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Water Chemistry of WWER Nuclear Power Plants

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FOREWORD

Chemistry control is one of the most important disciplines and activities in NPP operation. WWERs are currently in operation in a number of countries (Russia, Ukraine, Hungary, Czech Republic, Slovakia, Bulgaria, Armenia, Finland, China) and will shortly start operating in Iran and India, all of which have different national capabilities and, in a number of cases, different circuit chemistry guidelines, criteria and the philosophy underlying the control and management of water chemistry. The position with WWER guidelines is that there is no single document that describes the rationales for controlling individual chemical species and the limit values recommended. There are standards produced by design and research organisations, but no document has been prepared by a wider chemistry community that includes plant chemists from different WWER operating countries, which addresses operational chemistry optimisation issues and is available to WWER operators in all countries.

In contrast with this position, there are three major sets of PWR chemistry guidelines: the EPRI guidelines, the VGB standards and the EDF specifications, which generally follow very similar water chemistry control principles.

The need to harmonise WWER water chemistry regimes, to disseminate best practices and to incorporate advanced PWR water chemistry experiences has been repeatedly expressed in many occasions. Such a harmonised approach to WWER water chemistry would be helpful and PWR water chemistry experiences could then be used to improve WWER water chemistry performance.

The subject of this publication was suggested by the IAEA Technical Working Group on Life Management of Nuclear Power Plants. The activity was organised in 2006-2007 under the IAEA program on nuclear power plant operating performance and life cycle management.

This Nuclear Energy Report (NER) describes specific guidance and the technical bases for the control of chemistry parameters, impurity effects and the application of action levels and zones for WWER NPPs. It covers primary and secondary systems, as well as auxiliary systems. It is intended to be useful to water chemists and chemistry supervisors at all WWER NPPs, to chemistry specialists in WWER plant engineering and fuel design institutes, to nuclear regulatory bodies and to researchers in technical support organisations.

The report is intended to be used as a reference document. It is not mandatory and the different guidance specified for some of the more important circuits in each country are reported. A more consistent approach may follow in future from the information presented. The document is also intended to serve an additional important function, which is to educate or inform any personnel that may be involved with WWER plants in the important aspects of water chemistry strategy and control.

When any NPP, including any WWER NPP, is first commissioned, it is normal for it to operate to the manufacturer's or designer's specifications for the initial warranty period of power operation. In producing this IAEA NER, and where they are available, the design and research organisation specifications have been considered as part of the assessments made by the expert group that produced the document. In a number of cases, impurity limits proposed in this document are more stringent than those specified by the manufacturer or designer, since there are other potential plant operational issues that must be assessed by the Plant Operator in addition to the material warranty issues alone. For example, dose rate limits, liquid waste reduction, safer and longer steam generator operation and feedwater train corrosion product transport limits may not be fully covered by the designer's requirements, but are the responsibility of the Plant Operator.

Finally, it is a Regulatory Body's right to decide on the technical support that must be used to meet any requirements it imposes on the Plant Operator. Although this IAEA document is not mandatory, it is acknowledged that the Regulatory Body of some countries with WWER may include this document in their review when discussing with the Plant Operator what regulation should be applied. IAEA has no right and no desire to interfere in such discussions.

The work of all the contributors to the drafting and review of this publication who are listed at the end of this report is greatly appreciated. IAEA acknowledges the contributions of: K. Garbett (UK), F. Nordmann (France), V. Yurmanov (Russian Federation), J. Schunk (Hungary), I. Smiesko (Slovakia), V. Hanus (Czech Republic) and V. Kozlov (Ukraine). The IAEA officer responsible for this publication was H. Cheng of the Division of Nuclear Power.

1 INTRODUCTION

Nuclear power plants with WWER (Light Water Cooled and Moderated Nuclear Reactors) have a large number of different water systems that are essential to their safe and reliable operation. Of these systems, the primary and secondary side systems are the most obvious important circuits, but there are a number of auxiliary and safety systems with water that are equally essential to reactor operation. The latter include the reactor safety systems containing borated water, the spent fuel storage pond, refuelling pond, primary and secondary circuit make-up systems, a number of closed cooling water systems and service water systems.

Each water system in a WWER serves a different function and has its own chemical dosing and chemical control requirements. These are specified in this NER, but may differ in each country that operates this type of reactor. In this NER all the significant water circuits at WWER plants are considered, the basis of the control and diagnostic parameters specified are outlined and the options based on long-term WWER plant good practice for the different water chemistries that can be used are discussed.

1.1 Scope and Objectives of the Publication

This publication describes the specific guidance and technical bases for the control of chemistry parameters, impurity effects and actions that should be taken in response to abnormal chemistry conditions in WWER NPPs. It is intended to help WWER operating plants understand the important issues of water chemistry control and improve water chemistry program performance.

1.2 Other IAEA publications and activities

The publication was organised under the IAEA programme on nuclear power plant operating performance and life cycle management of 2006-07. For water chemistry control and management in general, there is an IAEA Safety Guide “Chemistry Programme for Water Cooled Nuclear Power Plants (DS 388), under preparation in 2006-08” [1], whilst a number of related IAEA publications are listed in References 2 to 5.

In parallel with this programme, there is an on-going Coordinated Research Project entitled “Optimisation of Water Chemistry Technologies and Management to ensure Reliable Fuel Performance at High Burnup and in Ageing Plants” (FUWAC, 2006-2010), which aims to understand the mechanisms of the following phenomena, taking into account high burn-up operation, mixed cores and plant aging:

- Deposit Composition and Thickness on the Fuel,
- Crud Induced Power Shift (CIPS) and Power Limitation,
- Fuel Oxide Growth and Thickness,
- Corrosion Related Fuel Failure,
- Crud Induced Localized Corrosion (CILC).

1.3 Structure of the publication

Chapters 2 and 3 of the report cover the primary and secondary coolant systems, respectively. Each of these sections has four sub-sections. The first sub-section describes the main design characteristics of the system, the second describes the important issues that must be addressed, the third discusses possible chemistry regimes and the final sub-section proposes operating control parameters and limits. Chapter 4 covers the auxiliary systems used in WWER NPPs. Finally, the report has three appendices that describe the overall design characteristics of WWER NPPs, pH and conductivity calculations and chemical quality requirements.

1.4 Historical Development of WWER Designs

WWERs are a type of pressurised water reactor developed in the former Soviet Union that are in operation in Russia, Ukraine, Hungary, Slovakia, Czech Republic, Bulgaria, Armenia, Finland and China. Two major types are in operation or under construction, the 6-loop designs rated at 440 MWe (1375 MWth) and the later 4-loop designs rated at 1000 MWe (3000 MWth) [6 to 8].

Thirty-six WWER-440 MWe units have been built, of which eight have shut down, and eleven further units were cancelled or still await completion. There are two basic WWER-440 designs. These are the first generation WWER-440s, which includes the initial V-179 design, the V-230 design and the V-270 design with enhanced seismic features. The second generation WWER-440 is standard V-213 design with a full accident confinement system.

Twenty-seven WWER-1000 MWe units have been completed and nine further units are still under construction. Further planned units were cancelled, but there are plans to build additional units in Russia and elsewhere. There are a number of WWER-1000 variants, the initial prototype V-187 design, the V-302 and V-338 designs and standard V-320 design. The new export V-392, V-428, V-466, V-412 variants have enhanced safety features, but are otherwise similar to the V320 design. All the WWER-1000 units have a full containment building. The following stations completed or are nearing completion:

List of WWER units that were completed or are under construction

	WWER-440		**WWER-1000**
V-179	Novovoronezh 3 and 4 (Russia)	V-187	Novovoronezh 5 (Russia)
V-230	Kola 1 and 2 (Russia)	V-302	South Ukraine 1 (Ukraine)
V-230	Kozloduy 1 to 4 (Bulgaria)	V-338	South Ukraine 2 (Ukraine)
V-230	Bohunice 1 and 2 (V-1, Slovakia)	V-338	Kalinin 1 and 2 (Russia)
V-230	Greifswald 1 to 4 (Eastern Germany)	V-320	Balakovo 1 to 4 (Russia)
V-270	Armenia 1 and 2 (Armenia)	V-320	Rovno 3 and 4 (Ukraine)
V-213	Loviisa 1 and 2 (Finland) (Containment Version)	V-320	Zaporozhe 1 to 6 (Ukraine)
V-213	Kola 3 and 4 (Russia)	V-320	Kozloduy 5 and 6 (Bulgaria)
V-213	Rovno 1 and 2 (Ukraine)	V-320	South Ukraine 3 (Ukraine)
V-213	Bohunice 3 and 4 (V-2, Slovakia)	V-320	Khmelnitski 1 and 2 (Ukraine)
V-213	Paks 1 to 4 (Hungary)	V-320	Temelin 1 and 2 (Czech Republic)
V-213	Dukovany 1 to 4 (Czech Republic)	V-320	Volgodonsk/Rostov 1 (Russia)
V-213	Greifswald 5 and 6 (Eastern Germany)	V-320	Kalinin 3 (Russia)

V-213	Mochovce 1 to 2 (Slovakia)	V-428	Tianwan 1 and 2 (China)
		V-412	Kudankulam 1 and 2 (India)
		V-446	Bushehr 1 (Iran)

Of the WWER-440 units that commissioned, Armenia 1, Greifswald 1 to 5, Kozloduy 1 to 4 and Bohunice-1 have been shut down, Greifswald 6 was cancelled before fuel was loaded, Greifswald 7 and 8 were cancelled before commissioning and Mochovce 3 and 4 remain part-complete. The cancelled units were Zarnowiec 1 to 4 (V-213 design, Poland) and Juragua 1 and 2 (V-318 containment version, Cuba). Currently, Armenia 1, Kozloduy 3 and 4 and Bohunice-1 remain in a state where they could be restarted.

Three lower power prototype designs (Novovoronezh 1 and 2 (WWER-210 and WWER-365) and Rheinsberg (70 MWe, Germany) were built in the 1960s, but these are now shut down [6 to 8]. Five further standard WWER-1000 V-320 units, Balakovo 5, Volgodonsk 2, Kalinin 4, and two V-466 units at Belene have been ordered, but some earlier planned V-320 units were cancelled, including Temelin 3 and 4, Stendal and the original Belene project units.

Modified export versions of the WWER-1000 design are under construction or planned. Originally these were given the generic V-392 designation, but they now carry site-specific designations shown in the list above. Of these stations, the two units at Tianwan (China) have AES-91 power plants with a slightly taller reactor pressure vessel and greater passive safety features, whilst the two units at Kudankulam (India) have AES-92 power plants with extra seismic protection. Of these new units, Tianwan 1 and 2 are operational and Kudankulam 1 and 2 are under construction. In addition, one AES-92 unit is under construction at Bushehr (Iran) and two further units AES-92 V-466 units have been ordered for construction at Belene (Bulgaria).

There are plans to construct standardised evolutionary WWER-1200 (AES-2006 power plant) units at Leningrad (V-491) and Novovoronezh (V-392M) in Russia based on the WWER-1000 design and further units are planned.

An overall description of these types of WWER NPP unit is given in Appendix A1.

REFERENCES TO CHAPTER 1

[1] Chemistry Programme for Water Cooled Nuclear Power Plants, IAEA Safety Guide x.x, DS 388, 2008 (?).

[2] High Temperature On-line Monitoring of Water Chemistry and Corrosion Control in Water Cooled Power Reactors, IAEA-TECDOC-1303, 2002.

[3] Water Chemistry and Corrosion Control of Cladding and Primary Circuit Components, IAEA-TECDOC-1128, 1999.

[4] Influence of Water Chemistry on Fuel Cladding Behaviour, IAEA-TECDOC-927, 1997.

[5] Safety Aspects of Water Chemistry in Light Water Reactors, IAEA-TECDOC-489, 1988.

[6] US Department of Energy, Overall Plant Design Descriptions WWER Water-Cooled, Water-Moderated Energy Reactor, DOE/NE-0084 Revision 1, October 1987.

[7] US Department of Energy, Department of Energy’s Team’s Analyses of Soviet Designed WWERs, DOE/NE-0086 Revision 1, September 1989.

[8] R Roofthooft, 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 WWER Power Plants, Unipede Report, 02004 Ren9653, 1996.

