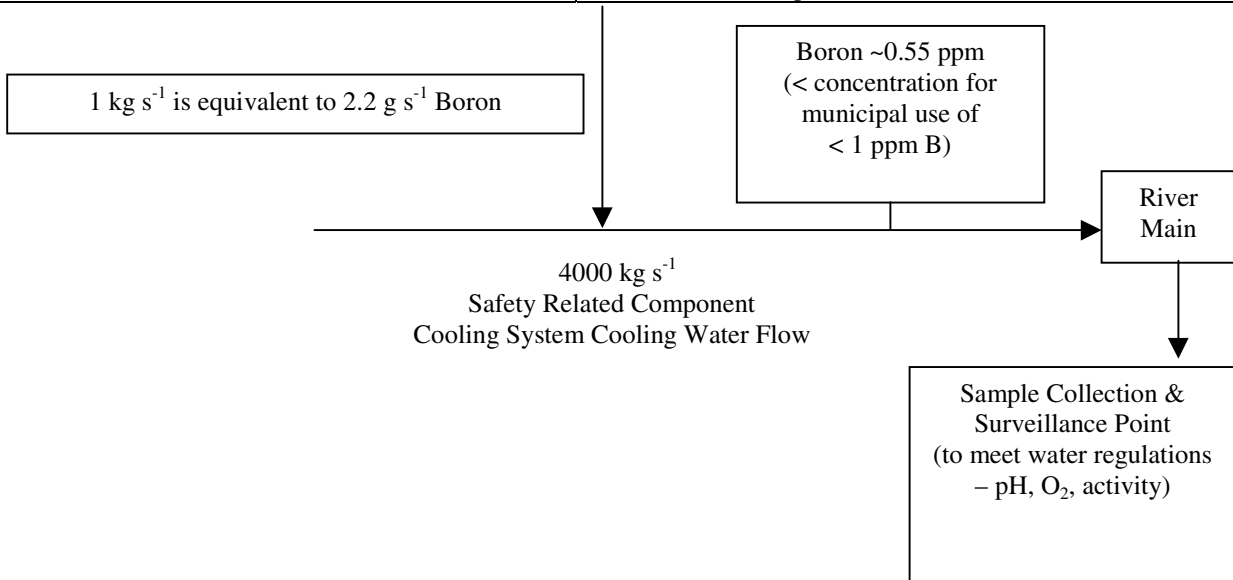


Figure 3-2
Boron Disposal Route at Grafenrheinfeld (3-1)

Change to Enriched Boric Acid in Siemens PWRs

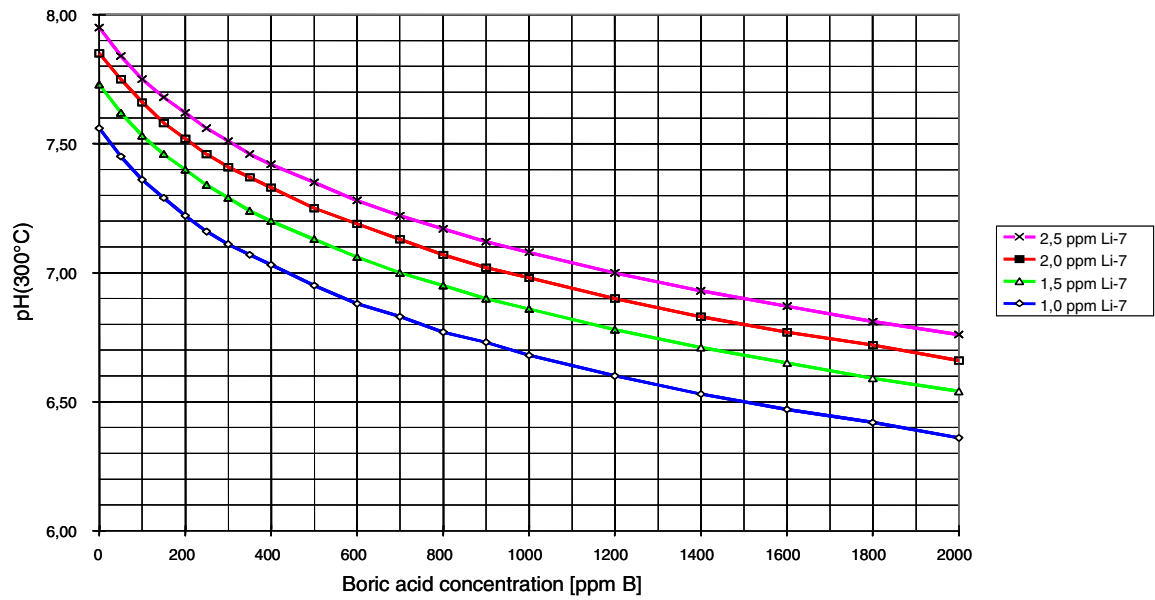


Figure 3-3
pH_{300°C} as a Function of Boric Acid Concentration at Constant ⁷Lithium Hydroxide (3-3)

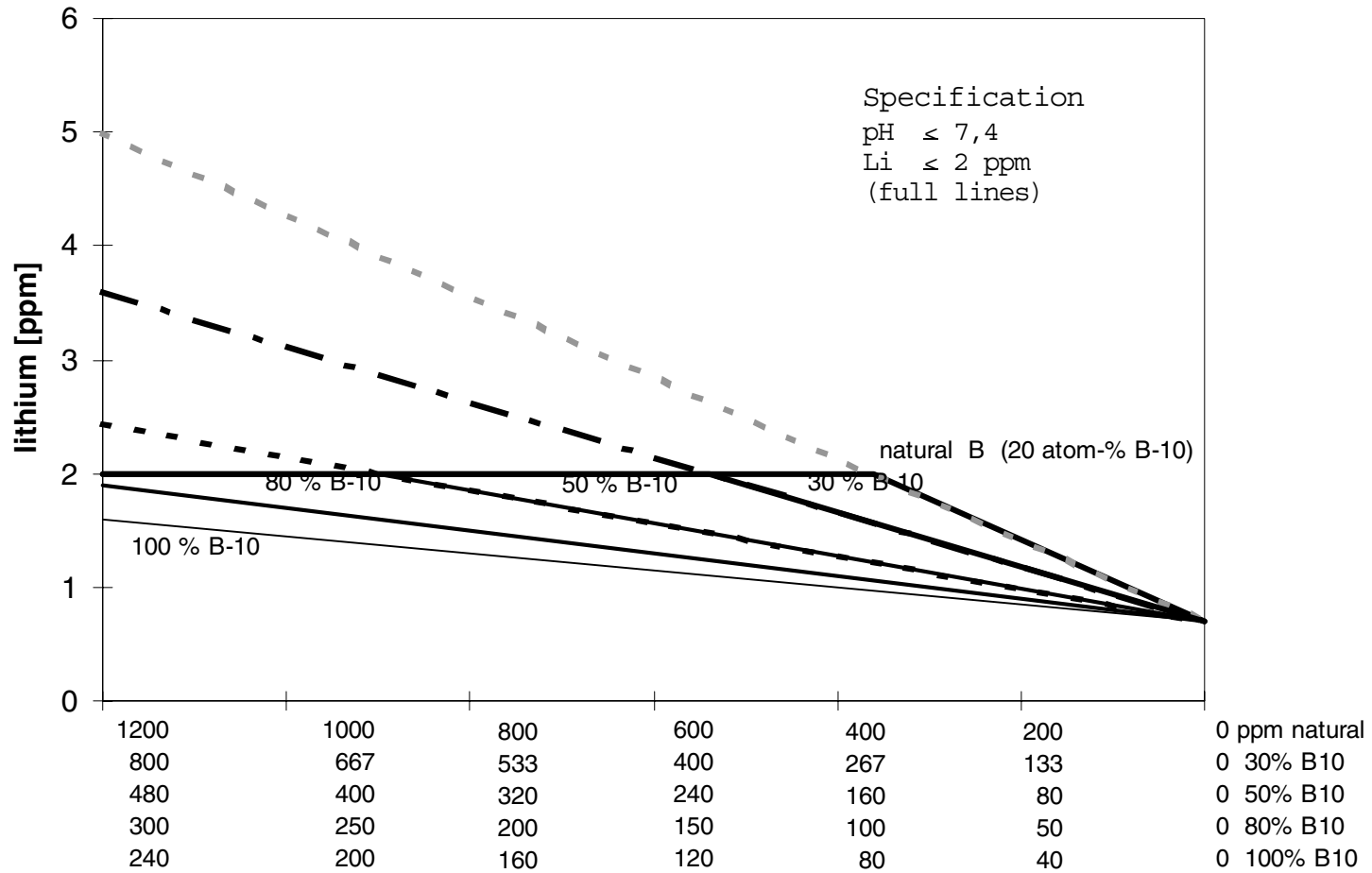


Figure 3-4
⁷Lithium Concentration for Various ¹⁰B Enrichment Levels (3-3)

Change to Enriched Boric Acid in Siemens PWRs

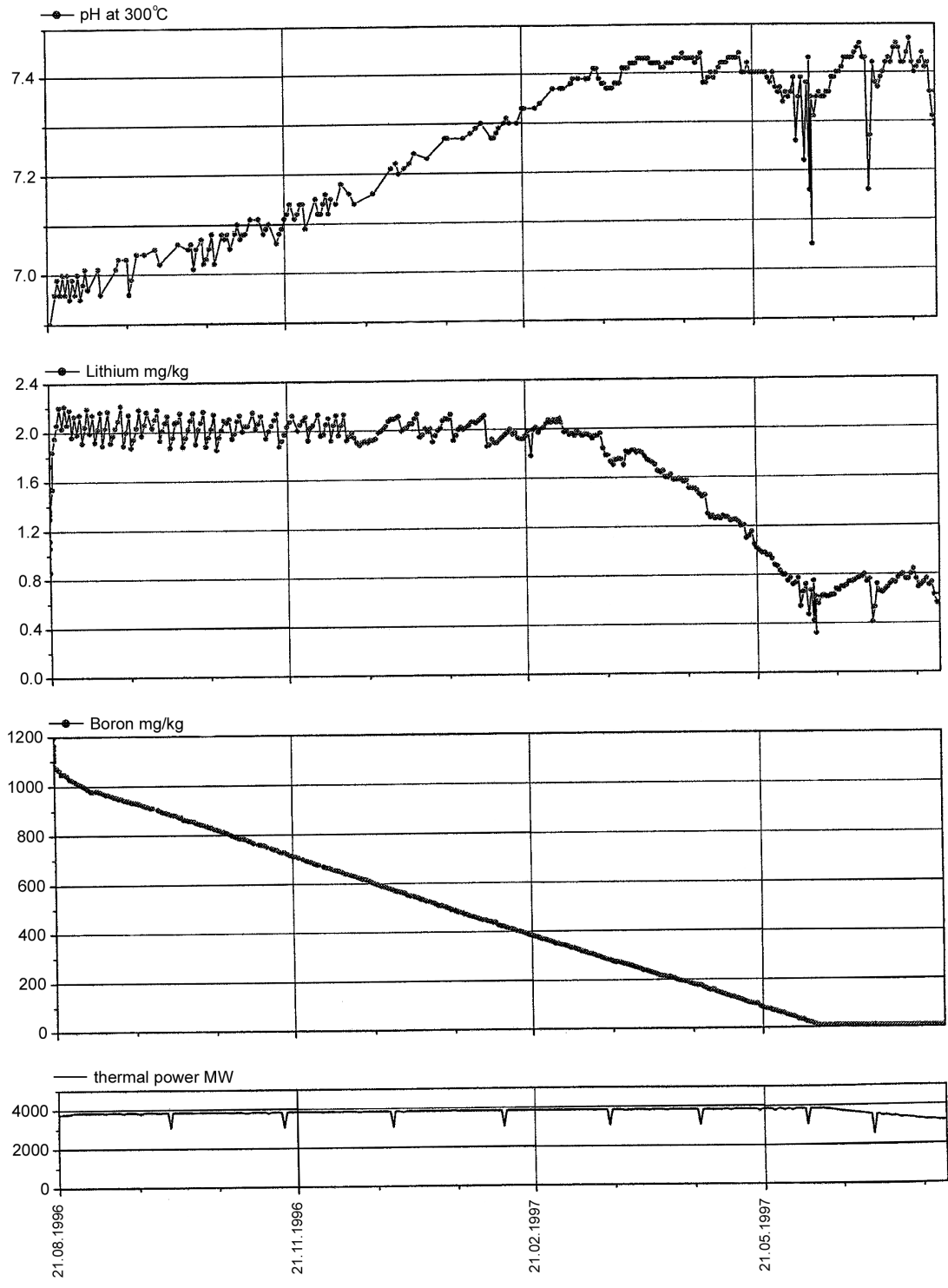


Figure 3-5
Primary Coolant Chemistry in Cycle 12 at Philippsburg 2 Before the Change to EBA (3-8)

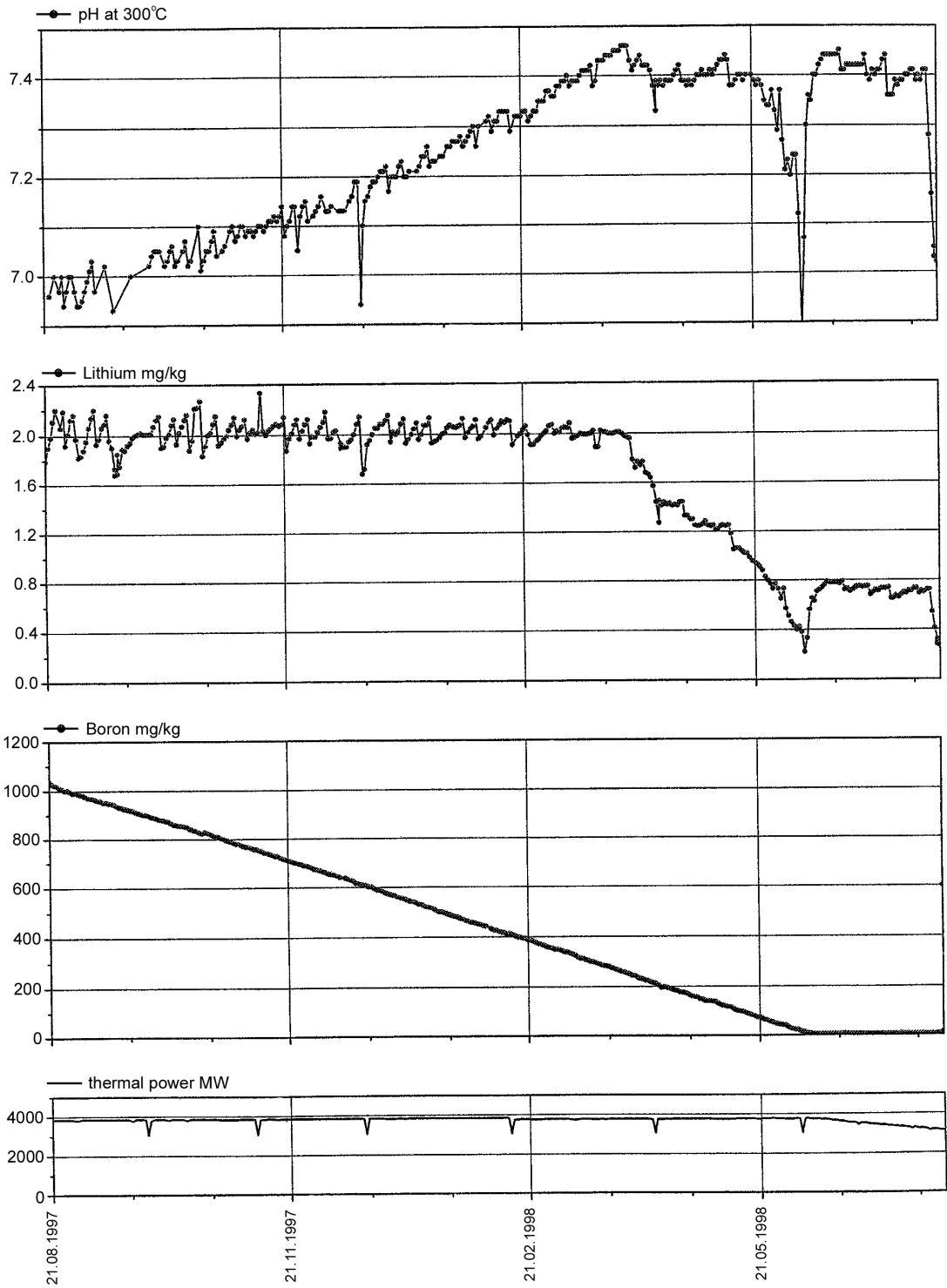


Figure 3-6
Primary Coolant Chemistry in Cycle 13 at Philippsburg 2 Before the Change to EBA (3-8)

Change to Enriched Boric Acid in Siemens PWRs

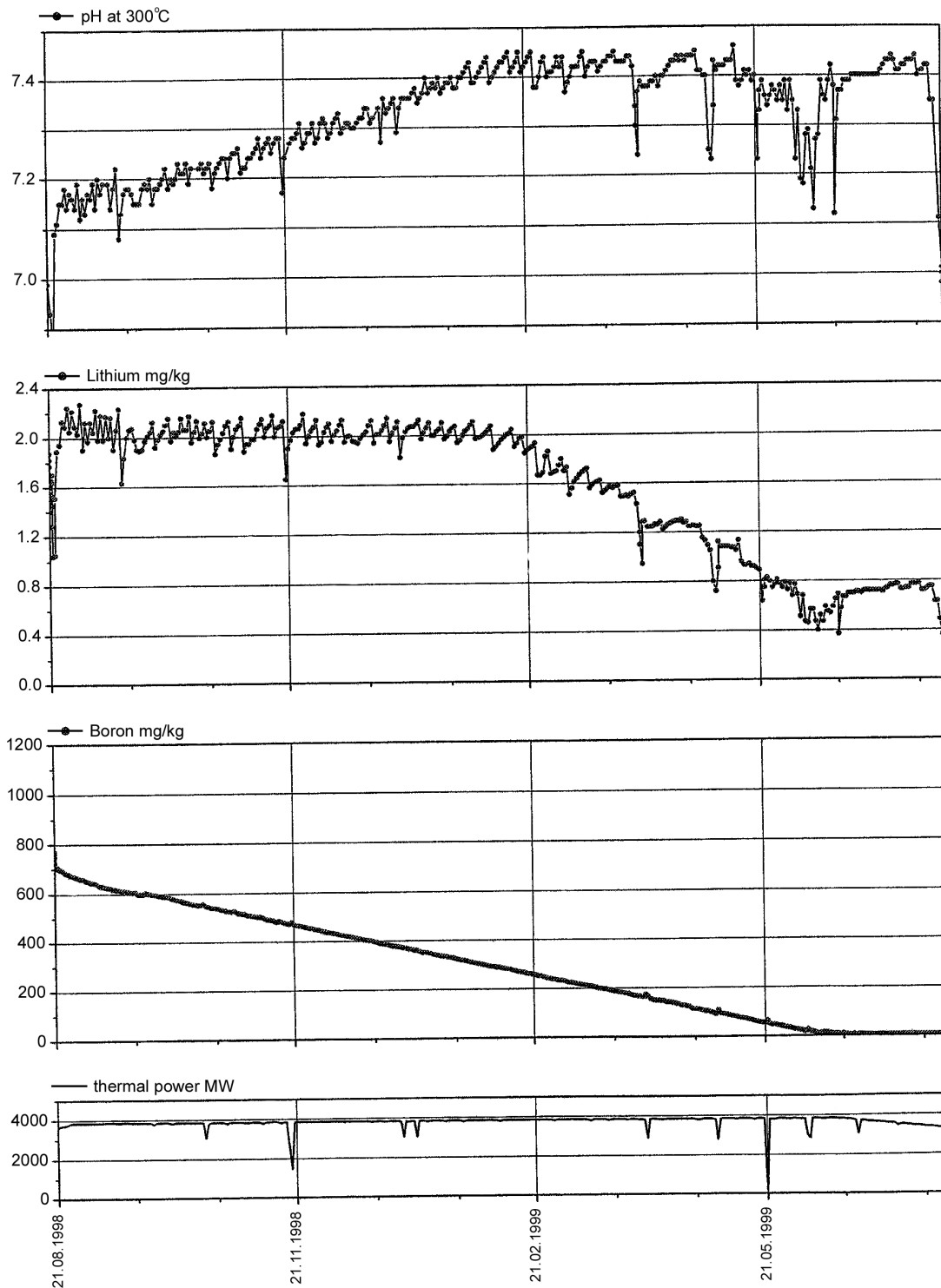


Figure 3-7
Primary Coolant Chemistry in Cycle 14 at Philippsburg 2 After the Change to EBA (3-8)

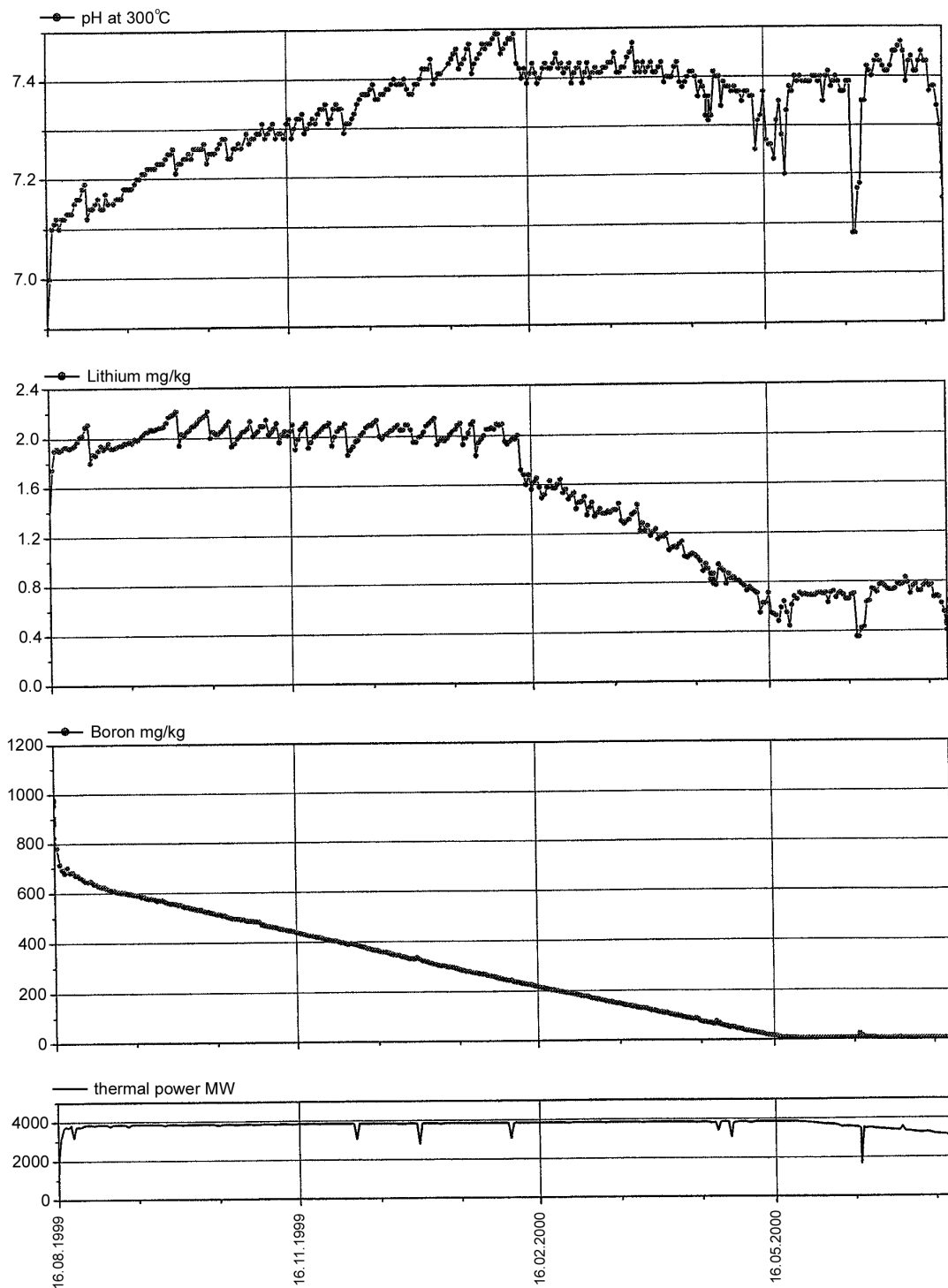


Figure 3-8
Primary Coolant Chemistry in Cycle 15 at Philippsburg 2 After the Change to EBA (3-8)

4

COMPARISON WITH U. S. EVALUATIONS

A number of cost assessments have been made on the application of EBA in U.S. and other similar PWRs (4-1 to 4-9). While many of the technical aspects in any conversion will inevitably be similar, it must be appreciated from the outset that the U.S. and other EBA assessments are based on a fundamentally different principal cost-benefit basis from those in the applications successfully carried out in Siemens PWRs.