2 PRIMARY SYSTEM

2.1 WWER Primary Circuit Design Characteristics

The following sections summarise the design characteristics of the primary circuits of the main types of WWER reactors, the characteristics of the fuel, the purification and auxiliary circuits associated with the primary circuits and the primary circuit safety systems. Schematic layouts of the primary and auxiliary circuits in WWER-440, V213 units and corresponding layouts for WWER-1000, V-187, V302, V-338 and V320 units are shown in Appendix A1.

2.1.1 Primary Circuit

WWER-440 Designs

The primary circuits of the WWER-440, V-179, V-230 and V-213 designs have a reactor pressure vessel (RPV) and six loops, each consisting of a hot leg, a horizontal steam generator (SG), and a cold leg in which is mounted a main circulating pump (MCP). Two isolation gate valves are fitted to the hot and cold legs of each loop, one between the RPV and SG and one between the RPV and RCP. These enable individual loops to be drained for inspection and repair, whilst circulation is maintained in the other loops. There is no separate residual heat removal system and decay heat is removed via the steam generators. A pressuriser (compensator tank) is connected to the cold leg of one of the loops (to two loops at Loviisa) and a spray line to the cold leg of the same loop (two spray lines, one to each loop, at Loviisa). Typical operating conditions are T_{hot} 297°C, T_{cold} 267°C, 12.3 MPa. When Loviisa was uprated, T_{hot} was increased by 3°C.

The compositions of the most important steels are given in Table 2-1 and cobalt impurity levels and surface areas are given in Tables 2-2 and 2-3 [1]. All primary circuit surfaces in contact with the primary coolant are either made from stainless steel (main loop pipework, main coolant pumps, steam generator tubing, steam generator tube headers (collectors), gate valves and auxiliary systems pipework), from low alloy steel (reactor pressure vessel) or carbon steel (pressuriser, type-22K carbon steel) weld clad with stainless steel. Stainless steel components, pipework including SG tubing and the pressuriser clad are normally made from the Russian-type titanium stabilised stainless steel 08Cr18Ni10Ti, (08X18H10T equivalent to AISI (ANSI) 321). The reactor pressure vessels are made from low alloy steel (15Cr2MFA; Loviisa 12Cr2MFA), weld clad internally with two stainless steel layers. The inner layer is a non-stabilised stainless steel (Sv-07Cr25Ni13, similar to AISI 309) and that in contact with the coolant is a niobium stabilised stainless steel (Sv-08Cr19Ni10Mn2Nb (Loviisa Sv-07Cr19Ni10Nb), both equivalent to AISI 347). Recent surveys at the Finnish stations Loviisa 1 and 2 show that considerable numbers of Stellite™ valves are present in the auxiliary circuits and some antimony/graphite in the main coolant pump seals of these stations [1], but other stations do not use components or valves having Stellite™ hard facing alloys.

WWER-1000 Designs

The primary circuits of all WWER-1000 designs have a reactor pressure vessel (RPV) and four loops, each consisting of a hot leg, a horizontal steam generator (SG), an intermediate leg, a main coolant pump (RCP) and a cold leg. The early V-179, V-302 and V-338 designs have two isolation gate valves fitted to the hot and cold legs of each loop, but the V-320 and the new export designs do not include isolation valves. A pressuriser (compensator tank) is connected to the hot leg of one of the loops and the spray line to the cold leg and auxiliary sprays are connected to the charging line beyond the regenerative heat exchanger. Operating conditions are T_{hot} 322°C, T_{cold} 290°C, 15.7 MPa.

Steel compositions, cobalt impurity levels and surface areas are also given in Tables 2-1 to 2-3 [1 and 2]. All primary circuit surfaces are either made from, or are clad in, stainless steel [2]. 08X18H10T stainless steel (08Cr18Ni10Ti, AISI 321) is used for the core structures, main coolant pumps and steam generator tubing, whilst the main loop pipework and steam generator collectors are made from type 10GN2MFA carbon steel, clad internally with 08Cr18Ni10T stainless steel. The pressuriser is also made from 10GN2MFA carbon steel, clad with an inner layer of Sv-07Cr25Ni13 (similar to AISI 309) stainless steel and two layers of Sv-08Cr19Ni10Mn2Nb niobium stabilised stainless steel (similar to AISI 347). The reactor pressure vessel and head is made from the low alloy steel 15Cr2MNFA, also clad with an inner layer of Sv-07Cr25Ni13 stainless steel and two layers of the niobium stabilised stainless steel Sv-04Cr20Ni10Mn2Nb (again similar to AISI 347). Small amounts of other grades of stainless steel and ferritic stainless steel are also present in the core internal structures, but no Stellite™ hard facing alloys are present in the primary or auxiliary circuits.

The primary circuits of the new AEA-91 and AES-92 WWER-1000 reactors are identical to those used in the WWER-1000 V-320 (and V-392) models, although Tianwan 1 and 2 do not have high temperature titanium sponge filters installed (see Appendix A1). The primary circuit of the new evolutionary AES-2006 WWER-1200 V-491 design is based on the existing WWER-1000 design and will also be similar, but will have a higher core power (3200 MWth initially) and will operate at slightly higher pressure (16.2 MPa) and temperature (T_{hot} ~330°C), have a slightly larger reactor pressure vessel, slightly larger steam generators and be designed for fuel cycle lengths of 12-24 months and have a design life of 60 years. These three designs all have greatly enhanced safety features (see Section 2.1.4).

2.1.2 Fuel

All WWER cores are based on a hexagonal geometry, with the individual fuel assemblies and control rods having hexagonal symmetry. WWER-440 fuel assemblies have a hexagonal cross section that contain fuel rods arranged on a triangular pitch, which are contained within an outer solid sheath that limits cross flows. Perforated sheaths are used in the fuel for the first WWER-1000 unit, Novovoronezh 5, but other WWER-1000 units do not have a sheath.

A WWER-440 core contains 349 fuel assemblies, each having 126 fuel rods. In V-230 and V-213 cores there are 37 control assemblies. The control assemblies are twice as long as the standard assemblies, with the upper half made from a hexagonal boron-steel (20%Cr, 16%Ni, 2%B) absorber segments in a Zr-2.5%Nb sheathed tube. The lower part (fuel follower) is similar to a standard fuel assembly. In normal operation thirty control assemblies are totally withdrawn and the lower fuel section forms part of the core. The remaining seven control assemblies are used for reactor power regulation. In a reactor trip all the control assemblies are inserted (by gravity) so that the absorber section lies within the core and the fuel section sits below the core. At Loviisa, Bohunice V-1, Kola 1 and 2 and Novovoronezh 3 the outermost 36 fuel assemblies were replaced with dummy steel assemblies to limit neutron irradiation of the reactor pressure vessel.

Except for Novovoronezh 5 where there are 151 fuel assemblies, all WWER-1000 unit cores have 163 fuel assemblies, each containing 312 fuel rods. In WWER-1000 units the control assemblies used in the WWER-440 design was replaced by sixty-one PWR-type reactor control rod clusters (RCCAs) containing either boron carbide (Russian fuel) or silver-indium-cadmium absorber (Westinghouse fuel).

Standard Russian fuel supplied by TVEL has uranium dioxide pellets with a central hole. The fuel has a zirconium-1% niobium alloy (Є-110) clad and when outer sheaths are used they are made from zirconium-2.5% niobium alloy. Spacer grids and end caps were made from the same 08X18H10T stainless steel as used in other parts of the primary circuit up to about 1998, but later Russian fuel has Zirconium-1% niobium alloy spacer grids. Fuel supplied by Westinghouse and BNFL has either Zircaloy-4 or ZIRLO clad and Zircaloy-4 spacer grids.

Standard WWER-1000 Russian TVEL fuel also has zirconium-1% niobium clad and 08X18H10T spacer grids and end caps. With the exception of Novovoronezh 5, WWER-1000 fuel assemblies do not have an outer sheath. At Temelin, Westinghouse fuel with Zircaloy-4 clad and spacer grids was loaded from the first start-up and ZIRLO clad fuel is now loaded, but Westinghouse fuel will be replaced by TVEL fuel from 2010, whilst Westinghouse fuel with ZIRLO clad is being tested at South Ukraine 3.

Until 1998-2000, WWER fuel cycles were essentially always 12-month cycles and the fuel loaded had an enrichment of up to 3.6% ^{235}U in WWER-440 units and 4.4% in WWER-1000 units. The burn-up is up to 40 GWd tU^{-1} ^{i}n a typical lifetime of four fuel cycles. Higher enrichment next generation fuel (‘profiled’ fuel) with an enrichment of 3.82% ^{235}U has been loaded from 1998 and fuel assemblies with enrichments of up to 4.25% ^{235}U containing gadolinium burnable poison and a lifetime of up to five fuel cycles and a burn-up of up to 57 GWd tU^{-1} were being loaded by 2005-2006.

Newer fuel designs with higher enrichments of up to 4.95% ^{235}U and design burn-ups of up to 68 GWd tU^{-1}, also supplied by TVEL, are being tested at a number of Russian, Ukrainian and Bulgarian WWER-1000 units. In addition, longer fuel cycles are under consideration and tests are underway in the Ukraine into load-following operation for the WWER-1000 units. These new fuel designs will be used in the AES-91 and AES-92 reactors being constructed at Tianwan, Kudankulam, Bushehr and Belene.

For the evolutionary WWER-1200 reactors the active length of the fuel in the fuel assemblies will be increased from 3.53 to 3.78 m, the top and bottom end-cap lengths reduced and the central fuel pellet hole eliminated. This will enable the fuel mass to be increased by 18%, compared with the TVEL advanced fuel supplied for WWER-1000 reactors.

2.1.3 Purification and Auxiliary Systems

All WWERs have a number of coolant purification (SVO = Special Purification Circuit) and auxiliary systems designed to carry out the following overall functions:

- purification of the primary coolant and the recovery of the boric acid and water discharged from the primary system during a fuel cycle for later reuse,
- minimisation of the volume of radioactive wastes that must be stored as radwaste, and
- removal of the main radionuclides generated during a fuel cycle (^{137}Cs and ^{60}Co) on to solid ion exchange or other substrates for long-term storage as solid radwaste.

- control of primary chemistry (potassium and ammonia concentrations)

The purification systems provided for the primary system, reactor coolant system (RCS), include the following subsystems:

(1) Primary Coolant Letdown Purification System (SVO-1)
(2) Letdown Purification System (SVO-2)
(3) Leakage and Drains Water Purification System (SVO-3)
(4) Fuel Cooling Pool and ECCS Tank Water Purification System (SVO-4), and
(5) Boric Acid Concentrate Purification System (SVO-6)

All valves and pipework and most equipment in the SVO-1, SVO-3 and SVO-6 systems are made from 08Cr18Ni10T stainless steel, but the main structural material in the SVO-2 and SVO-4 systems are made from 08Cr18Ni9T stainless steel.

The two main coolant purification systems are SVO-1 (otherwise called the High Pressure Primary Coolant Purification System) and SVO-2 (otherwise called the Low Pressure Primary Coolant Purification System). The SVO-1 and SVO-2 systems installed in WWER-440 and WWER-1000 units differ significantly, as do the purification systems in the different WWER-440 and WWER-1000 variants. The principal differences are given in Table 2-4. The two purification systems have the following main functions:

SVO-1 (a) Primary coolant impurity and radionuclide clean up using either ion exchange resins beds (WWER-440 and early WWER-1000) or high temperature filters (WWER-1000 V-320).

(b) Removal of excess alkali metals and boric acid from the coolant during the fuel cycle.

SVO-2 (a) Clean-up to remove corrosion and fission products from the coolant let down from the controlled leakage system from both the main coolant pumps and primary make-up water pumps.

(b) Clean-up to remove corrosion and fission products from the coolant discharged to the boron recovery system as part of the daily boric acid dilution programme.

(c) Removal of excess alkali metals and boric acid from the coolant during the fuel cycle.

The way that these purification circuits interlink with the primary circuit are shown in Appendix A1, Figures A1-3, A1-6 and A1-7 and the details of each circuit are summarised below. The volumes of the resin beds at each type of station are summarised in Table 2-5 and the characteristics of the high temperature filters installed in WWER-1000 V320 are given in Table 2-6.

WWER-440 Designs

SVO-1 (Primary Coolant Letdown Purification System)

In WWER-440 V-230 units SVO-1 consists of a single loop operating at full circuit pressure driven by the pressure drop of 0.52 MPa across the main coolant pumps. In later units (e.g., Bohunice and Kozloduy) SVO-1 circuit has three vessels containing ion exchange resin mixed-beds in the K^+-NH_4^+/borate form, a cation bed in the H^+ form and an anion bed in the OH^- form. It does not contain a resin catcher filter. It takes and returns its flow to all six loops. Normally, only the mixed bed is used continuously to remove fission and corrosion product radionuclides, but the anion bed is used periodically to reduce boric acid concentrations when the concentration falls below 0.3 to 1.0 g/kg and to remove anionic impurities if necessary. The cation bed is used periodically to adjust the potassium and/or ammonium concentrations and cations. The flow rate is normally 15 to 30 tonnes/h and, since there is only a single clean-up loop, total coolant purification rates are 50% of those in the V213 design. Earlier V-230 units have slightly different ion exchange resin bed configurations. Thus, Novovoronezh 3 and 4 have one anion and one mixed-bed ion exchange bed, whilst Kola 1 and 2 have one cation and one anion ion exchange resin bed (Table 2.4).

In WWER-440 V-213 units (including Loviisa 1 and 2) SVO-1 consists of two loops, each connected to three of the primary circuit loops, one loop containing a single mixed bed ion-exchange resin in the K^+-NH_4^+/borate saturated form and the second two separate cation and anion ion-exchange resins. At most stations the separate cation and anion beds also operate in K^+/NH_4^+ and borate saturated forms. The two SVO-1 loops are connected across the main coolant pumps and operate at full primary circuit pressure. The primary coolant is cooled to 45 to 60°C, which is close to the upper limit for ion exchange resin operation) by a regenerative heat exchanger, followed by a non-regenerative heat exchanger. The loops are located entirely within the primary circuit hermetically sealed confinement area, except at Loviisa where they are in the containment. There are no purification loop pumps and the 0.4 MPa pressure drop developed across the main coolant pumps drives the purification flow. Each loop contains a resin fines catcher filter (absent at Loviisa). At most stations the two loops take water from the downstream sides of three of the main coolant pumps and return it to the upstream sides of the main coolant pumps in the same three loops. Differences exist in the groupings used at each unit. At Dukovany the loop containing the mixed-bed resin is supplied by RCS loops 2, 3 and 4 and that containing the separate cation and anion beds is supplied by RCS loops 1, 5 and 6. In other Russian stations the equivalent groupings are RCS loops 1, 2 and 6 and RCS loops 2, 3 and 4, whilst at Loviisa both SVO-1 loops take water from the downstream side of the pumps in loops 2, 5 and 6 and return it to loops 1, 3 and 4, but in one case it is returned to the hot legs upstream of the steam generators and in the other to the cold legs upstream of the main coolant pumps. The operating pressure is 12.3 MPa and flow is controlled at 20-25 tonnes/h (m^3/h) (27 tonnes/h at Loviisa) in each loop by a flow-regulating valve; the design pressure is 18.0 MPa.

SVO-1 can be operated in a number of ways. At Loviisa, Dukovany and Bohunice 3 and 4 (V-213 design) all beds operate saturated with respect to K^+, Li^+, NH_4^+ and borate and at Loviisa and Bohunice 3 and 4 both purification loops operate at all times (the flow rate of 50 tonnes/h corresponds to 0.12 % of the total primary coolant flow). However, only one loop is used at Dukovany, and this is alternated from cycle to cycle (with the second loop operated periodically to maintain the bed at equilibrium with the coolant). At Bohunice 1 and 2 (V-230 design) only the mixed bed is operated in the saturated form and the separate cation and anion beds are used in the H^+ and OH^- forms to adjust the potassium/alkali and boron concentrations. Separate anion and cation beds are also used at shutdown at Paks. At Loviisa, Mochovce and Bohunice 3 and 4 the potassium concentration during the fuel cycle is controlled by reducing the ammonia concentration. This alters the K^+/Li^+/NH_4^+ equilibrium on the cation resins, enabling the resin beds to retain more potassium as the cycle proceeds. At all stations the saturated K^+/NH_4^+ cation resins also equilibrate with respect to the lithium as Li^+ is formed during the cycle. Although the ion exchange beds are designed to be regenerated, they are replaced when their capacity is exhausted every two years at Dukovany, three to five years at Bohunice 3 and 4 and four years at Paks.

SVO-2 (Letdown Purification System)

SVO-2 is a low pressure primary coolant purification loop in the Letdown and Make-up System that in most units operates at 0.2 MPa and at 20-40 m^3/h and the design temperature is 50°C. In both V-230 and V-213 units, SVO-2 is used to purify the "Organised Primary Coolant Drains" (all boric acid solutions that can be reused), which are stored in the "Dirty Condensate" tanks (capacity 1000 m^3). SVO-2 takes water from downstream of the main thermal deaerator and after purification either returns the water to the second thermal deaerator, or to contaminated water (boron recovery) hold up tanks. The purified boric acid leaving the system is normally concentrated by evaporation and re-used. In V-230 units SVO-2 cannot be used for low pressure coolant purification during normal operation, as there is no continuous primary make-up under these conditions. In V-213 units SVO-2 can be used during normal operation for "direct" coolant purification. At both Bohunice and Dukovany the SVO-2 resin beds are regenerated if they exhaust. Alternatively they were regenerated before the annual shutdown (Dukovany), or if they are expected to exhaust during the shutdown (Bohunice). At Loviisa the beds are replaced before the shutdown. The V-230 units have three beds, two cation beds and one anion bed (in the borate form)

In all V-213 units, SVO-2 has a single train of four resin beds, each of 3 m^3. These are a cation bed in the H^+ form (used to remove potassium during the cycle), an anion bed in the borate form (used to remove anionic impurities during normal operation and shutdown after the main coolant pumps have been stopped) and two anion beds in the OH^- form (used to reduce boron concentrations at end-of-cycle when the boric acid concentration is <0.2-0.5 g/kg). However, Loviisa has three beds, of which the cation bed (H^+) and the anion bed (borate form) are used for coolant purification, both mainly during the shutdown. The third larger anion bed (OH^- form) intended for boron removal is not used and no resins are loaded.

Letdown and Make-up System

In V-213 units, SVO-1 and SVO-2 are both linked to the Letdown and Make-up System. The Letdown and Make-up System takes letdown from SVO-1, reduces the pressure and passes the letdown to a thermal deaerator operating at ~104°C, 0.12 MPa. The deaerator has a gas/vapour flow of 130 kg/h that flows to hydrogen re-combiners in the off-gas system. After deaeration, the coolant is returned to the Primary Circuit Purification System via charging pumps operating at 13.5 MPa. At most V-213 plants part of the charging flow is routed to the main coolant pump seals (except at Loviisa where the pump seals are mainly supplied from downstream of the SVO-1 ion-exchange beds). Pump seal leak-off (~50% of the total) is returned to a collection tank (which is part of the Controlled Leakage System) and from there either to the charging pump suction line, or to the inlet of the thermal deaerator. Excess charging flows and leak-off from the charging pumps is routed to the thermal deaerator. At Dukovany and Bohunice 3 and 4 most make-up enters the primary circuit via the main coolant pump seals, although more commonly part or most of the make-up is added via the charging line.

In V-230 units, the absence of main coolant pumps with shaft seals means that only small amounts of coolant are routed continuously to the Letdown and Make-up System during normal operation. Therefore, only a single deaerator is installed in the letdown system and there is no means of purifying the coolant using the Letdown Clean-up System, SVO-2. The small quantity of coolant that passes to the Controlled Leakage System is collected in a Controlled Leakage collection tank from which it is routed either back to the primary make-up deaerator, or to the ‘Dirty Condensate’ tank and the contents are processed periodically by the boron recovery system.

WWER-1000 Units

The coolant purification and letdown and make-up system installed in the earlier V-187, V-302 and V-338 designs are similar to those installed in WWER-440 V-213 units (see Figure 2.3). However, each loop only contains a single mixed-bed ion exchange vessel and a resin catcher filter. Each loop operates at 20-30 m^3/h and at about 40°C. In these plants SVO-2 is identical to that in the WWER-1000 V-320 units.

SVO-1 (Primary Coolant Letdown Purification System)

In WWER-1000 V320 units the Primary Circuit Letdown Filtration System (SVO-1) is located in the containment. It has of four identical loops each containing a high temperature-high flow rate mechanical filter containing a titanium metal sponge filter medium, followed by a catcher filter. The four loops are connected across each of the GTsN-195 main coolant pumps and the flow rates are determined by the pressure (0.62 MPa) developed across each pump. The filters operate at 290°C, 15.7 MPa and have a design flow rate of 60 to 80 tonnes/h per loop (100 tonnes/h per loop maximum, maximum 0.5% of the total coolant flow). The loops are intended to remove fine particulate thus reducing radiation fields, but as the coolant should normally contain only small concentrations of particulate they are probably only effective at start-up and shutdown. The characteristics of the filters are given in Table 2.5.

SVO-2 (Letdown Purification System)

In V-320 units the low pressure SVO-2 Controlled Leakage Filtration System is located outside the containment in the Auxiliary Building. It has two parallel ion-exchange resin bed trains, each of which has two separate cation beds in the H^+ and K^+-NH_4^+-Li^+ forms, respectively (i.e., six beds overall), a single anion bed in the borate form and a resin fines catcher filter. The normal SVO-2 flow rate through the resin beds is 30 tonnes/h at 0.2 MPa (0.035 % of the total primary circuit flow for each stream) and a temperature of about 30°C.

Letdown and Make-up System

In V-320 units the Letdown and Make-up System includes SVO-2. Letdown flow is taken continuously from the intermediate legs of two of the primary circuit loops (in practise from the hot filtration loops) and flows in turn through a regenerative heat exchanger, a non-regenerative heat exchanger and one of two pairs of pressure reducing valves, all of which are located in a containment. The flow at about 30°C is then directed to the SVO-2 system. After purification, the coolant passes to the thermal deaerator operating at ~104°C, 0.12 MPa (130 kg/h gas/vapour flow to the hydrogen re-combiners in the off-gas system) in the Letdown and Make-up System and then to two out of three charging pumps, which return the make-up at

17.8 MPa to the cold legs of all four primary circuit loops via the regenerative heat exchanger. Part of the charging flow is routed to the No.1 seals of the main coolant pumps and the leak-off is returned to the letdown upstream of the thermal deaerator.

AES-91, AES-92 and AES-2006 Units

The coolant purification and letdown and make-up systems installed in the new AES-91, AES-92 and AES-2006 designs are similar to those installed in the earlier WWER-440 V-320 units, but with the following changes:

- The two AES-91 units at Tianwan (WWER-1000 V-428) both have a single coolant purification train installed, consisting of a continuously operated mixed-bed resin and two periodically operated cation and anion resin beds. No SVO-1 high temperature titanium filters are fitted.

- The AES-92 units at Kudankulam (WWER-1000 V-412), Bushehr (WWER-1000 V-446) and Belene (WWER-1000 V-466) all follow the standard WWER-1000 V-320 coolant purification circuit configurations and all have four high temperature titanium filters and two coolant purification trains, each with two cation beds and one anion bed.

- The coolant purification trains to be installed in the AES-2006 units is still to be finalised.

In addition to these design changes, the new reactors have adopted the later German VGB standard Identification System for Power Stations, KKS (Kraftwerk-Kennzeichnungssystem) first used for nuclear power stations in the Siemens ‘Konvoi’ PWR design in the mid-1980s. Other plants use the earlier VGB AKW system identifications. These are all defined in the Glossary, paragraph 3 under SVO definition.

2.1.3.1 Other Purification Circuits

Purification circuits are installed in a number of other systems, particularly those in the radwaste plant. The systems associated with the primary circuit are the Leakage and Drainage Water Purification System (SVO-3), the Cooling Pool and ECCS (Emergency Core-Cooling System) Tank Water Purification System (SVO-4, which is also used to purify the refuelling cavity) and the Boric Acid Concentrate Purification System (SVO-6), as the contents of these systems can mix with, or can be added to, the primary coolant.