In all U.S. studies the main cost-benefit is predicted to be the saving in radiation exposure costs, i.e. personnel doses (person-rem), due to the reduction in the plant radiation fields. Other benefits include reduced fuel corrosion rates and, more recently, the prevention of AOA. In addition, the earliest detailed study (4-3) included a predicted additional major saving from retaining the existing Boric Acid Tanks (BATs), but with the boric acid concentration reduced from 21000 ppm B (12% boric acid) to 5250 ppm B (3% boric acid), which would avoid trace heating and reduce maintenance costs. Changing to EBA is also expected to reduce steam generator degradation rates, lithium costs and solid radwaste, and should enable the fuel cycle to be extended without incurring higher fuel clad corrosion rates (4-1, 4-2, 4-3, 4-4, 4-6). Later studies emphasised the savings that would follow from reduced personnel doses, reduced fuel clad corrosion from the higher pH achievable during extended cycles using higher burn-up fuel and from avoiding the costs associated with additional boric acid storage volumes. Potentially there may be additional saving from preventing AOA (4-5). All these studies considered higher ^{10}B enrichments than those implemented in Siemens PWRs, since these would allow operation at $\text{pH}_{\text{Tave}}7.4$ throughout an 18-month cycle and would, therefore, maximise the benefits.

In Siemens PWRs while the benefits identified in the U.S. assessments were recognised as significant, the main cost-benefit from using EBA comes from the improved fuel economy that accompanies its use, especially the reduced cost of new fuel assemblies and the “back-end” costs of fuel storage, transport and disposal. An equally important consideration is minimising waste production and discharges, both during the initial change to EBA and during later normal operation.

In the discussion given below, the most significant U.S. assessments are reviewed, and the proposed method of changing to EBA is compared with that used in Siemens PWRs. The latter comparison concentrates on the costs of the change to EBA and on the ongoing costs of EBA operation. In each case the waste volumes and costs of the change have been recalculated using the approach used at Grafenrheinfeld, in Table 3-1 (see Appendix A) and using the latest EBA cost, so that direct comparisons can be made with the Siemens PWR approach. Note that in these recalculations, the initial concentration in the primary circuit is taken as 0 ppm B, since the change is assumed to occur as the coolant is borated at EOC during the shutdown itself (as it is in

the Siemens PWRs), and that the recalculations are based on a target enrichment of 30 weight % ^{10}B , i.e. 28.05 atom % ^{10}B . The comparisons do not consider ALARA issues.

4.1 Method of Changeover to EBA

The method proposed by Westinghouse was for EBA enrichments varying from 30% to 90 atom % ^{10}B (4-1 to 4-4) and differed principally from that used in Siemens PWRs by only changing the Spent Fuel Pool (SFP) to EBA before the refuelling shutdown. All other systems are converted to EBA after shutdown while the reactor is refuelling. While this method can be used successfully, it increases the initial production of boric acid waste. It does, however, ensure that the RWST volume is always above the minimum Tech. Spec. limit, which is not possible in the Siemens PWR method. Westinghouse also suggest that it may be possible to save costs by not changing the Spent Fuel Pool (SFP) and the Refuelling Water Storage Tank (RWST) to EBA, since together these tanks contain 80-90% of all the boric acid in a PWR. Such a step would not be allowed in Siemens PWRs (or other European PWRs) on safety grounds (boron dilution accident). A final point to note is that Westinghouse assessed the change to EBA assuming that 92 weight % ^{10}B boric acid would be used. However, Siemens PWRs use 96 weight % ^{10}B boric acid since the latter minimises waste production when enriching a 7000 ppm B boric acid solution to 30 atom % ^{10}B . 96 weight % ^{10}B boric acid is used for the recalculations.

The sequence proposed by Westinghouse is:

- (1) Reduce the SFP boron concentration before the shutdown by a “feed and bleed” method to a concentration where the addition of solid 92 weight % ^{10}B boric acid will bring the SFP to the correct total B concentration and ^{10}B enrichment. Mix the tank and associated system contents using the SFP cooling and purification systems. The discharged boric acid is collected in the Boron Recycle Hold-up Tanks and then passed through the Liquid Radwaste System mixed-bed demineralisers and particulate filters to remove activity, before it is discharged via the Circulating Water System to the river or the sea.
- (2) Shut down the plant for refuelling as normal, transferring the original contents of the RWST to the reactor cavity. Any additional boric acid in the RWST, above that required for the conversion to EBA, is discharged to waste. Some mixing of EBA from the SFP and the normal boric acid in the reactor cavity will occur (~15%, 4-5), which will need to be corrected after the plant has returned to power by adding further solid 92 weight % ^{10}B boric acid to bring the SFP to the correct ^{10}B enrichment. On completing the refuelling, the natural boric acid in the reactor cavity is discharged to waste. All boric acid in the reactor cavity and the RWST is first passed through the SFP mixed-bed filters (demineralisers), before being routed to the Boron Recycle Hold-up Tanks and the Liquid Radwaste System.
- (3) The partly drained RWST is refilled with a mixture of reactor coolant make-up water (demineralised primary water) and 92 weight % ^{10}B boric acid solution. At this stage the EBA enrichment in the RWST is such that it will give the correct final enrichment and total boron concentration when the contents of the RWST are mixed with the contents of the primary circuit (RCS), the Chemical and Volume Control System, the Residual Heat Removal System and the Safety Injection System. The 92 weight % ^{10}B boric acid solution

is prepared in the Boric Acid Batching Tank. At this stage the RCS will only be partially filled.

- (4) The Boric Acid Tanks (BATs) are drained to the level where adding 92 weight % ^{10}B boric acid solution will bring them to the correct enrichment and total boron concentration. The 92 weight % ^{10}B boric acid solution is prepared in the Boric Acid Batching Tank. The contents of the BATs should be above the minimum stated in the Tech. Specs., but sufficient volume must be left in the BATs so that they can be filled with EBA recovered from the RCS during start-up and then re-concentrated by evaporation. The natural boric acid drained from the tanks is discharged to waste via the Liquid Radwaste System.
- (5) The partially filled RCS is filled with EBA “blend” from the BATs and the Reactor Coolant Make-up Water Tank.
- (6) The Accumulators are emptied and the contents discharged to waste. They are refilled from the RWST; this will not reduce the RWST volume below the Tech. Spec. limit.
- (7) The plant is started-up as normally, but the EBA discharged from the RCS during heat-up and dilution to criticality must be routed to an empty Boron Recycle Hold-up Tank to avoid it mixing with natural boric acid awaiting discharge. After start-up, the contents are concentrated by evaporation and they are returned to the BATs.
- (8) Any further concentrated boric acid in the BATs is prepared by using solid boric acid of the correct enrichment.

4.2 Twin Unit PWR Evaluation

The earliest of the detailed studies in 1989 (4-3) was that for a twin 4-loop Westinghouse PWR (which can be identified as Zion), which had common SFP, BATs and Boron Recycle Hold-up Tanks. A further complication was that the two units operated on 18-month cycles out of phase, so that when one was at EOC or BOC, the other was in mid-cycle. Finally, the normal strength in the BATs was 12% boric acid (21000 ppm B). The assessment considered EBA enrichments of 35, 50 and 75 atom %.

At 12% boric acid, the tanks and lines have to be trace heated to keep the boric acid in solution, and there were significant maintenance problems. At the time of the assessment the station had plans to replace the BATs with ones of larger capacity that would enable the boric acid strength to be reduced to 4% (7000 ppm B), but at the same time the station also planned to remove the boric acid evaporators. An important aspect of the assessment for 75 weight % EBA was the cost saving that would result if the tanks were not replaced, but instead changed to operation with 3% boric acid. In the assessments, one of the largest savings was predicted to be that from not replacing the existing BATs. However, in practice EBA was not adopted and the planned BAT replacement was carried out in ~1992. Further major savings were expected to arise from the reduction in the radiation fields, from reducing the amount of $^7\text{LiOH}$ required during the cycle.

The proposed procedure for the first unit essentially followed that described above (Section 4.1) with small variations to cater for the different enrichments. Conversion of the second unit would follow in a similar manner, either when it was shut down for refuelling or during power operation immediately after the first unit was converted to EBA during its shutdown. Since the

Comparison with U. S. Evaluations

BATs and Boron Recycle Hold-up Tanks were common to both units, during the conversion of the second unit, one hold-up tank and one BAT would have to be reserved for operation with the first unit and would be unavailable. Table 4-1 summarises the volumes and quantities involved in changing the two units to EBA. Notably, the total amount of 92 weight % ^{10}B boric acid for the initial conversion ranges from 1565 to 3629 kg, depending on the enrichment, and 4850-9450 m^3 boric acid would be discharged to waste. At the current cost of $\$2.07 \text{ g}^{-1}$ for 92 atom % ^{10}B , the cost of boric acid used in the initial conversion ranges from $\$3.24\text{m}$ to $\$7.51\text{m}$.

Although it is difficult to make a direct comparison with the approach followed in Siemens PWRs, it is possible to use the Siemens' method to estimate the quantities of 96 weight % ^{10}B boric acid that would be required to convert the Twin U.S. stations to 28 atom % (30 weight %) ^{10}B boric acid and the amount of waste discharged. The result is given in Table 4-2, both for the original configuration with three BATs containing 12% boric acid and the current configuration with 4% boric acid. The analyses show very clearly that the cost of the EBA added is similar for the Westinghouse method ($\$3.24\text{m}$ for 35 atom % ^{10}B , Table 4-1) and the Siemens method ($\$3.68\text{m}$ for 28 atom % ^{10}B , Table 4-2). However, the waste volumes generated using the Siemens PWR approach are very much reduced, approximately a seven fold reduction, which would be accompanied by a similar reduction in the amount of SFP resin used. These reduced amounts represent a significant cost saving.

There are, however, two drawbacks in the Siemens PWR approach that will make it difficult to apply to U.S. stations. The first is that it is only designed for an EBA enrichment of 30 atom %, and for higher enrichments a similar "feed and bleed" method to that proposed by Westinghouse will be necessary. The second is that the changeover of the RWST would first require the discharge of 184 m^3 2000 ppm B boric acid, before adding the calculated volume of 7000 ppm B 96 weight % ^{10}B EBA. This step would reduce the RWST volume from 389000 U.S. gallons to 340400 U.S. gallons (87.4% volume), which is below the minimum Tech. Spec. limit of 350000 U.S. gallons (90% volume). Unless a temporary alleviation is permitted by NRC, the overall process would need to be modified, with a consequent increase in the amount of boric acid waste discharged. Most probably a combination of reducing the level initially to the Tech. Spec. minimum volume, fill and bleed, and then adding 7000 ppm B 96 weight % ^{10}B EBA would generate the minimum amount of waste.

During normal operation few consequences of a change to EBA were predicted in the Westinghouse evaluation, although it was considered that a daily measurement of the ^{10}B concentration would be essential. Experience in Siemens PWRs shows that this is not necessary and that monthly determinations of the isotopic ratio are all that is required. Load following was also identified as a potential problem, but non-recoverable boron losses to the Boron Recycle Hold-up Tanks would be minimal if the Boron Recycle System evaporators were used efficiently to recover any boric acid letdown from the RCS. Finally, it was noted that carryover in the evaporators could mean that recovered distillate routed to the Reactor Water Make-up Tank could contain up to 10 ppm B, which towards EOC would need to be removed by the BRS demineraliser. In Siemens PWRs such losses are lower, with the distillate normally containing <1 ppm B.

The final important aspect in estimating the ongoing costs of EBA is the amount of boric acid lost during the cycle. At this twin unit station boric acid losses were identified as being due to:

- (1) Discharge of letdown boric acid from the Boron Recycle Hold-up Tanks via the Liquid Radwaste System,
- (2) Uncontrolled leaks from the primary circuit routed to the Liquid Radwaste System,
- (3) Losses of boric acid with spent anion exchange resin,
- (4) Burn-up, and
- (5) Primary to secondary leakage.

At the time of the assessment no boric acid was recovered at this station and it was all was discharged. Letdown and uncontrolled leaks combined were 6-7 U.S. gallons per minute ($1.36-1.58 \text{ m}^3 \text{ h}^{-1}$). Assuming 90% recovery if the Boron Recycle Evaporator was re-commissioned, the estimated loss was 215 lb (97.7 kg) ^{10}B per year. Spent mixed-bed ion exchange resin generation was estimated at 677.6 ft^3 (19.2 m^3) per year. Excluding the Liquid Radwaste demineraliser, the anion resin used was 386.2 ft^3 (10.9 m^3), which corresponded to a loss of 386.2 lb. (175.5 kg) boron, equivalent to 49.2 kg ^{10}B at 30 atom %. Compared with these losses, losses due to burn-up were predicted to be small (30 lbs. or 13.6 kg ^{10}B per year), as were losses due to primary to secondary circuit leaks (8 lbs. or 3.6 kg ^{10}B per year). Thus, the estimated total, assuming 30 atom % EBA, is 164.1 kg ^{10}B for the two units, i.e. 82 kg ^{10}B per unit per year. Losses in Siemens PWRs have been emphasised as being one of the most important controllable costs during normal operation. Compared with the range reported for Siemens PWRs (10-55 kg ^{10}B per year), the losses at this station were high, as would be the annual replacement EBA costs (\$177000 per unit per year at $\$2.16 \text{ g}^{-1}$).