All the ion exchangers installed in these purification systems are designed to be regenerated periodically to restore the exchange capacity of resin. The process includes: back-washing, regeneration, post-regeneration washing, hydraulic discharge of the spent resin, and hydraulic loading of a fresh resin. During regeneration, the filters are disconnected from the main flow line.

SVO-3 (Leakage and Drains Water Purification System)

The leakage and drainage water purification system (SVO-3) is used to treat primary and other water that has been lost by leakage (leakage water) or is otherwise unsuitable for reuse in the primary circuit and, separately, to treat boron-containing water (borated water) discharged from the primary system during normal control of the boric acid concentration during the fuel cycle (boron control), as well that discharged during reactor cool down, refuelling and start-up.

The system typically consists of several parts: active liquid radwaste collection, borated water collection, filtration and collection of leakage water, evaporation of the collected liquids, condensation and degassing of the steam produced by the evaporators and final purification of distillate. There are two nominally interchangeable evaporators used to process the borated water and leakage water, each of which has a capacity of 7 tonnes/h and operates at 0.25 MPa (in a heated chamber), two purification loops containing a charcoal filter, a cation bed in the hydrogen ion form and an anion bed. The purification loops can be connected to either evaporator, however in practice one evaporator is dedicated to boron recovery and second for waste treatment. Essentially identical systems are installed in all WWER units.

Leakage and rinse water ('wash' water) is collected in leakage water sumps, which in WWER-440 units serve both units in the reactor building. The water and other liquid radwaste are pumped from the sumps by lift-pumps and then through leakage water filters for remove mechanical impurities. After filtration, the leakage water is collected in leakage water tanks (normally with a capacity of 250 m^3) and is pumped to the leakage water evaporator. The concentrate (salt concentrate) produced by evaporation of the leakage water is transferred to the liquid waste storage tanks and the distillate is re-used for primary system make-up and for auxiliary purposes, or if it is unsuitable for reuse it is discharged as liquid effluent. The leakage water is concentrated to a salt concentration of 60 g/1 and is distributed under gravity from the base of the evaporator to a second evaporator, where it is concentrated further to 200 - 400 g/1 ('still' residue). The secondary steam produced by the second evaporator is returned to the main evaporator and the 'still' residue is pneumatically transported to the 'still' residue tank in the liquid radioactive waste storage.

Borated water and primary coolant discharged during the fuel cycle and that discharged during start-up and shutdown is collected in 'dirty' condensate tanks (with capacities of 636 and 534 m^3 in earlier V-230 units). The contents of these tanks are transferred by 'dirty' condensate pumps to the boron recycle evaporator and the pumps can also be used to pump the liquid to the SVO-2 system for purification to remove potassium and lithium. The 'dirty' condensate system in WWER-440 units serves the two units housed in the reactor building. Concentrated boric acid and pure water ('clean' distillate) produced when borated water is processed are both re-used in the RCS. The borated water is concentrated in the evaporator to 40-50 g/l and is distributed under gravity to the boric acid sump tank of the SVO-6 system for further purification and recycling in RCS.

Secondary steam from the evaporators is condensed in the condenser-degasser and the condensate is pumped out through filters to remove any oil. Some condensate is returned to the evaporator to wash down the secondary steam. Non-condensed steam and gaseous impurities from the condenser-degasser are removed via a relief device. The gases are purified before they are discharged, whilst the condensate is returned to the condenser-degasser. After filtration, the oil-free condensate is cooled in a condensate cooler, passed through ion exchange filter beds and a mechanical filter trap and is finally collected in 'check' tanks (normally of 70 m^3 capacity). After radiochemical analysis, the condensate is pumped to the 'clean' condensate tanks for re-use in RCS, but any poor quality condensate can be returned to leakage water tank for treatment and radwaste storage.

SVO-4 (Fuel Cooling Pool and ECCS Tank Water Purification System)

The cooling pond and ECCS tank water purification system (SVO-4) is used to purify the boric acid solution used in the fuel cooling pool (spent fuel pool), refuelling cavity, the ECCS tanks and, in WWER-440 V-213 units, the bubble condenser trays. Its function is to remove chemical, radiochemical and corrosion products (from structural materials) impurities during normal operation (to maintain the required water chemistry) and after an accident (to prevent environmental radioactivity release). The system is only operated periodically during normal power operation.

Boric acid solution from ECCS tanks, the cooling pool and the bubble condenser is pumped by the corresponding pumps to the SVO-4 system, where it is treated in a single train consisting of two cation and one anion exchangers, followed by resin filter trap, and it is returned to the ECCS tanks, the cooling pool and or the bubble condenser. If the required purity standards are not achieved in the SVO-4 system, the liquid can be drained to the ‘dirty’ condensate tanks for further processing by the leakage water evaporator.

In the early first generation WWER-440, V-179 and V-230 units, both units of the twin reactors contained within the single reactor building were provided with only a single train consisting of a charcoal filter and ion exchange vessels. In the later WWER-440 V-213 units each reactor has a separate interchangeable SVO-4 ion exchange train. At the WWER-1000 V-320 units at Temelin, SVO-4 consists of a single train containing two cation exchange beds in the H^+ form (the first of which is called a mechanical filter) and finally a single anion exchange bed in the OH^- form. At Loviisa the spent fuel pool purification system has two mechanical filters followed by a cation bed and then an anion bed and is also used for the clean up of the emergency coolant tank. At Temelin, SVO-4 is used in a similar manner, in addition to if main function of removing caesium from the spent fuel pool.

Some of WWER plants use additional filtration system to provide high transparency of water in reactor and refuelling cavity during reactor refuelling. For example, Paks, Novovoronezh, Balakovo use BALDUF/GAARD glass fibre-based cartridge filter candles for fine filtration.

SVO-6 (Boric Acid Concentrate Purification System)

The boric acid concentrate purification system (SVO-6) is designed to purify the boric acid concentrate produced by treatment of the borated water and drain water discharged from the RCS for reuse in the fuel cycle. The system consists of a cooler, sump tanks, pumps and two ion exchange beds, a cation bed in the hydrogen ion form and an anion bed in the borate form. Boric acid concentrate supplied from the boron recycle evaporator is cooled in the cooler and is collected in the sump tank (normally of 8 m^3 capacity), from which it is pumped through cation and anion exchangers designed to operate at 1 MPa and 50°C and a resin trap. An additional pump is used to recirculate the concentrate through a boron meter. The purified concentrate is passed to the boric concentrate tanks. During normal system operation, the boric acid concentration is controlled automatically by changing the flow rate of concentrate supplied from the evaporator.

2.1.4 Primary Circuit Safety Systems

WWER-440 Units

WWER-440 V-230s were originally designed without an emergency core-cooling system (or secondary-side auxiliary feedwater systems), although some later units (e.g., Bohunice V-1) were fitted with both these systems and a spray system [3]. The original accident localisation system (which acts as a reactor confinement system, but was of small volume) had a poor leak tightness and a poor hydrogen mitigation capability, and was only designed to cope with a 100 mm pipe rupture with a hole of 32 mm diameter. If a large LOCA occurred, the accident location system was designed to vent to the atmosphere when the internal pressure reached 0.02 to 0.05 MPa overpressure.

These safety systems features were modified in the WWER-440 V-230 units that were still operating in the mid to late-1990s (Novovoronezh 3 and 4, Kola 1 and 2, Bohunice 1 and 2 and Kozloduy 1 to 4) to improve their ability to respond to major LOCAs. The measures taken included:

- Annealing of the reactor pressure vessels.
- Reducing primary system leakage rates,
- Rebuilding the emergency core-cooling system to provide two fully independent trains for each unit,
- Installing additional confinement area spray systems to provide two fully independent trains for each unit,
- Installing primary and secondary circuit bleed and feed accident management systems,
- Improving the leak tightness of the confinement system by factors of up to forty and fitting confinement boundary isolation valves,
- Installing hydrogen monitors and recombination units, and
- Improving the fault diagnosis, emergency control, electrical, seismic, ventilation and fire systems.

WWER V-213 units were designed with an emergency core cooling system (ECCS), several secondary-side cooling systems to remove heat from the steam generators following an accident and an engineered accident localisation system capable of coping with a 500 mm main loop pipework break [3]. The former include four accumulators connected to the upper part of the reactor pressure vessel and three emergency 200% redundancy high pressure and low pressure core cooling trains (plus two auxiliary feedwater trains, see Section 4). The latter comprises a hermetically sealed confinement space, which is designed to withstand an overpressure of 0.15 MPa, but do not have the same leak-tightness that characterises a full containment building. In a LOCA, the confinement vents to four large receiver volumes that act as air traps through a ‘bubble condenser’ tower where the pressure is reduced in large pressure suppression trays filled with boric acid solution which will also partly remove (scrub) some fission product gases from the steam-water mixture released in the LOCA. The boric acid for the three emergency high pressure and low pressure core cooling trains is taken from high pressure injection/recirculation system borated water storage tanks containing 40 g/kg boric acid and later from the low pressure injection/recirculation borated water storage tanks containing 12 g/kg boric acid.

The ECCS comprises three independent sub-systems, which give full protection across the entire spectrum of loss of coolant accident (LOCA) break sizes. The systems are:

(1) The core flooding system (CFS),
(2) The high-pressure injection/recirculation system (HPS) and

(3) The low-pressure injection/recirculation system (LPS).

The high-pressure injection system (HPS) prevents core uncover in a small LOCA, when the high system pressure is maintained, and it delays core uncover for intermediate sized LOCAs. The passive CFS is an additional method of adding coolant into the primary system and due to high pressure set point for discharging coolant from the accumulator, this system support the function of HPS during small and intermediate sized LOCAs. Under certain conditions (e.g., a small break LOCA with secondary "feed and bleed" cooling), the CFS may even replace the short term cooling function of the high-pressure injection system. The low-pressure injection/recirculation system (LPS) is designed to recover the core cooling at low pressures. For larger LOCAs, up to a double-ended guillotine failure of the main coolant pipework, the LPS and the CFS operate together providing coolant to cool the core. The recirculation mode of the LPS is designed to permit boron concentration control and long-term core cooling after a LOCA.

Secondary side cooling systems are important mitigation systems for very small LOCAs and for small LOCAs when the HPS is totally unavailable. Secondary side cooling is achieved by delivering feedwater to steam generators using emergency feedwater or auxiliary feedwater systems, whilst simultaneously dumping steam the secondary circuit via the SG safety relief valves, or by atmospheric steam dump or process condenser steam dump stations (part of secondary decay heat removal system).

The reactor building pressure suppression system and the reactor building spray system prevent overpressure of the accident localization compartments during a LOCA and, in addition, remove (scrub) fission products from the steam-water mixture as it is discharged to the atmosphere. The pressure suppression trays are filled with 12 g/kg boric acid solution. The reactor building spray system (RBS) is designed to prevent overpressure of the localization compartments if ‘feed and bleed’ core cooling via HPS is used. There are three reactor building spray systems, which take their spray water from the three low pressure emergency core cooling trains, to which hydrazine and potassium hydroxide is added from three separate hydrazine-dosed spray additive tanks that also contain boric acid. Later the sprays take their water from the building sumps. These spray water in to the reactor compartments following a LOCA or a steam line break limiting pressure rises and the release of fission products to the environment. Operation of the pressure suppression and spray systems do not affect operation of ECCS, but if successful mitigation of the LOCA cannot be achieved and core melt ensues, the consequences of any accident will be reduced if the functions of containment overpressure protection and radioactivity removal are performed.

At Loviisa, the standard WWER V-213 safety features were replaced by a full PWR-type containment building, within which these safety features were installed. The containment building was also fitted with ice condensers to reduce temperature and pressure if a large LOCA occurred.

WWER-1000 Units and New Reactor Designs

WWER V-1000 units are all fitted with a containment building and have four accumulators connected to the upper part of the reactor pressure vessel and three high pressure and low pressure emergency core cooling trains (plus two auxiliary feedwater trains) [3]. There are also three reactor building spray systems, which initially take their spray water from three low pressure emergency core cooling trains, to which hydrazine and potassium hydroxide is added from three separate small hydrazine-dosed spray additive tanks (of 10 m^3 volume in WWER-440 V-213 units and 6.5 m^3 in WWER-1000 V-320 units), and later from the containment sumps. These sprays are designed to limit containment pressure and iodine volatility following a LOCA or a steam line break.