4.3 Millstone 3 Evaluation

The Millstone 3 study in 1991 (4-4) closely followed the procedure recommended for the earlier twin PWR, but attention was also focussed on the impact that the presence of a BTRS and the unusually large RWST at Millstone had on the method and costs of the change. At Millstone 3 the RWST is approximately twice the size of those installed at other 4-loop Westinghouse PWRs, which was a consequence of the use of a sub-atmospheric containment at this station. Because of this the RWST and SFP combined contain ~90% of the total station boron inventory, with 66% being in the RWST alone. Since the BTRS could be used to retain all the EBA at EOC, the possibility was also investigated of not changing the RWST and SFP to EBA to save costs and of carrying out the shutdowns still using natural boric acid. At the time of the evaluation Millstone 3 was converting to 18-month cycles and increasing the shutdown boron concentration to 2700-2900 ppm B. The target enrichment was 70 atom %, which would allow operation at $\text{pH}_{\text{Tave}} 7.4$ throughout the cycle without exceeding 2.2 ppm lithium, although lower enrichments were also considered. At Millstone 3 the Boron Recycle Evaporator was normally used to recover boric acid, thus eliminating the main route for boric acid losses during normal operation.

The procedure recommended for the full conversion of the plant follows that summarised in Section 4.1. For the SFP, “feed and bleed” would again be used, in this case to reduce the concentration from 2900 ppm B to 250 ppm B, before solid 92 atom % ^{10}B EBA was added to

Comparison with U. S. Evaluations

increase the enrichment to 70 atom % ^{10}B . For the RWST the contents transferred to the reactor cavity would be discharged at the end of refuelling, as would an additional volume from the RWST to enable it to be brought up to the target pre-mixing enrichment by adding 92 atom % ^{10}B from the Boric Acid Tanks. For an enrichment of 70 atom % ^{10}B , 3669.3 kg 92 atom % ^{10}B would be required to change the entire station systems, which at the current price of $\$2.07 \text{ g}^{-1}$ for 92 atom % ^{10}B would cost $\$7.60\text{m}$. Equivalent figures for 30 atom % ^{10}B are 1765.2 kg and $\$3.65\text{m}$, respectively. By not converting the RWST and SFP, the initial EBA requirement at 70 atom % ^{10}B was reduced to 370 kg ^{10}B . Details of the volumes that would need to be discharged and resin usage, etc. for converting both the RWST and SFP were not given, but must be in the order of 3000000 U.S. gallons ($\sim 11500 \text{ m}^3$ boric acid).

Tables 4-3 and 4-4 reanalyse the Millstone data using the approach followed in Siemens PWRs, both for the case when the shutdown concentration is 2200 ppm B (to enable a direct comparison with the Siemens PWR data) and for 2900 ppm B. The results show that for 28 atom % (30 weight %) EBA, the cost of the 96 weight % EBA needed is rather higher than that estimated by Westinghouse ($\$5.35\text{m}$ v. $\$3.65\text{m}$), although this is an artefact of the different ways of estimating the amount of enriched boric acid needed to raise the ^{10}B enrichment. As expected, the amount of EBA required is greater for a shutdown concentration of 2900 ppm B and once again the waste volumes generated using the Siemens PWR approach are very much reduced, $\sim 820 \text{ m}^3$ v. $\sim 11500 \text{ m}^3$, which would be accompanied by a similar reduction in the amount of SFP mixed-bed resin used.

Once again the drawbacks in the Siemens PWR are that a “feed and bleed” method must be used for higher enrichments than 28 atom % and that the changeover of the RWST will reduce the volume below the Tech. Spec. limit, since the initial discharge of 568 m^3 would reduce the RWST volume to 1050000 U.S. gallons (87.5% volume), which is below the minimum Tech. Spec. volume of 1166000 U.S. gallons (97.2% volume). Again, unless NRC permits a temporary alleviation, the overall process would need to be modified, with a consequent increase in the amount of boric acid waste discharged.

During normal operations no significant issues were identified, although some Tech. Spec. revisions would be required. During normal operation, Westinghouse (4-4) reported that boric acid loss routes were similar to those summarised in Section 4.2, with the exception that plant data indicated that losses from the Boron Recycle Evaporator were negligible. Primary to secondary circuit losses were also negligible. The estimated losses were: 113.6 kg boron per year (84.4 kg at 70 atom % and 34.1 kg ^{10}B at 30 atom %) in spent mixed-bed resins (5.66 m^3 resin discharged per year), 13.6 kg ^{10}B per cycle for an 18-month cycle due to burn-up (9.9 kg ^{10}B per year) and 501.2 kg boron per year (312.5 kg ^{10}B at 70 atom % and 150.4 kg ^{10}B at 30 atom %) from the Liquid Radwaste System. Overall, the estimated losses were 406.6 kg ^{10}B per year at 70 atom % and 194.4 kg ^{10}B per year at 30 atom %. Again, compared with the figures for Siemens PWRs (10 to 55 kg ^{10}B per year) the losses and associated costs would be very high.

4.4 Re-evaluation of EBA Benefits

The latest U.S. assessment in 1998 (4-5) reconsidered the benefits of implementing EBA, supporting this with data for a typical 4-loop Westinghouse PWR. In addition to the factors

considered in the earlier assessments, it included additional factors in the analysis. These included higher benefits due to the reduction in radiation exposure (person-rem costs) and the savings if Axial Offset Anomalies (AOA) could be avoided, which were partly offset by the higher costs associated with longer cycle-higher core duty operation and the costs due to increased Primary Water Stress Corrosion Cracking (PWSCC) from the higher lithium concentrations in longer cycles. It also outlined the plant requirements for demonstrating EBA use in a U.S. PWR. The study targeted operation at $\text{pH}_{\text{Tave}} 7.4$, with maximum lithium concentrations of either 2.2 or 3.5 ppm and enrichments of 30 to 75 atom % ^{10}B EBA.

In terms of fuel corrosion the view taken was that clad corrosion for Zircaloy-4 clad fuel would be reduced by limiting lithium to 2.2 ppm by operating at an EBA enrichment of 75 atom % ^{10}B , but that with ZIRLO™ clad the same benefit could be obtained at 3.5 ppm lithium by reducing the EBA enrichment to 40 atom % ^{10}B . Under the latter conditions, burn-ups up to 75000 MWd tonne U^{-1} would become possible. In addition, both AOA and burnable poisons were considered. While the risk of AOA could be minimised by operation at $\text{pH}_{\text{Tave}} 7.4$ during the cycle, the consequential risks were also higher, since if it did occur AOA could be worse with EBA present in the coolant. It was concluded that EBA should only be used if there was no risk of AOA. For burnable poisons there was no impact for cycle lengths up to 24 months. Overall, the benefits of permitting operation to higher burn-up were recognised, but a low benefit of only \$270000 per year for savings in the number of Zircaloy-4 and ZIRLO™ clad fuel assemblies was estimated. This differs from the two main basic cost-benefit elements for operation with EBA in Siemens PWRs, i.e. the savings in the cost of new fuel assemblies and the “back-end” costs of long term storage and disposal. The latter aspect of the cost-benefit analysis was omitted, since the storage costs are expected to be much lower in U.S. PWRs than in Siemens PWRs, although they are not zero. There is, of course, no current intention to reprocess spent fuel from U.S. PWRs so that reprocessing and transport costs are much less.

In normal operation the latest assessment again states that the ^{10}B isotopic ratio may need to be monitored during operation. As noted above, experience at Siemens PWRs shows that continuous or frequent isotopic measurements are not necessary, although they are required at monthly to three monthly intervals. The latest assessment also states that the typical minimum boron concentration in the primary coolant at EOC is 10 ppm B, which would reduce core life by 11 days at an 80 atom % ^{10}B enrichment. This loss can be avoided if a BTRS or a deborating anion resin bed is used at EOC. A further problem is the increasingly large volume of demineralised water necessary to dilute the coolant at very low EOC boron concentrations. Siemens PWRs use neither a BTRS nor a deborating anion resin bed, yet report no operational problems from these issues. Thus, while a BTRS may be an advantage, it is not essential.

Since the 1980s, PWRs with mill annealed Inconel 600 steam generator tubing have suffered from PWSCC, which statistical analysis suggests is made worse by 10-35% on increasing lithium from 0.7 to 3.5 ppm (4-5). While the effect is small, the latest evaluation considers that EBA would be beneficial in PWSCC susceptible plants.

In normal operation, increasing the natural boric acid concentration potentially causes a number of problems. These are those associated with a positive BOC moderator temperature coefficient, with the rate of achieving the cold shutdown concentration during a shutdown, with emergency

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boration rates, with boric acid solubility in the RWST and reducing the containment sump pH following a LOCA. Use of EBA would remove most of these concerns, either by reducing the total boron concentrations, or by maintaining the existing total boron concentration in the various systems. Both approaches would avoid installation of costly additional storage tanks. Maintaining the existing total boron concentration in the various systems is the option followed in Siemens PWRs.

Because of the problems due to AOA and the potentially greater effect of boron hideout on AOA with EBA present in the primary coolant during operation later in the fuel cycle, one option considered was operation with EBA for the first part of a cycle and then reverting to natural boric acid. While this was considered feasible, it was concluded that it could only be achieved if a mid-cycle shutdown and possible core off-load was carried out. All European assessments rule out any mixed EBA-natural boric acid operation, because of the risk of a boron dilution accident. A further option considered was not to enrich the spent fuel pool. Again this would not be permitted in Siemens or other European PWRs.

A new cost-benefit analysis was carried out using data for a generic 4-loop PWR operating at $\text{pH}_{\text{Tave}} 7.4$ with EBA enrichments of 45 and 80 atom % ^{10}B . For these enrichments the initial fill requirements were estimated at 2200 kg ^{10}B for an 80 atom % ^{10}B enrichment and 736.6 kg for 45 atom % ^{10}B , equivalent to \$4.95m and \$1.66m at \$2.25 g^{-1} . A similar amount was estimated in the earliest study, although detailed data were not presented (4-1). Comparable results for a generic 4-loop PWR and a Standardized Nuclear Unit Power Plant System (SNUPPS) PWR (i. e., Callaway and Wolf Creek) calculated using the Siemens approach are included in Tables 4-3 and 4-4. Once again the initial fill quantities are similar, although the Westinghouse assessment again predicts a lower quantity, but again it is certain that the amount of waste boric acid discharged will be much less. For a SNUPPS PWR, the Siemens approach requires that 198.3 m^3 of boric acid be discharged from the RWST, reducing its volume to 366600 U.S. gallons (87.5% volume), which again is below the Tech. Spec. limit of 394000 U.S. gallons (94.0% volume).

During normal operations U.S. experience indicates that ~ 127 kg ^{10}B in natural boric acid is lost to waste each year (corresponding to 181.6 kg for 30 atom %), 56.8 kg ^{10}B on spent anion resins, 10 kg ^{10}B due to burn-up and a small amount at EOC on deborating resins (~ 1.5 kg for 30 atom %). Again the total losses of ~ 250 kg ^{10}B are very high compared with Siemens PWR experience (13-55 kg ^{10}B per 12 month cycle, Section 3.4).

A final feature noted was the impact on silica levels in the primary coolant of high silica concentrations in the Spent Fuel Pool due to Boraflex fuel racks, if all boron was recovered via the Boron Recycle System. It was noted that a reverse osmosis plant might be required to remove silica from the SFP. While Siemens PWRs do not have a specific Boraflex problem, they do operate with higher BOC silica concentrations without any deleterious effect.

4.5 References

- 4-1 J A Battaglia and J Roesmer, "Utilisation of Enriched Boric Acid in Pressurised Water Reactor Plant", Proceedings of the EPRI Seminar on PWR Primary Water Chemistry and Radiation Field Control, Paper 34, 1988.

- 4-2 W B Rodill, “Enriched Boron Study Surry Power Station Units 1 and 2”, Proceedings of the EPRI Seminar on PWR Primary Water Chemistry and Radiation Field Control, Paper 35, 1988.
- 4-3 J A Battaglia, L A Lamata, R M Waters, C A Bergmann, J M von Hollen and S M Ditommaso, “Enriched Boric Acid for PWR Application, Cost Evaluation Study for a Twin-Unit PWR”, EPRI Report EPRI NP-6456, 1989.
- 4-4 Westinghouse Electric Corporation, “Final Report Cost Evaluation Study for the Application of Enriched Boric Acid in Millstone Nuclear Power Station Unit 3 for Northeast Utilities Service Company”, Westinghouse Report WP0606-1, 1991.
- 4-5 J Sejvar, C A Bergmann, W J Leech, J D Perock and R J Jacko, “Re-evaluation of the Benefits of Implementing Enriched Boric Acid”, EPRI Report TR-109992, 1998.
- 4-6 E G Lin, C G Lee, Y N Suh and G S Jun, “Technical Review of B-10 Enriched Boric Acid for Control Role in Pressurised Light Water Reactor”, J. Korean Nucl. Soc, Vol. 27(4), 591, 1995.
- 4-7 E K Kim, B S Choi, Y S Ko, Y D Hong, C K Lee, H L Chang, K S Chun and S N Kim, “Study on Chemical and Volume Control System Design Improvement of Pressurised Water Reactor to use the Enriched Boric Acid”, KAERI Report, KAERI/RR-1591/95, 1995.
- 4-8 T Ichimura, J Sevjar and H Takiguchi, “Evaluation of Dose Reduction Initiatives for Tsuruga Units 3 & 4”, 10th Pacific Basin Nuclear Conference, Kobe, Japan, October, 1996.
- 4-9 H Ocken, P Frattini and C J Wood, “Prospects for Enriched Boric Acid in U.S. PWRs”, Water Chemistry of Nuclear Reactor Systems 8, BNES, Vol 1, 49, 2000.

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**Table 4-1
Summary of Conversion Process Volume and Concentration Requirements (Zion) (4-3)**

	¹⁰ B Enrichment		
	75 atom %	50 atom %	35 atom %
Spent Fuel Pool			
Make-up water (m ³)	6440	3385	1845
92 atom % ¹⁰ B (kg)	864	707	512
SFP boron concentration (ppm)	504	778	1127
Resin used to process discharged boric acid (m ³)	6.65	3.48	1.90
Refuelling Water Storage Tank			
92 atom % ¹⁰ B (kg)	2 x 1344	2 x 709	2 x 506
RWST boron concentration before mixing (ppm)	912	901	1441
RWST boron concentration after mixing (ppm)	1055	1045	1515
Original RWST contents processed (m ³)	2 x 1507	2 x 1507	2 x 1507
Boric Acid Tank			
92 atom % ¹⁰ B (kg)	77	58	41
Original boric acid discharged	N/A	N/A	N/A
RCS Dilution and Expansion			
Dilution volume (m ³)	2276	3297	3298
BOC RCS boron concentration (ppm) (equivalent to 1100 ppm B)	275	427	619
Expansion volume (m ³)	891	891	891
Boron Recycle Hold-up Tank (RHUT)			
Volume from RCS dilution and expansion (m ³)	3138	4189	4189
RHUT boron concentration (ppm)	350	635	921
Concentrated volume (m ³) – 3 weight %	219	506	744
Concentrated volume (m ³) – 12 weight %	-	130	186
Total BAT Contents (m ³) – 3 weight %	411	795	1160
Total BAT Contents (m ³) – 12 weight %	-	202	290
TOTAL			
92 atom % ¹⁰ B (kg)	3629	2183	1565
Cost of 92 atom % ¹⁰ B (\$) (\$2.07 g ⁻¹ ¹⁰ B)	7512030	4518810	3239550
SFP Resin (SFP and 2 x RWST)	9.65	6.48	4.90
Volume discharged (m ³)	9454	6399	4859
Volume reprocessed (m ³)	3138	4189	4189

Table 4-2
Estimated Boric Acid Requirements and Waste Volumes for Converting Zion Units 1 and 2
PWRs to 30 weight% (28.05 atom %) EBA using the Siemens PWR Method

	Volume		Boron (ppm)	Addition (a) added as "blend" (m ³)		Waste volume (b) (m ³)	Mass added (kg)	
	(U.S. gallons)	(m ³)		96 weight % ¹⁰ B Boric acid	Demin- eralised water		As 96 weight % ¹⁰ B	As 96 weight % ¹⁰ B Boric acid
Original Configuration								
Spent Fuel Pool	600000	2271.2	2000	27.0	257.0	283.9 (284.9)	566.5	3442.2
RWST Unit 1	389000	1472.5	2000	17.5	166.6	184.1 (184.7)	367.3	2231.7
RCS Unit 1	85000	321.8	0	0	0	0	0	0
BATs (12% boric acid)	35646	134.9	2100 0	16.9	0	16.9 (16.9)	354.2	2152.6
Accumulators Unit 1	25435	96.3	2000	1.1	10.9	12.0 (12.1)	24.0	145.9
Miscellaneous Unit1	10000	37.9	1000	0	0	0	0	0
RWST Unit 2	389000	1472.5	2000	17.5	166.6	184.1 (184.7)	367.3	2231.7
RCS Unit 2	85000	321.8	0	0	0	0	0	0
Accumulators Unit 2	25435	96.3	2000	1.1	10.9	12.0 (12.1)	24.0	145.9
Miscellaneous Unit 2	10000	37.9	0	0	0	0	0	0
TOTAL	165451 6	6263.0	-	81.1	612.0	693.1	1703.3	10350. 1
Cost (\$) (\$2.16 g⁻¹ ¹⁰B)							3679037	
Current Configuration								
Spent Fuel Pool	600000	2271.2	2000	81.0	203.0	283.9 (284.9)	566.7	3443.4
RWST Unit 1	389000	1472.5	2000	52.5	131.6	184.1 (184.7)	367.4	2232.5
RCS Unit 1	85000	321.8	0	0	0	0	0	0
BATs (4% boric acid)	105000	134.9	7000	49.7	0	49.7 (49.7)	347.8	2113.6
Accumulators Unit 1	25435	96.3	2000	3.4	8.6	12.0 (12.1)	24.0	146.0
Miscellaneous Unit1	10000	37.9	1000	0	0	0	0	0
RWST Unit 2	389000	1472.5	2000	52.5	131.6	184.1 (184.7)	367.4	2232.5
RCS Unit 2	85000	321.8	0	0	0	0	0	0
Accumulators Unit 2	25435	96.3	2000	3.4	8.6	12.0 (12.1)	24.0	146.0
Miscellaneous Unit 2	10000	37.9	0	0	0	0	0	0
TOTAL	173387 0	6563.4	-	242.5	483.4	725.9	1697.3	10313. 9
Cost (\$) (\$2.16 g⁻¹ ¹⁰B)							3666192	

- Notes (a) Boric acid added as a 9.5% "blend" from a BAT containing 21000 ppm B or as a 28.5% "blend" from a BAT containing 7000 ppm B to systems at 2000 ppm B (see Appendix).
- (b) Main values calculated on the basis of diluting the ¹¹B concentration to 71.95 weight %. Comparative values in brackets on the basis of increasing the ¹⁰B concentration to 28.05 weight %.

Table 4-3
Calculated Enriched Boric Acid Requirements and Waste Volumes for Converting 4-Loop PWRs with Systems at 2200 ppm B to 28 atom % (30 weight %) EBA using the Siemens PWR Method

	Volume		Boron (ppm)	Addition (a) added as "blend" (m ³)		Waste volume (b) (m ³)	Mass added (kg)	
	(U.S. gallons)	(m ³)		96 weight % ¹⁰ B Boric acid	Demin- eralised water		As 96 weight % ¹⁰ B	As 96 weight % ¹⁰ B Boric acid
Millstone 3								
Spent Fuel Pool	454674	1721.1	2200	67.6	147.6	215.2 (215.4)	473.0	2874.1
RWST	1200000	4542.5	2200	178.3	389.6	567.9 (568.6)	1248.3	7585.5
RCS	87500	331.2	0	0	0	0	0	0
BATs	50600	191.5	7000	23.9	0	23.9 (23.9)	167.6	1018.7
Accumulators	25440	96.3	2200	3.8	8.3	12.0 (12.1)	26.5	160.8
Miscellaneous	10000	37.9	0	0	0	0	0	0
TOTAL	1828214	6920.5	-	273.6	545.4	819.0	1915.4	11639.2
Cost (\$) (\$2.5 g⁻¹ ¹⁰B)							413726	3
SNUPPS								
Spent Fuel Pool	410000	1552.0	2200	60.9	133.1	194.1 (194.3)	426.5	2591.4
RWST	419000	1586.1	2200	62.3	136.0	198.3 (198.5)	435.9	2648.6
RCS	90000	340.7	0	0	0	0	0	0
BATs	48000	181.7	7000	22.7	0	22.7 (22.7)	159.0	966.2
Accumulators	24400	92.4	2200	3.6	7.9	11.5 (11.6)	25.4	154.2
Miscellaneous	10000	37.9	0	0	0	0	0	0
TOTAL	1001400	3790.7	-	149.5	277.1	426.7	1046.8	6360.8
Cost (\$) (\$2.5 g⁻¹ ¹⁰B)							226102	3
4-Loop Generic Westinghouse PWR								
Spent Fuel Pool	410000	1552.0	2200	61.0	133.3	194.3 (194.3)	427.0	2594.8
RWST	500000	1892.7	2200	74.4	162.5	236.9 (236.1)	520.7	3164.3
RCS	90000	340.7	0	0	0	0	0	0
BATs	60000	227.1	7000	28.4	0	28.4 (28.4)	198.8	1207.9
Accumulators	20000	75.7	2200	3.0	6.5	9.5 (9.4)	20.8	126.6
Miscellaneous	10000	37.9	1000	0	0	0	0	0
TOTAL	1090000	4126.1	-	166.8	302.3	469.1	1167.4	7093.6
Cost (\$) (\$2.5 g⁻¹ ¹⁰B)							2521502	

- Notes (a) Boric acid added as a 31.4% "blend" from a BAT containing of 7000 ppm B to systems at 2200 ppm B (see Appendix).
- (b) Main values calculated on the basis of diluting the ¹¹B concentration to 71.95 weight %. Comparative values in brackets on the basis of increasing the ¹⁰B concentration to 28.05 weight %.

Table 4-4
Calculated Enriched Boric Acid Requirements and Waste Volumes for Converting 4-Loop PWRs with Systems at 2900 ppm B to 28 atom % (30 weight %) EBA using the Siemens PWR Method

	Volume		Boron (ppm)	Addition (a) added as "blend" (m ³)		Waste volume (b) (m ³)	Mass added (kg)	
	(U.S. gallons)	(m ³)		96 weight % ¹⁰ B Boric acid	Demin- eralised water		As 96 weight % ¹⁰ B	As 96 weight % ¹⁰ B Boric acid
Millstone 3								
Spent Fuel Pool	454674	1721.1	2900	89.3	125.9	215.2 (214.7)	625.2	3799.1
RWST	1200000	4542.5	2900	235.7	332.3	568.0 (566.8)	1650.1	10026.8
RCS	87500	331.2	0	0	0	0	0	0
BATs	50600	191.5	7000	23.9	0	23.9 (23.9)	167.6	1018.7
Accumulators	25440	96.3	2900	5.0	7.0	12.0 (12.0)	35.0	212.6
Miscellaneous	10000	37.9	0	0	0	0	0	0
TOTAL	1828214	6920.5	-	354.0	465.2	819.2	2477.9	15057.2
Cost (\$) (\$2.5 g⁻¹ ¹⁰B)							5352241	
SNUPPS								
Spent Fuel Pool	410000	1552.0	2900	80.5	113.5	194.1 (193.6)	563.8	3425.8
RWST	419000	1586.0	2900	82.3	116.0	198.3 (197.9)	576.1	3501.0
RCS	90000	340.7	0	0	0	0	0	0
BATs	48000	181.7	7000	22.7	0	22.7 (22.7)	159.0	966.4
Accumulators	24400	92.4	2900	4.8	6.8	11.5 (11.5)	33.6	203.9
Miscellaneous	10000	37.9	0	0	0	0	0	0
TOTAL	1001400	3790.7	-	190.4	236.3	426.7	1332.5	8097.1
Cost (\$) (\$2.5 g⁻¹ ¹⁰B)							2878198	
4-Loop Generic Westinghouse PWR								
Spent Fuel Pool	410000	1552.0	2900	80.5	113.5	194.3 (193.6)	563.8	3425.8
RWST	500000	1892.7	2900	98.2	138.5	236.7 (236.1)	687.5	4177.8
RCS	90000	340.7	0	0	0	0	0	0
BATs	60000	227.1	7000	28.4	0	28.4 (28.4)	198.8	1207.9
Accumulators	20000	75.7	2900	3.9	5.5	9.5 (9.4)	27.5	167.1
Miscellaneous	10000	37.9	1000	0	0	0	0	0
TOTAL	1090000	4126.1	-	211.1	257.5	469.1	1477.6	8978.7
Cost (\$) (\$2.5 g⁻¹ ¹⁰B)							3191584	

Notes (a) Boric acid added as a 41.5% "blend" from a BAT containing 7000 ppm B to systems at 2900 ppm B (see Appendix).

(b) Main values calculated on the basis of diluting the ¹¹B concentration to 71.95 weight %. Comparative values in brackets on the basis of increasing the ¹⁰B concentration to 28.05 weight %.

5

DISCUSSION

Although most of the recent Siemens PWRs have converted to EBA, thus far no other European or U.S. PWRs have converted, although a number of cost assessments have been made on the application of EBA in U.S. and other similar PWRs. Many technical aspects in any conversion will inevitably be similar. However, different cost-benefit approaches were used, and there are different operational restrictions that influence the approaches followed or proposed. These issues are discussed below.