The AES-91, AES-92 and AES-2006 designs all have a double containment building and have enhanced active and passive safety systems that meet Russian, IAEA and European Reactor Requirements. All are designed to cope with both design-basis and beyond-design-basis accidents and have the following systems installed [4]:

Active Pumped Safety Systems:

- Active Emergency Core Cooling and Containment Spray Systems.
- Active Heat Removal via the Steam Generators.
- Active Containment Annulus Ventilation System.

Passive Natural Circulation Safety Systems

- Passive Quick Boron Supply System.
- Passive Sub-system for Reactor Flooding HA-1 (first-stage hydroaccumulators).
- Passive Sub-system for Reactor Flooding HA-2 (second-stage hydroaccumulators).
- Passive System to Maintain Low Inter-containment Gap (annulus) Atmospheric Pressure.
- Passive Residual Heat Removal System via the Steam Generators (PHRS).
- Passive Core Catcher

Table 2.1 Compositions of Important Alloys in Contact with the Primary Coolant in WWER Primary Circuits

ALLOY	**COMPOSITION (PERCENT BY WEIGHT)**								
	C	**Si**	**Ni**	**Cr**	**Fe**	**Mn**	**Co**	**Others**	**Zr**
07Cr25Ni13	≤0.09	≤1.2	11/14.5	22/ 26.5	Bal.	0.8/2.0	≤0.05	-	-
08Cr18Ni10Ti (a)	≤0.08	≤0.8	9/11	17/19	bal.	≤1.5	≤0.05	Ti≥5C-0.6	-
08Cr19Ni10Mn2Nb	≤0.10	≤1	8.5/11	17.5/ 20.5	bal.	1.3/2.5	≤0.05	Nb=0.7/1.2	-
04Cr20Ni10Nb (b)	0.03	0.6	10	18	bal.	1.7	≤0.05	Nb=0.7	-
Zircaloy-4 (c)	≤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.
ZIRLO	0.005/ 0.022	-	0.03-0.08	0.03/ 0.08	0.07/ 0.14	-	-	Sn=0.9/1.5 Nb=0.5/2	bal
Zirc.1 % Niobium	≤0.05	≤0.05	≤0.025	-	≤0.07	≤0.002	≤0.007	Nb=0.8/1.2, O≤0.1	bal.

Zirc.2.5 % Niobium (b)	≤0.027	≤0.012	≤0.007	≤0.02	≤0.15	≤0.005	≤0.007	Nb=2.4/2.8, O=0.09/0.13	bal.

(a) Early WWER-440, V-230 units (excluding Bohunice 1 and 2) used 12Cr18Ni12Ti stainless steel; Loviisa used 08Cr18Ni12Ti for loop pipework (see Table 2-3).
(b) Russian data quote 04Cr20Ni10Mn2Nb (0.04%C, 20%Cr, 10%Ni, 2%Mn, 0.5%Nb)
(c) ASTM Standard, Zr-1%Nb is Russian type Э-110
(d) WWER-1000 primary circuit weld metal – 04Cr19Ni11Mo3

Table 2.2 Cobalt Impurity Levels in WWERs

Alloy	Composition	Impurity Level (Percent by Weight)		
		WWER-440		WWER-1000
		Specification	Loviisa (a)	
Stainless Steel	Core Internals	≤0.05	-	≤0.025
	Main Coolant Pipework	≤0.05	0 - 0.04	≤0.025
	RPV/SG Clad	≤0.05	-	≤0.025
	SG Tubing	≤0.05 (b)	0.03 - 0.06	≤0.025
	RCP Bearing Rings	≤0.05	0.0012 –0.14	≤0.025
	Fuel Assemblies/ Dummy Elements	≤0.05	0 - 0.12	≤0.025
Zirconium 1 % Niobium	Fuel Clad	-	<0.00003	-
Zirconium 2.5 % Niobium	Fuel Assembly Outer Sheath	-	-	-

(a) Actual Values
(b) Russian manufactured SG tubing in Paks 1 to 4: 0.04 - 0.06 % Co
Russian manufactured SG tubing in Bohunice 1 and 2: 0.03 - 0.04 % Co
Russian manufactured SG tubing in Dukovany 0.05-0.07% Co.
Czech manufactured SG tubing in Bohunice 3 and 4 and Dukovany 1 to 4: 0.015 to 0.02 % Co.
Dukovany 3 has three Czech and three Russian manufactured SGs.
Dukovany 2 has five Czech and one Russian manufactured SGs.
Dukovany 1 and 4 only have Czech manufactured SGs.

Table 2.3 Surface Areas of WWER stations

Alloy	COMPOSITION	Surface Area (m^2)	
		WWER-440	WWER-1000 V320
Stainless Steel	Core Internals	402.8	980
	RPV Clad RPV Head	 150	

	Main loop Pipework	15300	700
	SG tubing		16400
Zirconium 1 % Niobium	Fuel Clad	3200	4870
Zirconium 2.5 % Niobium	Fuel Assembly Sheath	920	-

Table 2.4 Examples of Configuration of SVO-1 and SVO-2 Resin Beds and High Temperature Filters in WWER Designs

NPP unit	Power, MWe	Cation Exchanger	Anion Exchanger	Mixed bed	High Temp. Filter
Novovoronezh 3-4 (V-179)	440	-	1	1	-
Kola 1-2 (V-230)	440	1	1	-	-
Bohunice 1-2, Kozloduy 1-2	440	1	1	1	-
V-213 Units	440	1	1	1	-
Novovoronezh 5, Kalinin 1-2. S. Ukraine 1-2	1000	4	2	2	-
V-320 units	1000	4	2		4

Table 2.5 Examples of Volumes (m^3) of Ion Exchange Resin in the Primary Coolant Purification System

Type	**Primary Coolant Purification System**	
	WWER-440 (1)	**WWER-1000 (2)**
Mixed Bed	1 x 1.0	-
Cation Bed	1 x 1.0	4 x 1.2
Anion Bed	1 x 1.0	2 x 1.2

(1) SVO-1 Coolant Purification System, which has two loops in the V213 design and one loop in the V230 design.
(2) V-320 design.

Table 2.6 Operating Parameters for WWER-1000 Titanium High Temperature Filters

Parameter	**Value**

Maximum Flow Rate, tonne h^{-1}	100 per filter
Nominal Flow Rate, tonne h^{-1}	60 to 80 per filter
Operating Temperature, °C	288
Operating Pressure, bar	157
Maximum Pressure Drop, bar	4
Volume of Titanium Sponge Sorbant, m^3	0.7
Average Grain Size, mm	1.3
Bulk Density, g cm^{-3}	1.4
Linear Flow Rate of Filter, m h^{-1}	100-150
Filtration Efficiency, %	80

2.2 Rationale for Chemistry Control Measures

The main aim of any primary water chemistry regime adopted for WWER primary circuits is to create conditions that will:

(1) Ensure the integrity of the primary system pipework, vessels, and other components
(2) Ensure the integrity of the fuel assembly cladding,
(3) Minimise the formation and transport of corrosion product radionuclides around the primary circuit, so as to minimise out-of-core radiation fields and personnel doses,
(4) Minimise fuel crud deposition on the fuel to avoid CIPS (Crud Induced Power Shift),
(5) Suppress the products of radiolysis, and
(6) Optimise the ammonia concentration to minimise radwaste and carbon-14 formation.

In general, these aims are achieved by operating under mildly alkaline reducing conditions, where the hydrogen used to create reducing conditions also suppresses the products of coolant radiolysis. Alkaline conditions are achieved by adding potassium hydroxide to counteract the boric acid present in the coolant to control core reactivity and reducing conditions by adding ammonia, which is decomposed to hydrogen in the core. As many corrosion processes are accelerated by impurities in the coolant, these must also be minimised, and as corrosion product formation and transport are dependent on coolant alkalinity, pH_t must be optimised. The presence of other materials that can become highly activated must also be minimised.

The following sections describe the main processes that must be controlled.

2.2.1 Structural Materials

2.2.1.1 General Corrosion and Oxide Formation

Primary circuit stainless steel alloys in WWER units undergo general corrosion in high temperature, deoxygenated, mildly alkaline solution to form thin oxide films. The oxide films are protective and diffusion control gives an oxide film whose thickness, x, ideally varies parabolically with time, t (i.e., $x^2 = kt$). The corrosion rate of 08Cr18Ni10Ti (08CH18N10T) stainless steel is a function of the temperature, redox conditions and pH_t, but at WWER operating temperatures data from different sources show that after several thousand hours the corrosion rate is <0.1 µg m^{-2} sec^{-1} (<0.4 mg m^{-2} h^{-1}) [2] or ~0.07 µg m^{-2} sec^{-1} [1 and 5]. In-pile loop tests show corrosion rates are largely unaffected by the different chemistries used in WWERs, although some loop results suggest that corrosion rates increase in the order "Hydrazine Water Chemistry" < "Standard Water Chemistry" < "High pH Chemistry" [5].

Normally, duplex oxide films are formed, although all or part of the outer layer is lost by dissolution into the coolant and is replaced by an outer deposited oxide layer. For stainless steel, the inner layer is an iron-chromium-nickel inverse spinel (iron chromite), enriched in chromium and depleted in iron and nickel relative to the bulk metal. The outer layer is an iron-nickel spinel (effectively a substituted magnetite) containing some chromium and trace amounts of other transition metals [1 and 5 to 18]. Chromium is retained in the inner oxide layers because it has low solubility in the coolant under reducing conditions. The inner oxide thickness is normally about 5-10 µm thick on primary circuit stainless steel surfaces and <1 µm thick on the steam generator tubing. In WWERs, the outer oxide layer instead of being formed entirely by diffusion from the metal, contains material deposited from the coolant and the very outer surface is usually covered by small amounts of loose particulate material. Thick outer layer oxides are found in a number of stations after many years of operation (e.g., the loop pipework at Bohunice, [19], which are due to the prolonged deposition of corrosion product oxides over many years operation [6 to 8].

Stainless steel corrosion rates are influenced by the surface finish [5 and 6], which affects surface micro-roughness and modifies surface properties. Both determine the lifetime corrosion rate, as only a few microns of the metal corrode over the lifetime of any WWER station. Machining or grinding increases micro-roughness and introduces sub-surface damage, which increases grain boundary diffusion rates leading to a higher corrosion rate and thicker oxides. Conversely, electropolishing removes sub-surface damage and produces a thin smooth chromium rich surface layer, giving a low corrosion rate and a thin oxide layer. Cast or weld clad surfaces do not contain damaged surfaces and, moreover, initially have a thin air grown oxide film. These differences result in the following order for the corrosion rates and activity uptake [20 to 25]:

Machined ≈ Coarse Ground > Fine Ground > Electropolished ≈ Cast/Weld Deposited

Activity uptake on machined surfaces can be up to five times higher than on electropolished surfaces, because of the differences in surface state. These differences are the reason for the much thicker inner layer oxides found on the rougher (commonly machined or ground) stainless steel surfaces of the primary circuit pipework [6 and 7], compared with the very thin inner layer oxides on the smooth drawn surfaces of the steam generator tubes, even though the machined main loop pipework and the drawn SG tubing are made from the same type of stainless steel. Decontamination using concentrated solutions also produces a relatively rough surface, which has a high corrosion and corrosion release rate and tends to have a high activity uptake and recontamination rates (although recontamination rates at Loviisa 2 were low). The high post-decontamination release rates are the basic reason for the problems experienced at Paks and Novovoronezh, and to a lesser extent Loviisa 2, where increased corrosion and corrosion release resulted in fuel deposits.

Although the normal oxides formed on stainless steel are protective duplex oxides, this is not always the case. At Loviisa 2 the rapid increase in radiation fields after 1988 was due to the formation of an anomalous thick (15 µm) non-duplex iron-nickel chromite oxide layer that did not have an outer nickel ferrite layer on the cold leg primary circuit surfaces. To minimise personnel doses during work planned for the 1994 annual refuelling, a full-system decontamination was carried by Siemens using the HP/CORD UV process (permanganic acid/oxalic acid), after which radiation fields returned similar values to those at Loviisa 1, indicating that normal duplex oxides had developed after the decontamination [26].