5.1 Cost-Benefit Bases for Changing to EBA

In all U.S. studies the main cost-benefit is predicted to be the saving in radiation exposure costs, i.e. personnel doses (person-rem), due to the reduction in the plant radiation fields, coupled with reduced fuel corrosion rates and, more recently, the prevention of AOA (5-1 to 5-5). In addition, the earliest study included the additional major saving that was expected if the Boric Acid Tanks (BATs) were not replaced (see Section 4.2). Changing to EBA is also expected to reduce steam generator degradation rates, lithium costs and solid radwaste, and should enable the fuel cycle to be extended without incurring higher fuel clad corrosion rates (5-1 to 5-4, 5-6). All these studies considered higher ^{10}B enrichments than those implemented in Siemens PWRs. These enrichment levels would allow operation at $\text{pH}_{\text{Tave}}7.4$ throughout an 18-month cycle, thereby maximising the benefits. It was also assumed that EBA costs would reduce significantly as EBA usage increased. Although these early assessments were not sufficiently cost-beneficial for EBA to be used in an operating PWR, they did show that operation with EBA was feasible. However, initial costs were high, as were the operating costs due to the relatively high losses of EBA to waste.

In recent years U.S. interest in EBA has been re-awakened by problems arising as a result of the general change to extended fuel cycles in U.S. PWRs and the accompanying moves towards better fuel economy. Improved fuel economy is achieved by core uprating, loading “low leakage” cores, loading more highly ^{235}U enriched fuel, operating to higher fuel burn-up, and increasing boiling duty in-core. Unfortunately, in a number of 4-loop PWRs these changes also resulted in the onset of Axial Offset Anomalies (AOA), caused by boron hideout under sub-cooled nucleate boiling conditions in porous fuel crud deposits in the upper part of the core. Although the full explanation for AOA is not yet known, it is believed that operation at lower pH in the early part of an 18-month cycle is one of the factors responsible, since it promotes fuel crud deposition (5-7). Using EBA to enable operation at $\text{pH}_{\text{Tave}}7.4$ throughout an 18-month cycle should minimise fuel crud deposition and is clearly an option for minimising AOA, in addition to the other benefits identified in earlier studies. However, there is no certainty that EBA will prevent AOA, since factors other than the coolant pH may be more important (5-8). Therefore, the most recent U.S. assessment (5-5) again assesses the main cost-benefit as being that due to

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reduced radiation exposure and only assigns a small part of the overall cost-benefit to improved fuel behaviour, which is due to reduced fuel clad corrosion. In addition, no benefit is assessed for any potential savings in the costs of new fuel assemblies (due to concerns that AOA may occur) or from the storage and disposal of the spent fuel, the latter of which may or may not be significant. Finally, operation with MOX fuel was not considered, since reprocessing and reuse of plutonium from spent fuel is not, generally, U.S. policy.

An extra option considered in U.S. assessments was the conversion of only the primary circuit and its related systems to EBA, leaving the RWST and SFP still filled with natural boric acid. This approach would save on the cost of the initial EBA fill, since the two tanks together contain 80-90% of the total boric acid inventory of a station. However, the presence of both natural boric acid and EBA at the same time in an operating station increases the risks of accidents similar to boron dilution accidents, and would not be permitted in any Siemens PWR or, more generally, in European PWRs.

In Germany, and to a lesser extent other European countries, the basis for using EBA is very different. The major cost-benefit comes from the improved fuel economy that EBA operation supports (5-9, 5-10), while the benefits from reduced radiation exposure and reduced fuel clad corrosion are only minor contributors. With respect to radiation exposure, this is because radiation fields in Siemens PWRs are already low. Indeed, five of the eight Siemens PWRs (including here Neckarwestheim 2) that operate with EBA have reduced Stellite™ inventories, which have produced very low radiation fields and radiation exposures (5-11). With respect to clad corrosion, this is less of a problem in Siemens PWRs because Siemens Fuel Division set an upper limit of 2.0 ppm lithium in all plants currently operating, or likely to operate, with EBA.

In many respects improved fuel economy in Siemens PWRs comes from similar steps to those being followed by U.S. PWRs (i. e., core uprating, loading “low leakage” cores, loading more highly ²³⁵U enriched fuel, operating to higher fuel burn-up and increasing boiling duty in-core). Of these, higher ²³⁵U enrichments are one of the most important factors, since they enable the fuel to be used to higher burn-up, which in turn permits the fuel assemblies to be used for more fuel cycles (5-9, 5-10). Fewer new fuel assemblies are, therefore, required each cycle and “back-end” costs of fuel storage, transport, reprocessing and waste management are reduced. In German stations these costs are high and the initial cost outlay for EBA can be recovered in only 1-2 years; there will also be ongoing savings in storage and final disposal costs. Figure 5-1 illustrates the link between ²³⁵U enrichment, burn-up and the numbers of fuel assemblies that must be reloaded (5-9, 5-12).

However, unlike the experiences in U.S. PWRs, these changes have not been accompanied by the onset of AOA, even though boiling duty in some of these stations (e. g., Gösgen) is higher than in most U.S. PWRs. The reason for the absence of AOA is not well established, but may be linked to the fact that Siemens PWRs only operate on 12-month fuel cycles (allowing the pH to be always $\geq \text{pH}_{300^\circ\text{C}} 6.9$ throughout a cycle), or to the different corrosion product balance in the coolant (5-13). It has been pointed out (5-14) that using Incoloy 800 steam generator tubes makes the overall primary circuit alloy mass balance in Siemens PWRs iron-rich, rather than nickel-rich as in Westinghouse PWRs with Inconel 600 or 690 tubed steam generators. Further, corrosion release rates are lower for Incoloy 800 and Inconel 690, than for Inconel 600. These

differences are reflected in the corrosion product concentrations in the coolant, which are similar for circulating ferrous iron (1-6 ppb), but significantly lower for circulating nickel (0.020-0.080 v. 0.100-0.700 ppb) (5-15). AOA is associated with the formation of porous nickel oxide containing deposits in the upper part of a core. Therefore, it is possible that either the greater iron excess in the coolant or the low nickel concentration inhibits nickel oxide formation and, therefore, the porous deposits responsible for AOA. As with U.S. PWRs, increasing the fuel duty does not necessarily require changing to EBA in Siemens PWRs and in at least two of the Siemens stations the cold shutdown concentration has been increased (2400 ppm B at Neckarwestheim 2 and 2500 ppm B at Gösgen). However, it is considered that the loading of more highly ^{235}U enriched fuel is, in itself, sufficient to warrant the change to EBA.

Loading MOX fuel is part of the overall improved fuel economy strategy in Siemens PWRs and is part of the wider strategy to improve the overall utilisation of the original ^{235}U in the fuel by reprocessing. In this case the cold shutdown boron reactivity worth has to be increased, but if the same total boron concentration of 2200 ppm B is retained, this can be achieved with the EBA enrichment increased to only ~27-30 weight % ^{10}B .

Although higher EBA enrichments (70-80% ^{10}B) could be used, an equally important consideration in Siemens PWRs is the reduction in the amount of waste produced and in the amount of processed waste discharged to the local river. At an enrichment of only ~30 weight % ^{10}B both waste production and discharges are minimised, whilst at the same time there is sufficient ^{10}B present to ensure that there is an adequate cold shutdown margin. For this approach to be effective there must be no additional compelling need to operate at the higher primary coolant pHs that can be achieved with a higher EBA enrichment. This is indeed the case for Siemens PWRs, all of which operate on 12-month fuel cycles allowing them to operate at higher average cycle pHs, do not suffer from AOA, even though they operate with highly rated fuel, and will not benefit greatly from reducing primary circuit radiation fields. It is the combination of the need to minimise waste production and the absence of a need to increase the primary coolant pH greatly, that leads to the chosen enrichment of ~27-30 weight % ^{10}B and to the minimum cost of converting to EBA.

Overall, the use of EBA in Siemens PWRs is justified primarily on fuel economy grounds, whereas in U.S. PWRs, if it is to be used, it will mainly be justified on reduced radiation exposure and improved corrosion product behaviour grounds, but including a contribution from reduced fuel clad corrosion. However, if AOA can be prevented, then the use of EBA in U.S. PWRs may also become justifiable on fuel economy grounds. Whereas the cost-benefit in Siemens PWRs includes the “back end” fuel costs, no account of these is taken for U.S. PWRs. In addition, in U.S. PWRs no account is taken of the cost-benefits that might accrue if the ongoing costs of EBA losses during the fuel cycle are reduced to Siemen PWR levels. If these are factored in or minimised, then using EBA in U.S. PWRs may become more justifiable.

5.2 Methods of Initial Conversion to EBA Enrichment

In addition to the different cost-benefit bases, the methods used, or proposed, for the initial conversion to EBA and the target enrichments for Siemens PWRs are significantly different from those proposed for U.S. PWRs. In principle, the Siemens PWR method is a “drain and fill”

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method mainly carried out during normal operation, while the U.S. Westinghouse method is a mixture of “fill and bleed” and “drain and fill” stages mainly carried out during refuelling. While these differences may be linked mainly to the different target enrichments, other factors also support the different approaches, e.g. Tech. Spec. limits in U.S. PWRs and waste discharge costs in Siemens PWRs.

In the “fill and drain” method used in Siemens PWRs, the important factors governing both the method and the choice of ^{10}B enrichment are:

- (1) Enrichment to 30 atom % ^{10}B is sufficient to give the necessary cold shutdown margin without increasing the total boron concentration above the normal value of 2200 ppm B for a 12-month cycle.
- (2) Waste discharges associated with increasing the ^{10}B enrichment in the Boric Acid Tanks (BATs) to 30 atom % ^{10}B are minimised by discharging excess natural boric acid and then adding the same volume of 96 weight % ^{10}B boric acid. In other systems, waste discharges are minimised by adding a 31% “blend” of 7000 ppm B, 30 atom % ^{10}B boric acid.
- (3) Because there are four redundant Residual Heat Removal and Emergency Core-Cooling trains, these can be converted to EBA in turn during normal operation, as can the Extra (emergency) Boration System, the Spent Fuel Pool (SFP) and the Boric Acid Tanks (BATs). The Emergency Core-Cooling trains include the Flood Tanks, which are the equivalent of the Refuelling Water Storage Tank (RWST). However, at least at Grafenrheinfeld, the Accumulators were converted to EBA after shutdown during the refuelling.
- (4) The primary circuit and Chemical and Volume Control System are converted to EBA as the primary circuit is borated during the shutdown for refuelling. This is possible because Siemens PWRs operate in stretch-out mode at EOC, and because all other associated systems are changed to EBA in the final months of normal operation.

This method ensures that no aspect of normal operation, shutdown or start-up is altered, other than those linked to the increase in the boron isotopic ratio. Therefore, changes to plant safety analysis assessments (FSARs and Tech. Specs.), corrosion rates, materials degradation effects and safety system operations do not arise. However, there are safety implications during the change to EBA, and the implications of the higher boron reactivity worth per ppm boron during operation have to be considered. In practice, the approach taken is the simplest possible, since it involves the minimum disturbance to the normal operation of the plant and the minimum production of waste boric acid during the change. Finally, it must be emphasised that Siemens PWRs always operate with very low boric acid losses during a fuel cycle, which has a significant impact on the ongoing costs of using EBA and on the success of the change to EBA. All these aspects are important, since Siemens PWRs normally have very short refuelling shutdowns and because PWRs in Germany and Switzerland are effectively “zero” discharge stations. The costs of processing the waste natural boric acid or of discharging it are, therefore, significant factors in the overall costs of the conversion.

In contrast with the method used in Siemens PWRs, the U.S. assessments assume that only the SFP can be changed over to EBA during normal operation and that all other circuits must be converted during refuelling. They also consider higher ^{10}B enrichments than those used in

Siemens PWRs. The Westinghouse method proposes a “fill and bleed” method to reduce the natural boric acid concentration in the SFP before adding solid 92 weight % ^{10}B boric acid to give the correct enrichment. It also assumes that the entire contents of the RWST will be replaced with EBA as the reactor is refuelled, and that the original contents will be discharged to waste when the refuelling cavity is emptied after refuelling is complete. The Accumulators and BATs would also be changed to EBA during refuelling. The advantage of the Westinghouse method is that it can be used for essentially any EBA enrichments. Its great disadvantage is that it produces large quantities of waste natural boric acid and could impact upon the outage time if a rapid refuelling shutdown is planned. It is not clear how important it is to minimise waste processing and/or discharge costs in U.S. PWRs and how these factors affect the overall cost-benefit justification for converting to EBA.