2.2.1.2 Stress Corrosion Cracking and Pitting

In addition to general corrosion, 08Cr18Ni10Ti stainless steel can also suffer from pitting, intergranular attack and stress corrosion cracking. Intergranular attack or pitting has not been reported on the inner surfaces of the primary circuit of WWER reactors operated in accord with the operating specifications for the primary circuit and the main cause of any primary-side degradation that occurs is probably due to a high chloride contamination during manufacturing, transportation and lay-up of steam generator tubing in a new plant.

Transgranular stress corrosion cracking (TGSCC) of 08Cr18Ni10Ti stainless steel does occur, but only from the secondary side of the steam generators, where higher chloride concentration can occur (e.g., in steam generator tube support crevices) [27] and it can also occur due to intergranular stress corrosion cracking of the steam generator tubing, where it originates from secondary-side pits and general corrosion in crevice environments with high impurity concentrations [28]. Tests carried out in France showed that there is a risk of stress corrosion cracking in cold worked stainless steels in concentrated potassium hydroxide environments, compared with lithium hydroxide, but such environments do not exist in WWERs and no examples of WWER primary-side stress corrosion cracking have been reported.

2.2.1.3 Corrosion Release

Corrosion causes both the formation of an adherent oxide layer and the dissolution of some part of the metal into the circulating coolant. The latter is termed corrosion release. Corrosion release has a similar time dependence to that for corrosion [11 to 14 and 29], which is also due to the low cation diffusion coefficients for the inner chromium-rich oxide layer, which control iron and nickel transport from the metal surface to the outer layer and their dissolution into the coolant. As the inner layer thickness increases with time, diffusion rates reduce and corrosion release rates reduce. In experimental work, up to half of the total possible oxide thickness tends to be released, accounting for the majority of the outer oxide, whilst the less soluble inner layer is always retained. The corrosion release rate is, therefore, tied to the local corrosion rate and this gives it a similar time dependence. For 08Cr18Ni10Ti stainless steel, the corrosion release rate is 30 to 60% of the corrosion rate [12]. Although most corrosion release processes probably decrease initially with time, they will always tend towards a constant rate as the processes of net oxide formation and release become equal because of removal via coolant purification and deposition on the fuel.

2.2.1.4 Effect of Impurities and Chemicals and on the Corrosion of Structural Materials

2.2.1.4.1 Dissolved Oxygen

Minimising coolant oxygen concentrations will minimise both general corrosion of the stainless steel primary circuit surfaces and the risk that stress corrosion cracking will occur. Low oxygen concentrations are achieved by degassing the make-up water and by adding hydrazine to the coolant during start-up. At power the steady state oxygen concentration is effectively zero at normal primary coolant hydrogen concentrations and any oxygen added to the primary circuit in the make-up water or boric acid will react radiolytically with excess dissolved hydrogen in the coolant in the first few centimetres of the core. At PWR and also WWER operating temperatures and neutron fluxes, a concentration of only ~1 to 5 Nml/kg hydrogen is required to suppress radiolysis and to prevent the creation of oxidising conditions in the coolant that would favour stress corrosion cracking. [30 and 31]

2.2.1.4.2 Dissolved Hydrogen

Dissolved hydrogen is required to maintain primary circuit reducing conditions to minimise any risk of stress corrosion cracking. As indicated above, ~1 to 5 Nml/kg will suppress radiolysis at normal WWER primary circuit operating temperatures, but this increases to about 10-15 Nml/kg at ambient temperature (<50°C).

In WWERs, hydrogen is formed *in situ* by the radiolytical decomposition of ammonia (either added directly or produced by the decomposition of hydrazine) in the primary coolant. Ammonia breaks down to a mixture of hydrogen and nitrogen, which are removed in the thermal degasser in the letdown and make-up system and are replaced by ammonia added in the make-up water added to the primary coolant. The specified primary coolant hydrogen concentration at power is 2.2 to 4.5 mg/kg (25 to 50 Nml/kg). At Temelin NPP the lower hydrogen concentration limit specified is 20 Nml/kg in order to limit ammonia primary coolant concentration, thus reducing the volume of liquid radwaste produced; an ammonia concentration of about 15 mg/kg gives a hydrogen concentration of 20 Nml/kg H_2.

Although the hydrogen concentration range is similar to that in reactors where hydrogen gas is added directly, in WWER reactors the ammonia and hydrogen concentrations in the primary coolant are steady state concentrations determined by the letdown rate and pump seal leak-off rate to the thermal degasser and the corresponding make-up water rate.

Hydrazine is added instead of ammonia to generate hydrogen in a few of WWER reactors. This decomposes in a similar way to ammonia, producing mainly a mixture of ammonia, hydrogen and nitrogen and only a small steady state hydrazine concentration. There are indications that the steady state hydrogen and ammonia concentrations in WWERs that add hydrazine are higher than in those that add ammonia.

It is planned to inject hydrogen gas into the primary coolant make-up water at the WWER-1000 stations South Ukraine 1 and 2, replacing the ammonia additions used currently, but this has not yet been carried out. Here, the objective is to avoid the drawbacks of ammonia presence described in Section 2.2.1.4.7, mainly its impact on resin behaviour. Similar proposals were made previously for both Temelin and Kalinin.

2.2.1.4.3 Chloride, Fluoride and Sulphate

Chloride-induced stress corrosion cracking occurs when austenitic stainless steel is exposed to chloride ion in high temperature, particularly in solutions containing oxygen. However, experimental data indicate that the risk of SCC is extremely low at normal WWER primary coolant hydrogen and oxygen concentrations. Nevertheless the chloride concentration is controlled at low concentration to avoid any risk of SCC occurring. Although fluoride ion concentrations are normally controlled to limit fuel clad corrosion, fluoride-induced stress corrosion cracking of austenitic stainless steel can occur at high fluoride concentration, but is suppressed if boric acid is also present. In practice, the limits imposed to prevent fuel clad corrosion are well below those required to prevent SCC. Both chloride and sulphate have been shown to cause SCC in stainless steels in non-stabilised stainless steels [32], but SCC does not initiate as rapidly in the stabilised 08Cr18Ni10Ti stainless steel used in WWERs [27, 33 and 34]. Sulphate has been shown to be at least as aggressive as chloride with respect to SCC of the non-stabilised austenitic type-304L stainless steels used in Boiling Water Reactors operating under oxidising conditions [32], but the risk of sulphate-induced SCC for the titanium-stabilised stainless steel used in WWERs is not as well characterised as that for chloride. Most experts consider that the sensitivity to SCC due to sulphate ions is not greater than that of chloride and that it is the acidity or the simultaneous presence of oxygen are the key factors [32 and 33]. A specific study using the 08Cr18Ni10Ti stainless steel used in WWER concluded that the number of microcracks was lower in presence of sulphate than chloride. Finally, in presence of chloride and sulphate ion, sulphate was found to act as an inhibitor of chloride-induced SCC initiation [34]. However, since sulphate is an aggressive anion that can initiate SCC, it is now accepted that sulphate concentrations should be controlled in essentially all nuclear plants at similar content to the limits applied for chloride ion.

Of these anions, chloride ion mainly enters the primary coolant in the make-up water and is controlled by ensuring that the water supplied by the make-up water plant is of the correct purity. It may also be released from the anion resin in the coolant purification system by partial regeneration during injection of ammonia and potassium hydroxide (where the chloride accumulates on the resin over several years operation). Finally, chloride ingress can occur if the correct controls to exclude chloride-containing materials are not applied during fuel transport or maintenance activities (Foreign Materials Exclusion (FME) controls). While fluoride can enter the primary coolant in the make-up water, the main source is considered to be fluoride residues from fuel clad etching during manufacture and there is requirement to monitor fluorides for defined period after unit startup after refuelling outage. Other sources are either solid boric acid added to the coolant or weld fluxes used when repairing or modifying the primary circuit or its auxiliary circuits. The latter two sources can only be avoided by applying an appropriate specification when purchasing solid boric acid and by applying correct procedures to minimise contamination of the primary circuit during maintenance.

Sulphate ions can also enter the primary coolant in the make-up water, but its main source is the sulphonic acid functional groups on cation ion exchange resins in the SVO-1 and SVO-2 coolant purification systems. An especially high risk of contaminating the primary coolant is associated with the release of resin beads or resin fines into the primary system when they break down at primary circuit temperature to release sulphate into the coolant. This can be avoided if there are efficient mandatory protection measures, such as resin traps to prevent resin ingress and procedures in place to avoid operational errors. Equally serious, the cation resin in the spent fuel pool purification system is decomposed slowly by the hydrogen peroxide that builds-up in the spent fuel pool water, which in a PWRs fuel pool is typically about 4 mg/kg and a similar concentration should be present in a WWER fuel pool. In PWRs, examples have occurred when the sulphate concentration in the aerated spent fuel pool water has reached several mg/kg and where IGSCC of the non-stabilised 304L stainless steel fuel assembly upper guide tubes occurred [35]. This caused separation of the upper fuel assembly nozzles from the remainder of the fuel assembles when the fuel assemblies were moved. Normally, the anion resin in the mixed-bed charge removes any sulphate released, but in this case a layered bed was used and the sulphate was not removed. There have been no similar examples reported for the titanium-stabilised stainless steel used in WWERs, this steel is not expected to be immune from similar damage although crack initiation may be much slower.

2.2.1.4.4 Nitrate

Nitrate is normally an anionic impurity that is controlled by ensuring that the make-up water is of the correct purity. However, a number of the ion exchange resins used in the coolant purification circuits are designed to be regenerated and as nitric acid is used to regenerate the cation resin, there is a risk that nitric acid or nitrates will enter the primary circuit. Nitrate ingress during power operation has occurred at a number of WWER units, either through accidental ingress of nitric acid during the regeneration process or due to incomplete rinse down of the ion exchange beds before they are returned to service. In the most serious example of this type of ingress event, the protective oxide present on the inner surfaces of the primary circuit was also attacked, releasing large amount of corrosion product radionuclides into the coolant and, possibly, altering the surface roughness so that higher release rates of the type seen after primary circuit decontamination might result. It should be noted that not all WWER units, e.g., Loviisa, regenerate their resin beds and these stations are not normally susceptible to nitrate ingress.

Nitrates are not normally considered as impurities that induce stress corrosion cracking of austenitic stainless steels, but there is at least one report [36] that indicates that mg/kg nitrate levels will cause cracking of AISI 304 stainless steel under oxidising conditions at boiling water reactor operating temperatures (288°C). However, the main threat arises because nitrate reacts radiolytically with the hydrogen in the coolant and if large quantities enter the coolant it will cause the coolant to become oxidising. This then creates a risk that stress corrosion cracking of the stainless steel primary circuit alloys will initiate.

During normal operation, the build-up of nitrate concentrations is suppressed by the presence of hydrogen in the coolant, which ensures that reducing conditions exist and very low nitrate concentrations normally exist. However, during a shutdown under aerated oxidising conditions, the shutdown reactor gamma flux causes radiolytic oxidation of ammonia in the primary coolant and the nitrate concentration increases rapidly to mg/kg levels. However, the concentration falls rapidly when the SVO-4 circuit is in operation.

2.2.1.4.5 Organics

Organic materials can enter the primary circuit form a variety of sources, including the make-up water, ion exchange resin fines, oils and the chemicals added to the circuit, but one of the most important potential sources in WWERs are residues of the solutions used to decontaminate the primary side of the steam generators where iron oxalate precipitates are not easily flushed out after the decontamination. In general organic materials are not corrosive and they will normally be decomposed in the high temperature radiation field that exist in the core. In most cases the organic material will be converted into methane, plus some ethane, and will be removed by the thermal degasser. In larger amounts it may, however, be converted to graphite and be incorporated into the oxides present on the fuel and primary circuit surfaces.

In WWER units that have been decontaminated by high concentration reagents containing citric acid or oxalic acid, the oxides present on the primary coolant surfaces have been shown to contain relatively large amounts of carbon-based material. It is not known if this alters the protective nature of the oxide film present on the stainless steel surface, but it may be a factor in the high release rates observed in WWERs that have been decontaminated repeatedly and that have then suffered from increased deposition on the fuel clad and grid surfaces.