It is instructive to ask whether the method used in Siemens PWRs can be used in U.S. PWRs. In principle the data indicate that it is possible, but only up to the enrichments used in Siemens PWRs, i.e. 30 atom %, and even then changing the RWST during normal operation would reduce its volume by ~12.5%, which is below the minimum Tech. Spec. limit, at least temporarily. While it is possible that a temporary alleviation could be negotiated with NRC, it would have to be fully justified. At higher enrichments the “drain and fill” method used in Siemens PWRs cannot be used and a similar “fill and bleed” method to that proposed by Westinghouse would need to be employed. However, it might be possible to follow the Siemens PWR approach in part. For example, changing the SFP enrichment by “drain and fill”, instead of “feed and bleed”, might be an option. Whether this is worth doing will depend on the savings in waste processing costs that would result and on whether the required quantity of boric acid can be drained from the SFP without violating any Tech. Spec. limits.

5.3 Impact of EBA on Normal Operation

While the cost-benefit analyses and method of conversion chosen for the initial change to EBA are very important, clearly it is the impact on normal operations and replacement costs that are important for its continued use. Here the important questions are the influence on normal day-to-day reactivity and chemistry control, and the costs associated with EBA losses from the system.

In general, the experience reported by Siemens PWR chemists is that operating with EBA has no significant impact on station reactivity or chemistry control. The basic reason for this is that the amount of ^{10}B present during the cycle is identical for both natural boric acid and EBA and that ^{10}B burn-out already occurs during a fuel cycle without it having any significant impact on reactivity or chemistry control, even though all the stations operate as base load stations with few if any mid-cycle shutdowns. With EBA ^{10}B burn-out occurs at the same rate and to the same extent, and because of this, frequent redeterminations of the ^{10}B : ^{11}B isotopic ratio are unnecessary. The isotopic ratio can be measured at monthly, or even three monthly, intervals in the station laboratory using a commercial ICP-MS instrument. For routine daily boron concentration measurements, the standard semi-automatic boron auto-titrator is used as normally and its control room output can still be used to control the operation of the Boric Acid-Demineralised Water Control System. If there are frequent load changes (e. g., load following) or if there are mid-cycle shutdowns the effect of burn-out on core reactivity will be very much less, but again the effect on plant operation is no greater than would be the case with natural boric

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acid. Clearly, however, the approaches followed in Siemens PWRs can only be used if all the borated water systems have the same EBA enrichment. As a further back-up, it should be recognised that the daily control rod position changes are a direct indication of the ^{10}B reactivity worth of the coolant and will show whether there is a need to re-determine the ^{10}B : ^{11}B isotopic ratio. Early U.S. assessments (5-2) commented that control would be more difficult due to the lower accuracy of the boron determinations at lower concentration, but this does not appear to have any real impact in practice. Nor do concerns that it might be more difficult to determine the critical boron concentration during start-up (5-3). Although silica and lithium concentrations in the recovered boric acid in Siemens PWRs can be high, no deleterious effect on normal operations have been reported.

Although some impact on primary circuit radiation fields are predicted, in practice none has been found so far. The absence of any reduction in radiation fields is not easy to explain, particularly as this is the most important cost-benefit identified in the U.S. assessments. In part, the explanation will lie in the low enrichment used, which only produces a small coolant pH increase for the first few months of the 12-month cycles, and in-part to the slow decay in ^{60}Co levels already present in the out-of-core oxides. It must also be recognised that many of these stations already have low radiation fields due to their reduced Stellite™ inventories. Nevertheless, Siemens PWR operators expect that radiation fields will decay slowly.

It is the general experience that minimising EBA losses is one of the most important aspects of normal operation in Siemens PWRs, since this determines the ongoing costs. Burn-up losses are relatively small, ~ 10 kg ^{10}B per cycle, and if other losses can be kept small overall replacement costs will be equally small. At some stations total losses appear to be very low (~ 13 kg ^{10}B at both Brokdorf and Gösgen), which would imply essentially 100% recovery of all boric acid letdown from the primary circuit, or lost via the Plant Drains Systems, by the Coolant Treatment System (BRS) evaporator. In the worst case reported, the EBA losses were 55 kg ^{10}B . These values correspond to replacement costs of \$29k-\$120k per 12-month cycle. In the context of these losses it should be noted that no Siemens PWR operates with a BTRS or with EOC deborating ion-exchange resins and that they set limits of <1 ppm B in the distillate produced by the evaporators. They also minimise resin wastes by operating the mixed-bed filter to exhaustion (activity break-through), while the filters downstream of the mixed-bed filters normally last for a complete fuel cycle. Compared with the U.S. assessments the EBA losses are particularly low, and significant improvements may be necessary if U.S. PWRs are to minimise the ongoing costs and make EBA operation economic.

Most of the observations found for Siemens PWRs can be expected to apply to U.S. PWRs, but there may be additional constraints in AOA affected plants, especially if AOA is present in combination with high silica levels originating from SFPs with Boraflex fuel racks. What is clear, however, is that to minimise ongoing costs non-recoverable losses of EBA must also be minimised. This will mean that greater awareness is required to ensure that leakage from borated water systems is reduced to the lowest level possible and, possibly, that modifications to the plant drains systems similar to those fitted in Siemens PWRs may be required to recover any boric acid leakage. It will certainly mean that efficient use of the BRS evaporator is essential, as is control of EOC boron concentrations to <1 ppm B, as occurs in Siemens PWRs. If EOC boron

concentrations can be controlled, then a BTRS or beborating resins are not essential, but running resins routinely to exhaustion will be required.

5.4 References

- 5-1 J A Battaglia and J Roesmer, “Utilisation of Enriched Boric Acid in Pressurised Water Reactor Plant”, Proceedings of the EPRI Seminar on PWR Primary Water Chemistry and Radiation Field Control, Paper 34, 1988.
- 5-2 W B Rodill, “Enriched Boron Study Surry Power Station Units 1 and 2”, Proceedings of the EPRI Seminar on PWR Primary Water Chemistry and Radiation Field Control, Paper 35, 1988.
- 5-3 J A Battaglia, L A Lamata, R M Waters, C A Bergmann, J M von Hollen and S M Ditommaso, “Enriched Boric Acid for PWR Application, Cost Evaluation Study for a Twin-Unit PWR”, EPRI Report EPRI NP-6456, 1989.
- 5-4 Westinghouse Electric Corporation, “Final Report Cost Evaluation Study for the Application of Enriched Boric Acid in Millstone Nuclear Power Station Unit 3 for Northeast Utilities Service Company”, Westinghouse Report WP0606-1, 1991.
- 5-5 J Sejvar, C A Bergmann, W J Leech, J D Perock and R J Jacko, “Re-evaluation of the Benefits of Implementing Enriched Boric Acid”, EPRI Report TR-109992, 1998.
- 5-6 T Ichimura, J Sevjar and H Takiguchi, “Evaluation of Dose Reduction Initiatives for Tsuruga Units 3 & 4”, 10th Pacific Basin Nuclear Conference, Kobe, Japan, October, 1996.
- 5-7 “PWR Primary Water Chemistry Guidelines”, Revision 4, Volume 1, EPRI Report TR-105714-V1R4, 1999.
- 5-8 “PWR Axial Offset Anomaly (AOA) Guidelines”, EPRI Report TR-110070, 1999.
- 5-9 M Beer, R Güldner and E Weber, “Fuel Cycle Optimization for Pressurized Water Reactors”, Siemens AG Report, Power Generation Group, 1999 (Top Operation '99, Berlin Oct 24-26, 1999, atw – Internationale Zeitschrift für Kernenergie, 12, 733, 1999).
- 5-10 F Rurtak and P Urban, “High-Burnup Fuel Assemblies Reduce Fuel Cycle Costs”, atw – Internationale Zeitschrift für Kernenergie, 8/9, 549, 2000.
- 5-11 R Riess and T Marchl, “Radiation Fields in Siemens-Designed PWRs”, Water Chemistry of Nuclear Reactor Systems 8, BNES, Vol 1, 17, 2000.
- 5-12 Eagle-Picher Technologies LLC, “Enriched Boric Acid for Pressurised Water Reactors”, Brochure, 2001.
- 5-13 A A Strasser, H J Schröder and K D Sheppard, “ Primary Water Chemistry, Fuel Rod Corrosion, and Crud Deposition in PWRs, A Comparison of European and U.S. Plant Performance”, EPRI Report EPRI TR-107255, 1996.
- 5-14 R Riess, Personal Communication, 1999.
- 5-15 R Roofthoof, M C Thiry, A Cascia, K Garbett, M Halin, E F Lillo, K-H Walter and M Zmitko, “Primary Circuit Chemistry of Western PWR and VVER Power Plants”, Unipede Report, 02004Ren9653, 1996.

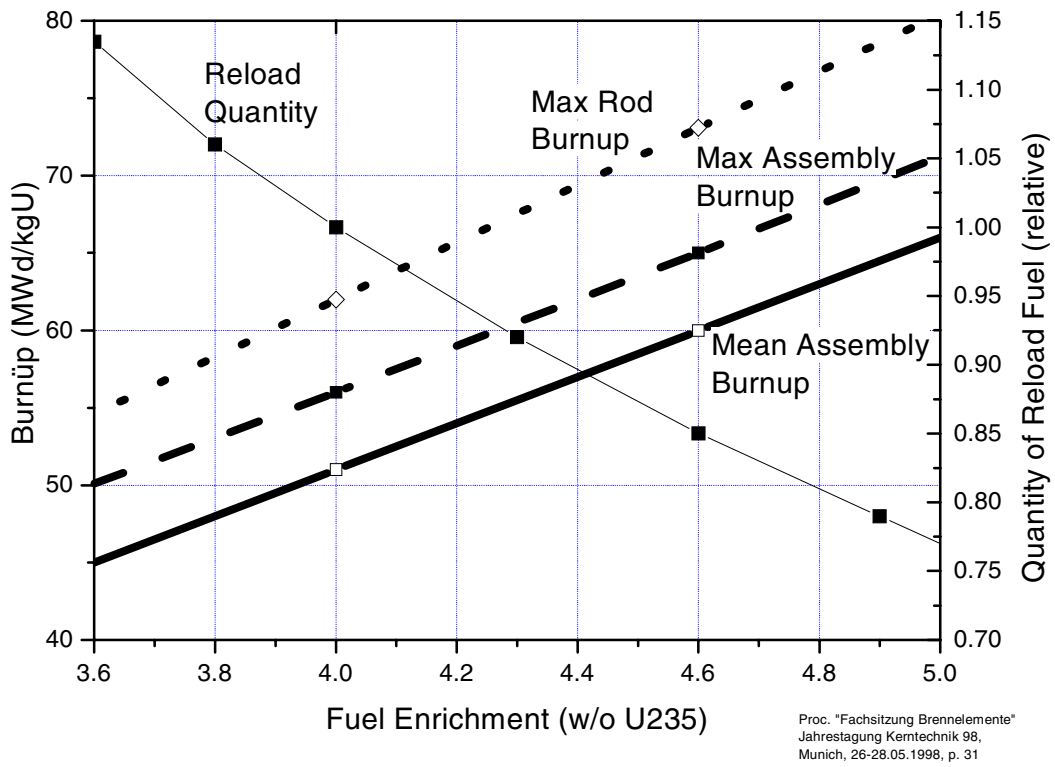


Figure 5-1
 Relationship Between Burn-up, Average Fuel Enrichment and Reload Fraction (5-9)

6

CONCLUSIONS

Operation with enriched boric acid (EBA) at an enrichment of 27-30 atom % ^{10}B has been adopted in most of the recent Siemens PWRs since 1997. This report describes why the change to EBA was made, how it was carried out, and the operational consequences. It also compares the experience in Siemens PWRs with the earlier assessments made for U.S. PWRs and discusses possible implications for U.S. PWRs. The conclusions reached are:

- (1) EBA can be used to give either improved pH control to reduce radiation exposure, fuel clad corrosion and, possibly, Axial Offset Anomalies (AOA), or to enable operation with more highly ^{235}U enriched or MOX fuel.
- (2) The main cost saving associated with the use of EBA in Siemens PWRs is the improved fuel economy, including the lower “back end” costs of storage and final disposal that result from the loading of more highly enriched ^{235}U and MOX fuel. Both contribute to the reduced numbers of new fuel assemblies required. Reduced radiation exposure is a minor factor. This is in contrast with the earlier U.S. PWR evaluations where improved radiation exposure was predicted to be the main benefit.
- (3) Seven of the most recent Siemens PWRs have been converted to operate with 27-30 atom % ^{10}B boric acid. These are Grafenrheinfeld (1997, 31%), Grohnde (1997, 27%), Gösgen (1997, 28%), Brokdorf (1998, 28%), Philippsburg 2 (1998, 29%), Emsland (2000, 28%) and Isar 2 (2000, 30%). Neckarwestheim 2 is planning to change to 27-28% EBA in 2002.
- (4) Siemens PWRs are all single unit stations, mainly with uprated cores of 3765-3950 MWth for the 4-loop stations converted to operate with EBA. Gösgen is a 3-loop 3002 MWth station.
- (5) While many details of Siemens PWR designs are similar to those in Westinghouse PWRs, there are some differences that influence the change to EBA. These include slightly smaller Spent Fuel Pools located in the containment building and four independent Residual Heat Removal and Emergency Core-Cooling trains, which include four Flood Tanks. The latter replace the single Refuelling Water Storage Tank present in Westinghouse PWRs. No Siemens PWR has a BTRS or deborating resin beds.
- (6) Siemens PWRs operate on a 12-month fuel cycle, which includes ~10 months full power operation, one-month stretch-out operation and a short refuelling shutdown. All operate to the VGB high pH water chemistry, which is the equivalent of the EPRI “Modified Chemistry”. Stations converted to operate with EBA load more highly ^{235}U enriched fuel and, except for Emsland, MOX fuel. None, however, has suffered from AOA.
- (7) Siemens PWRs recover essentially all the boric acid let down from the primary circuit and run all ion-exchange mixed-bed filters to exhaustion. The recovered boric acid contains both silica and some lithium, but this has no reported detrimental effect on operations.