2.2.1.4.6 Potassium, Lithium and Sodium

In WWER reactors a concentration of up to 20 mg/kg potassium, added as potassium hydroxide, is added at the start of each fuel cycle to create the alkaline conditions that minimise corrosion release and fuel crud deposition, which are the main factors in the generation of out-of-core radiation fields and potentially of Crud Induced Power Shifts. During the fuel cycle, the potassium concentration is reduced at the same time as the boric acid concentration, so as to maintain the optimum pH for radiation field development. However, lithium-7 is also produced during the fuel cycle via the $^{10}B(n,\alpha)^{7}Li$ moderation reaction, which makes simple control of the total alkalinity more difficult as it requires the control of more than of one alkali metal. The lithium-7 concentration reaches its maximum value in mid-cycle, when the concentration can reach 0.6 to 1.0 mg/kg. A further contribution to the pH is due to the sodium hydroxide contained as a minor component in the potassium hydroxide used in WWERs. The sodium concentration also changes throughout the fuel cycle, but is highest at start-of-cycle when the potassium hydroxide concentration is highest. The maximum sodium concentration is often ~0.35 mg/kg and falls to about 0.03 mg/kg by the end of the fuel cycle, but when good quality potassium hydroxide is used the sodium concentration is much lower (40-60 µg/kg at Temelin) and its contribution to pH_t is very low, compared with potassium.

To accommodate these three alkali metal ions, the alkalinity is normally controlled on the basis of the total alkali metal Molar concentration, but some older WWER plants still use an equivalent potassium concentration. These parameters are expressed either as a concentration in mg/kg or as a Molar concentration in mmol/litre of equivalent potassium or total alkali metals ($K^+ + Li^+ + Na^+$). To calculate the equivalent potassium, sodium concentrations are converted to equivalent potassium concentrations by multiplying by 39.1/23 and lithium-7 by multiplying by 39.1/7.

At Temelin NPP, sodium concentrations are <100 µg/kg and pH_t is controlled on the basis of on-line ammonia, Na^+, K^+, Li^+ and boric acid measurements, from which pH_t is calculated. Consequently, in this case, pHt is defined as a control parameter instead of total alkali in the plants operational procedures and pH_t is kept as constant as possible within the range 7.0-7.2 for the complete fuel cycle. A similar approach of using calculated pH_t as a control parameter may be used at other WWER units.

One advantage of the presence of potassium in the primary coolant is that the short-lived ^{42}K isotope ($t_{½}$ = 12.36 hours) can be used to monitor primary to secondary leakage.

2.2.1.4.7 Ammonia

Although ammonia is added to generate hydrogen by radiolysis, or is produced when hydrazine is added. It does not influence the primary coolant pH at high temperature significantly, as it is a very weak base at high temperature. However, this is not the case at low temperature in the SVO-1 and SVO-2 coolant purification circuits, where ammonia and the boric acid added to the coolant are partially ionised and ammonia affects the pH of the cooled coolant slightly. An additional consequence of the partial ionisation that occurs in the SVO-1 and SVO-2 circuits is that ammonium ion competes for the cation exchange capacity of the mixed-bed and cation resins, reducing its ability to remove potassium and lithium from the coolant. In practice, the cation resins all operate at equilibrium with respect to potassium, lithium, sodium and ammonium ions. This equilibrium is used at Loviisa, Mochovce and Bohunice 3 and 4 as a way of controlling coolant alkalinity, since reducing the ammonia concentration increases the alkali metal capacity of the cation resins and reduces the circulating alkali concentration.

Ammonia also causes radwaste processing problems in the SVO-3 system, where, at high pH, ammonia is removed in the steam from the evaporator. The ammonia collects in the evaporator distillate stream, which is purified by the SVO-3 ion exchange beds, increasing their exhaustion and regeneration rate. The regenerant liquors are returned to the evaporator, causing the ammonia to remain within the system and the main result is to increase the regeneration frequency of the cation resin in the ion exchange beds.

2.2.1.4.8 pH_t

The primary coolant pH at the primary circuit operating temperature determines the overall corrosion product behaviour in the primary circuit, as it determines the corrosion and corrosion release rates, the way that corrosion products precipitate out and deposit in the fuel clad, and, finally, the way that the activated corrosion product radionuclides deposit on out-of-core surfaces. This aspect is described in more detail in Sections 2.2.2, 2.2.3 and 2.2.4.

2.2.1.4.9 Additional parameters

In addition to the parameters discussed above, some WWER plants still measure the primary coolant conductivity and the pH at 25°C, whilst others measure the turbidity and suspended solids concentration. However, none of these parameters is of direct significance for the corrosion of the primary circuit structural alloys and they are only used as diagnostic measurements.

2.2.2 Fuel Clad Behaviour

In addition to stainless steel, the only other alloys present in most WWER primary circuit in a significant amount are the Zr-1%Nb fuel clad used in WWER-440 and WWER-1000 units and the Zr-2.5%Nb fuel sheath material used in WWER-440 units and at Novovoronezh 5. However, fuel supplied by Westinghouse and BNFL to Loviisa and Temelin reactors used Zircaloy-4 clad and the latest Temelin and South Ukraine fuel has ZIRLO clad.

The main function of the clad is to act as a barrier to fission product release during power operation, but the clad is thin to minimise the temperature gradient across the clad. As a result, the permissible amount of corrosion over the lifetime of the fuel is also small. For the Zr-1%Nb fuel clad in WWER-440 units the design basis corrosion limit for a LOCA is 17% of the fuel clad thickness of 0.685 mm (0.116 mm) [28], whereas for the Zircaloy-4 and ZIRLO fuel clad supplied by BNFL and Westinghouse the corrosion limit is equivalent to the formation of $\leq$100 µm zirconium dioxide corrosion film on the outer surface of the fuel clad. In practice, the fuel clad oxide thickness formed on WWER-440 Zircaloy-4 and Zr-1%Nb fuel clad is typically <5 µm after three cycles, but is somewhat greater in WWER-1000 units due to the higher operating temperature (8-12 µm generally and 10-15 µm at the end-plug welds [2]). More corrosion is expected when ZIRLO and, particularly, Zircaloy-4 fuel clad is used, but at Temelin and South Ukraine good clad corrosion behaviour has been observed, although whether this is due to the lower lithium concentration, the presence of potassium or differences in the fuel duty is not yet known. Under equivalent conditions to those quoted for Zr-1%Nb fuel clad above, the oxide thickness on Zircaloy-4 would be up to 40µm [2].

In normal operation no significant fuel crud deposits have been observed on either WWER-440 or WWER-1000 fuel [2], except under the abnormal conditions that existed in some WWER-440 units after repeated steam generator decontamination (see Section 2.2.1.1).

No corrosion occurs on the inner surface of the clad, which is in contact with the helium filled gap between the fuel pellets and the clad.

2.2.2.1 Fuel Clad Corrosion

Zirconium alloys corrode in high temperature water to form zirconium dioxide. Initially, corrosion forms a thin black protective layer of tetragonal zirconium dioxide, which is of the order of 2-5 µm thick. At greater oxide thickness, the form of the oxide changes to a lighter coloured oxide, which consists of alternating very thin porous bands of the tetragonal and monoclinic forms of zirconium dioxide. This oxide is not protective and in the absence of temperature changes the oxide thickness would be expected increase linearly with time. However, zirconium dioxide has poor thermal conductivity and the inner clad surface temperature rises as the oxide thickens. In turn, the higher inner clad wall temperature increases the corrosion rate. This feed-back mechanism is the main reason that clad corrosion rates accelerate with increasing fuel burn-up and oxide thickness, and is the reason for the limits placed on maximum burn-up for fuel assemblies with different zirconium alloy clad.

The underlying corrosion rate of all zirconium alloys is very dependent on:

(a) Minor alloying metals present in the alloy,

(b) Trace impurities present in the alloys, and

(b) The effects of species present in the coolant.

In addition, hydrogen is produced as the zirconium metal corrodes to form zirconium dioxide. Some of the hydrogen is absorbed into the clad, making it brittle and increasing the risk of fuel leaks due to hydriding failures.

Zr-1%Nb clad is currently available in two main forms. These are the standard Russian alloy Є-110 made from electrolytically produced zirconium metal, and the AREVA (Framatome) M5 clad and the new Russian clad used in advanced fuel assemblies, both of which are made from zirconium sponge produced by the Kroll process. In addition, the standard Russian alloy has an HF-etched outer surface, whilst M5 and the new Russian clad have polished outer surfaces. Standard Є-110 clad used in WWER fuel has been shown to have very good corrosion resistance, both in WWER-440s and WWER-1000 units. Operating data show that the maximum oxide thickness in WWER-440 units is typically <5 µm [37 and 38] and there is no transition to linear breakaway corrosion kinetics (at least up to 30000 hours exposure at ≤350ºC). In addition, its corrosion rate does not increase in a radiation field. However, it is more sensitive to oxygen levels than Zircaloy-4.

Two forms of Zr-1%Nb clad differ in their trace impurity levels. The sponge used in M5 clad is lower in fluoride, but is higher in calcium, magnesium, aluminium, iron and yttrium, whereas the electrolytic zirconium used in Є-110 clad is purer, but has a higher trace fluoride concentration derived from the molten salt bath. In addition the outer surface of Є-110 clad is higher in fluoride because of the acid etch treatment. Of these impurities, Ca, Mg, Al, Fe and Y are beneficial impurities with respect to oxidation, whereas F is detrimental towards oxidation [39].

In general, tests show that the ductility and oxidation behaviour of the different Zr-1%Nb clad alloys is very sensitive to the microchemical impurity composition and surface finish [39]. The current Є-110 clad has an optimal microstructure, but Zr-1%Nb clad made from zirconium sponge has a significant reduced oxidation rate and zero ductility threshold in LOCA (loss of cooling accident) tests, whilst polishing the clad surface gives an additional improvement in oxidation and ductility. The result is that whilst Є-110 clad appears to have a lower general corrosion rate than M5, it is worse under oxidising conditions when boiling is present and under LOCA conditions; however, M5 and the new Russian clad can be expected to behave essentially identically during power operation. Both types of Zr-1%Nb clad can be used in fuel assemblies designed to operate at burn-ups of up to 60-70 GWd/tU.

Zircaloy-4 clad containing 1.2-1.7% tin has a higher general corrosion rate than Zr-1%Nb clad and even when the alloying elements have been optimised for corrosion resistance, the zirconium dioxide film thickness can approach the 100 µm limit at high burn-up in PWRs (of the order of 50 GWd/tU). However, such high burn-ups are not currently reached in WWERs. ZIRLO clad containing both 1.2-1.9% tin and 1.3-1.9% niobium has a lower general corrosion rate than Zircaloy-4, but the rate is higher than that of all types of Zr-1%Nb clad. However, ZIRLO clad is still suitable for burn-ups of up to 60-70 GWd/tU in PWRs.

2.2.2.2 Effect of Impurities and Chemicals on the Fuel Clad

Fuel clad alloys do not suffer from enhanced corrosion due to the potassium, sodium or ammonia present in the primary coolant, but the corrosion rate is affect by oxygen, fluoride and lithium. They are also affected by species that form deposits on the fuel clad surface. These deposits include zeolites, formed from aluminium, calcium, magnesium and silica, and corrosion product species that form fuel crud deposited or grown on the fuel clad surfaces. These are summarised below.

2.2.2.2.1 Dissolved Oxygen

The corrosion rate of all zirconium alloys increases under oxidising conditions when there is a radiation field and in some alloys, e.g., Zircaloy-2, it can result in nodular corrosion. The corrosion rate of Zr-1%Nb clad increases under aerated conditions even when there is no radiation field and it has been shown that oxygen concentrations of between 0.5 and 6 mg/kg will accelerate the corrosion rate by a factor two to three times at 280-320°C. Even though oxygen accelerates Zr-1%Nb clad corrosion, in practice operating the primary circuit under reducing conditions prevents any additional corrosion during power operation. However, since hydrogen is only produced by radiolytic decomposition at power in WWERs, there is a finite risk that some corrosion will occur during start-up when the reactor is at full temperature and pressure, but is not yet critical. To avoid any risk, it is important that the coolant is deoxygenated fully by hydrazine additions before the temperature is raised above 100°C.