Conclusions

- (8) The change to EBA in Siemens PWRs is carried out by methods designed to give sufficient extra ^{10}B reactivity worth, while minimising waste boric acid discharges.
- (9) In Siemens PWRs the change is carried out so that there is no impact on plant safety at any time and with minimal impact on plant operations, and all borated water systems must be converted to the same ^{10}B : ^{11}B isotopic ratio.
- (10) In Siemens PWRs, with the exception of the primary circuit and the Coolant Volume and Chemistry Control System, all borated water systems are converted to EBA during the final months of normal operation. The primary circuit and Coolant Volume and Chemistry Control Systems are converted to EBA as they are borated during the shutdown.
- (11) Most Siemens PWRs have converted to EBA by a “drain and fill” “compensation method”, in which part of the boric acid is discharged to waste and is replaced by 96 weight % ^{10}B boric acid.
- (12) 96 weight % ^{10}B boric acid is used to convert the 7000 ppm B boric acid solution in the Boric Acid Tanks to 30 atom % ^{10}B , as this produces the minimum amount of natural boric acid waste. Systems containing 2200 ppm B boric acid can be converted to 30 atom % ^{10}B with minimum waste boric acid production by adding 7000 ppm B 30 atom % ^{10}B boric acid diluted to a 31.4% “blend” with demineralised water. For a 2900 ppm B solution the equivalent dilution would be 41.5%.
- (13) Gösgen converted to EBA by an “addition method”, in which the addition of 96 weight % ^{10}B boric acid also increased the total boric acid inventory.
- (14) Most Siemens PWRs discharge the waste natural boric acid after processing it through mixed-bed ion-exchange resin beds.
- (15) The change to EBA is reported to have no significant impact on either reactivity or chemistry control during normal operation. In addition, there are either no significant or only minimal effects on the operation of any other borated water circuit. In Siemens PWRs experience shows that it is only necessary to measure the ^{10}B : ^{11}B isotopic ratio at monthly, or even three-monthly intervals and that boron control can be achieved using the normal methods of analysis.
- (16) No significant changes in primary circuit radiation fields have yet been observed in Siemens PWRs, but this is not an unexpected result because the plants that have converted to EBA operate at only slightly higher pH levels than previously.
- (17) The most important ongoing cost of EBA operation in Siemens PWRs is the loss of EBA during the fuel cycle. Efficient recovery of EBA by the boron recycle evaporator is essential, as is the minimisation of EBA losses on anion resins by operating the mixed-bed filters to exhaustion.
- (18) U.S. PWR evaluations are based on a mixture of “feed and bleed” and “drain and fill” methods of conversion to EBA, which would mainly be carried out during the shutdown. Generally, higher EBA enrichments than those used in Siemens PWRs are proposed in order to permit operation at higher pH. While the most recent assessment considers the potential saving if AOA were to be prevented, it is not yet certain that EBA will prevent AOA. The resolution of this question will require experimental study and verification.

- (19) Comparison with U.S. PWR assessments shows that the Siemens method could be used in U.S. PWRs if a similar enrichment level is used, but that conversion of the RWST by a “drain and fill” method would violate the minimum Tech. Spec. limit during draining, and could only be used if a temporary alleviation was permitted by NRC. If higher enrichments were needed, then a “fill and bleed” method similar to that proposed by Westinghouse would have to be followed.
- (20) The U.S. assessments show that boric acid losses in U.S. PWRs are high. If EBA operation was adopted, these losses would need to be reduced significantly to reduce the ongoing EBA replacement costs during normal operation to the level found in Siemens PWRs.

A

EBA MASS BALANCE CALCULATIONS

This Appendix summarises the method used to calculate the amount of 96 weight % ¹⁰B boric acid added to convert tanks and systems to a specified ¹⁰B enrichment. It is believed that this method is the basis of the approach adopted in Siemens PWRs.

A1 Conversion of 7000 ppm B Natural Boric Acid Tanks to 30 Atom % (28.05 Weight %) ¹⁰B Boric Acid

The method outlined below can be used when the initial and final boron concentrations are identical, as is the concentration of the 96 weight % ¹⁰B boric acid added from the Boric Acid Batching Tank. It can be used equally for boron concentrations of 7000 or 21000 ppm total B.

Natural boric acid contains 18.34 weight % ¹⁰B, 81.66 weight % ¹¹B.

The EBA used contains 96 weight % ¹⁰B, 4 weight % ¹¹B.

The final target enrichment is 28.05 weight % ¹⁰B, 71.95 weight % ¹¹B.

If the tank volume is “v” m³, and the volumes of natural boric acid discharged and the 96 weight % ¹⁰B boric acid added are both “y” m³.

The ¹⁰B and ¹¹B mass balances are: -

Initial inventory	v (7000*0.1834) g ¹⁰ B	v (7000*0.8166) g ¹¹ B
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Discharge	y (7000*0.1834) g ¹⁰ B	y (7000*0.8166) g ¹¹ B
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Addition	y (7000*0.96) g ¹⁰ B	y (7000*0.04) g ¹¹ B
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Final inventory	v (7000*0.2805) g ¹⁰ B	v (7000*0.7195) g ¹¹ B
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For ¹⁰B: - $v (7000*0.1834) + y (7000*0.96) = v (7000*0.2805) + y (7000*0.1834)$

hence, $y = v \frac{(0.2805 - 0.1834)}{(0.96 - 0.1834)} = 0.124v$

For ¹¹B: - $v (7000*0.8166) + y (7000*0.04) = v (7000*0.7195) + y (7000*0.8166)$

hence, $y = v \frac{(0.7195 - 0.8166)}{(0.04 - 0.8166)} = 0.124v$

EBA Mass Balance Calculations

A2 Conversion of Systems Containing “z” ppm B Natural Boric Acid to 30 Atom % (28.05 Weight %) ¹⁰B Boric Acid using a “Blend” Containing 7000 ppm B 96 Weight % ¹⁰B Boric Acid

The method outlined below can be used when the initial and final boron concentrations are identical. 7000 ppm B 96 weight % ¹⁰B boric acid is added as a “blend” from a Boric Acid Tank diluted with Reactor Make-up Water. The method can be used for boron concentrations of 2000, 2200 or 2900 ppm total B.

Natural boric acid contains 18.34 weight % ¹⁰B, 81.66 weight % ¹¹B.

The EBA used contains 96 weight % ¹⁰B, 4 weight % ¹¹B.

The final target enrichment is 28.05 weight % ¹⁰B, 71.95 weight % ¹¹B.

If the system volume is “v” m³, the volume of natural boric acid discharged is “y” m³ and the volume of 96 weight % ¹⁰B boric acid “blend” added is also “y” m³. The system concentration is “z” ppm total B and the “blend” added is a “100w” % mixture.

The ¹⁰B and ¹¹B mass balances are: -

Initial inventory	v (0.1834 z) g ¹⁰ B	v (0.8166 z) g ¹¹ B
Discharge	y ₁ (0.1834 z) g ¹⁰ B	y ₂ (0.8166 z) g ¹¹ B
Addition w) g ¹¹ B	y ₁ (7000*0.96 w) g ¹⁰ B	y ₂ (7000*0.04 w) g ¹¹ B
Final inventory	v (0.2805 z) g ¹⁰ B	v (0.7195 z) g ¹¹ B

For ¹⁰B: -
$$v (0.1834 z) + y_1 (7000*0.96 w) = v (0.2805 z) + y_1 (0.1834 z)$$

hence,
$$y_1 = \frac{v z (0.2805 - 0.1834)}{(7000*0.96 w - 0.1834 z)}$$

For ¹¹B: -
$$v (0.8166 z) + y_2 (7000*0.04 w) = v (0.7195 z) + y_2 (0.8166 z)$$

hence,
$$y_2 = \frac{v z (0.7195 - 0.8166)}{(7000*0.04 w - 0.8166 z)}$$

For systems containing: -

2000 ppm B y₁ = y₂ if w = 0.285 i.e. 96 weight % ¹⁰B boric acid is added as 28.5 % “blend”

2200 ppm B y₁ = y₂ if w = 0.314 i.e. 96 weight % ¹⁰B boric acid is added as 31.4 % “blend”

2900 ppm B y₁ = y₂ if w = 0.415 i.e. 96 weight % ¹⁰B boric acid is added as 41.5 % “blend”

B

GLOSSARY

ALARA	As Low As Reasonably Achievable
AOA	Axial Offset Anomaly
BODE	Boron-demineralised water control (Bor-deionat Regelung)
BOC	Beginning (start) of cycle
BRS	Boron Recovery System
BTRS	Boron Thermal Regeneration System
CVCS	Chemical and Volume Control System
EBA	Enriched boric acid
EOC	End of cycle
FSAR	Final safety analysis report
PWSCC	Primary Water Stress Corrosion Cracking
RCS	Reactor Coolant System (Primary Circuit)
RWST	Refuelling Water Storage Tank
SFP	Spent Fuel Pool
STAFAB	Rod insertion limits (Stabfahrbegrenzung)
VCT	Volume Control Tank

Standard Abbreviations used in later Siemens PWRs (abbreviations used in earlier PWRs up to Brokdorf given in bold in parentheses)

FA	Storage of fuel assemblies and other radioactive components
FAA	New fuel store
FAB	Spent fuel pool (irradiated fuel store)
FAE	Reactor refuelling cavity (pool) (BE-becken, TG)
FAF	Reactor internal storage area (between refuelling cavity and spent fuel pool)
FAK	Fuel pool cooling system (TG)

Glossary

FAL	Fuel pool purification system (TG)
FKE	Decontamination plant
GHC	Demineralised water supply system (UD)
GHW	Seal water supply system
JDH	Extra boration system (Zusatzboriersystem) (TW)
JE	Reactor coolant system (HKML) (YA to YP)
JEA	Steam Generator (Dampfzuger, DE, YB)
JEB	Reactor coolant pumps (Hauptkühlmittelpump, HKMP) (YD)
JEC	Reactor coolant piping system (YA)
JEF	Pressuriser (Druckhalter) system (YP)
JEG	Pressuriser relief system (YP)
JET	Reactor coolant leak-off system
JEW	Seal water supply system
JN	Residual heat removal systems (TH)
JNA	Residual heat removal system (Nachkühlssystem) (TH)
JND	High pressure injection system (TH)
JNG	Accumulators (Druckspeicher) (TH)
JNK	Borated water storage system (Borwasserlagerung) (TH)
KA	Component cooling systems (TF)
KAA	Safety-related component cooling water system (TF)
KAB	Process component cooling water system
KB	Coolant treatment (TA to TD)
KBA	(level and) volume control system (TA)
KBB	Coolant storage system (TD)
KBC	Boric acid and demineralised water control system (TB)
KBD	Chemical control system (TB)
KBE	Coolant purification system (TC)
KBF	Coolant treatment system (including evaporators) (TD)
KBG	Coolant degasification system (TC)
KL	Heating, ventilation, air-conditioning systems (HVAC) in controlled areas.
KLA	Heating, ventilation, air-conditioning systems for the inner containment
KLB	Heating, ventilation, air-conditioning systems for the containment annulus
KLE	Heating, ventilation, air-conditioning systems for the auxiliary building

KP	Radioactive waste processing
KPA	Solid waste processing system
KPC	Radioactive concentrates processing system
KPE	Solid waste storage system
KPF	Liquid waste processing system (TR)
KPK	Liquid waste storage system (TR)
KPL	Gaseous waste processing system (TL, TS)
KT	Nuclear collecting and disposal systems
KTA	Drains system of nuclear systems in the containment
KTB	Drains system of nuclear systems in the containment annulus
KTC	Drains system of nuclear systems in the auxiliary building
KTE	Pressuriser and other SRV relief pipework to the pressuriser relief tank
KTF	Drains systems for the containment sump
KTG	Drains systems for containment annulus sump
KTH	Drains systems for auxiliary building sumps
KU	Nuclear sampling systems (TV)
LCQ	Steam generator blowdown system (DE-abschlammung) (RZ)



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