2.2.2.2.2 Fluoride

Fluoride has been shown to accelerate the corrosion rate of zirconium alloys including the Zr-1%Nb clad used in WWERs at a concentration of between 10 and 100 mg/kg. For this reason it is usual to include a fluoride limit in the primary coolant specifications, which is also intended to avoid any risk of SCC of the stainless steel primary circuit materials. A number of slightly different limits are in use in different WWER operating countries, but most apply a limit of <100 µg/kg fluoride during normal operation, although in some cases this values is set as a combined fluoride plus chloride limit.

2.2.2.2.3 Lithium, Potassium and Ammonia

In the absence of boric acid, lithium hydroxide is known to accelerate the corrosion rate of Zircaloy-4 used as PWR fuel clad. Tests showed that the corrosion rate was increased significantly at a lithium concentration of 70 mg/kg at 350°C and some increase was found at concentrations of as low as 7 mg/kg. However, in the presence of ~6 g/kg boric acid (~1000 mg/kg boron), there was very little effect even at a concentration of 100 mg/kg lithium. Since lithium will concentrate in thick porous oxides under boiling conditions, all PWR fuel manufactures impose an upper primary coolant lithium limit for plants operating with Zircaloy-4 clad fuel. This limit is also generally applied for fuel with ZIRLO clad. For many years the limit was set at 2 to 2.2 mg/kg lithium, but for 18-month fuel cycles this is now generally set at 3.5 mg/kg lithium (which is identical to the 0.5 mmol/litre total alkali metal limit specified for WWER units). In U.S. PWRs, a number of stations using ZIRLO clad are starting to operate with lithium concentrations of up to 6.5 mg/kg lithium at the start of each fuel cycle, so that they can operate at constant pH_t throughout the cycle to minimise fuel crud formation.

There is still considerable debate over the role of lithium in accelerating Zircaloy-4 corrosion in PWRs. Westinghouse use a model that includes a lithium-squared term. However, AREVA (formerly Siemens) use a model that only predicts a corrosion rate increase if the lithium content of the oxide is <100 mg/kg. Both models predict an increase in the corrosion rate due to lithium at high burn-up, when the zirconium dioxide layer is thick. However, fuel inspections have failed to show that any enhancement in the corrosion rate actually occurs. Thick oxides that increase the corrosion rate should not occur in WWER units operating with Zircaloy-4 clad fuel and no lithium effect is expected. This is also true for ZIRLO fuel clad, as the corrosion rate for this alloy is lower than that of Zircaloy-4. For Zr-1%Nb clad the type of thick oxide that is implicated in accelerated clad corrosion due to the presence of lithium in the coolant is absent and no lithium effect is expected. This view is supported by the fact that the maximum lithium concentration seen in mid-cycle in WWER units is only about 0.6-1.0 mg/kg, compared with 3.5 mg/kg lithium at the start of an 18-month PWR fuel cycle.

As stated earlier, the presence potassium and sodium in the coolant do not affect the corrosion rate of Zr-1%Nb clad, which is normally attributed to the much larger ionic radii of these cations, compared with the smaller ionic radius of lithium ion which allows lithium to be incorporated into the growing zirconium dioxide layer. Until the mid-1990s the maximum potassium concentration permitted by the Russian fuel manufacturer at the start of each fuel cycle was 16.4 mg/kg K^+. This was increased to 20 mg/kg K^+ in the mid-1990s after Zr-1%Nb clad corrosion tests at 20 mg/kg K^+ had showed no increase in the corrosion rate, compared with earlier tests at lower potassium concentration. Unfortunately, this concentration is not high enough to permit operation for a full fuel cycle at constant pHt, as is beginning to be adopted in PWRs. Ammonia has only a very small effect on high temperature pH in WWERs and because of this no effect on fuel clad corrosion is expected.

2.2.1.4.8 pH$_t$

One of the main objectives of pH optimisation is to minimise corrosion product deposition on to the fuel clad is to avoid CIPS (also called an Axial Offset Anomaly, AOA). Whilst this has occurred at some PWRs, there are three main reasons why it has not been observed in WWER plants:

a) The core power characteristics are lower in WWERs than in those PWRs that have suffered from CIPS,

b) WWER steam generators tubing material is 08Cr18Ni10Ti stainless steel, instead of the nickel base alloys used in most PWRs, where nickel released produces porous nickel-rich deposits within which boron species concentrate, and

c) Potassium salts are more soluble than lithium salts, as this may avoid the precipitation of the metaborate salts responsible of CIPS.

CIPS is being studied in detail in the IAEA Coordinated Research Project on the "Optimisation of Water Chemistry to ensure Reliable Water Reactor Fuel Performance at High Burn-up and in Ageing Plant (FUWAC).

2.2.2.2.4 Zeolite Forming Species

Aluminium, calcium, magnesium and silica, are known to be capable of forming insoluble zeolite deposits within the porous crud deposits that form on fuel clad. The reason is that most calcium, magnesium and aluminium oxides and silicates have retrograde temperature coefficients of solubility and tend to precipitate out in the hottest part of the circuit, which is the crud layer on the fuel clad. If this occurs, the zeolite deposits will tend to block the pores in the fuel crud, which reduces heat transfer to the coolant and increases the fuel clad surface temperature and, therefore, the corrosion rate.

For zeolites to form, both an alkaline earth metal cation (calcium, magnesium or aluminium) and silica must be present in the coolant. In general, alkaline earth metal ions are only present at very low concentrations, but silica is more common and at the start of a fuel cycle can be as high as 1 to 3 mg/kg. The latter is more common if the boric acid used to refill the primary circuit after each refuelling was recovered by evaporation and concentration in a boron recycle system. Little data exist on the risks from silica alone and limits of 1 to 3 mg/kg are applied in PWRs that operate with low levels of sub-cooled nucleate boiling in the core and <1 mg/kg in PWRs with higher core duties. When silica limits have been applied to WWER units, the value adopted ranges from <200 to 500 µg/kg.

For calcium, magnesium, aluminium and silica the main ingress route is the make-up water or the solid boric acid used to prepare the boric acid concentrate added to the coolant. However, they can also enter the primary coolant during refuelling when the coolant mixes with the water in the spent fuel pool. Additional sources are thermocouple and heater element packing materials (aluminium or magnesium) and the glass fibre matrix of some types of coolant purification filter (silica). Due to the nature of these sources, the main method of control must be the purity of make-up water and the purity of the solid boric acid used to prepare boric acid concentrate. However, because there are less easily monitored sources, the concentrations of these species should also be measured during normal operation.

2.2.2.2.5 Corrosion Product Deposits

In addition to the zirconium dioxide oxide film that forms on the fuel clad, corrosion products deposit to produce fuel crud that increases the fuel clad surface temperature and the clad corrosion rate under some circumstances. Normally, part or all of the crud deposits are formed by precipitation from dissolved iron and nickel from the coolant, but some originates from particulate in the coolant. Both precipitation and particulate deposition rates are higher on the heat transfer surfaces of the fuel, particularly if sub-cooled nucleate boiling occurs on some fuel assemblies. This aspect is considered more fully in Section 2.2.4.

2.2.3 Radiation Field Control

Inactive transition metal cations that deposit as fuel crud, plus any transition metals in alloys that form part of the fuel assemblies or in alloys in the core structure exposed to a significant neutron flux (e.g. the top and bottom core plates and the core barrel), are activated to form radioactive corrosion products. These activated species are then released into the coolant and deposit on out-of-core surfaces, which in turn become active, causing occupational radiation exposure (ORE) to personnel engaged in maintenance work during refuelling shutdowns [40]. There are two basic out-of-core activity production routes:

(1) Direct activation and release, where fuel assembly and pressure vessel internal parts are activated *in-situ* in the core neutron flux, are released and then deposit on out-of-core surfaces, and

(2) Indirect activation and release, where the parent elements are released primarily from out-of-core surfaces into the coolant, deposit on in-core surfaces (particularly the large fuel clad surface area), are activated and are then re-released into the coolant to re-deposit throughout the primary circuit.

In WWERs, the most important radioactive corrosion products contributing to radiation fields (or dose rates) are usually ^{60}Co and ^{58}Co, but in some WWER-440 stations ^{110m}Ag and ^{124}Sb are also significant contributors (e.g. Loviisa, Paks and Temelin). In addition, significant amounts of ^{51}Cr, ^{54}Mn and ^{59}Fe are present, although these are minor contributors to the radiation fields, and small amounts of ^{65}Zn, ^{95}Nb, ^{95}Zr, ^{122}Sb and ^{187}W are detectable on surfaces and in the coolant. In WWERs most of the personnel dose originates from ^{58}Co. In PWRs the main source of ^{60}Co is considered to be the hard facing material Stellite-6, but in WWERs high cobalt alloys are normally absent and cannot be the source of ^{60}Co. Here, differences in radiation fields are probably due to different cobalt impurity levels in SG tubing in steam generators [41 and 42]. At Loviisa, the auxiliary circuits contain considerable numbers of valves containing Stellite seats [1], but cobalt enrichment of the primary circuit oxides has not been observed and radiation fields are generally similar to those at other WWER-440 stations [7 and 8]. This observation suggests that auxiliary circuit sources are less important that primary circuit sources [43 and 44].

For indirect activation and release, the first stage in generating out-of-core radiation fields is the release of the elemental transition metals into the primary coolant. These are transported round the primary circuit before being deposited elsewhere on the primary circuit surfaces, with a proportion depositing on the fuel clad. After activation, some of the radioactive species are re-released to the coolant and re-deposit on out-of-core surfaces. Some of the transitions metals in the core structure are also activated, from which radioactive corrosion products can be released directly into the coolant. Coolant transport in the can occur via either soluble, colloid or particulate species, but soluble species are probably the most important under steady full power operating conditions (except when thick fuel clad deposits are present). Corrosion release from the coolant purification or make-up system pipework at low temperature is believed to be small. Some active corrosion products can be released by recoil following (n,p) fast neutron activation, but this is only possible for ^{58}Co and ^{54}Mn and is not the dominant re-release mechanism.

Although the same elemental and radionuclide corrosion products contribute to the radiation fields of both WWERs and PWRs, it is important to note is that the concentrations of the key species (nickel, cobalt, ^{58}Co and ^{60}Co) circulating in the coolant and incorporated into the out-of-core oxides are significantly less in WWERs than in most PWRs. This is because the nickel content of the materials in contact with the primary coolant is lower in WWERs, particularly that in the stainless steel steam generator tubing that forms the major surface area, which in many PWRs is made from Alloy 600 or Alloy 690. Consequently, the nickel corrosion release rate WWERs is lower, as are the nickel and ^{58}Co concentrations in the coolant [1] and the ^{58}Co surface activity on the primary circuit surfaces. In parallel with this change, elemental cobalt corrosion release rates, circulating elemental cobalt and ^{60}Co concentrations and ^{60}Co surface activities are also lower in WWERs as cobalt-containing hard facing alloys such as Stellite-6 are not used, whereas they are used in most PWRs. The effect of these differences is that whereas PWR primary circuit surfaces activities range from about 500 to 6000 kBq/cm^2 ^{58}Co and 50 to 2000 kBq/cm^2 ^{60}Co, the equivalent values in WWERs are 10 to 100 kBq/cm^2 ^{58}Co and 3 to 50 kBq/cm^2 ^{60}Co. However, it must be noted there is considerable variability from plant to plant amongst both PWRs and WWERs [45 to 53].

It would be expected that ^{54}Mn and ^{59}Fe activities should be similar in WWERs and PWRs, as the amounts present in the primary circuit structural materials are either similar or, for iron, greater. In practise, the surface activities are similar, although they still tend to be somewhat lower in WWER circuits due to the lower corrosion release rate for stainless steel. However, it could also be linked to the lower operating temperatures in WWER-440 units for which most data are available. The typical values reported are 20-200 kBq/cm^2 ^{54}Mn in PWRs versus 2-50 kBq/cm^2 ^{54}Mn in WWERs and 5-80 kBq/cm^2 ^{59}Fe in PWRs versus 1-40 kBq/cm^2 ^{54}Mn in WWERs.

In solution, soluble corrosion product ions are mainly removed rapidly from the coolant by adsorption onto the primary coolant surfaces, followed by absorption into the oxides. At low temperatures adsorption is almost completely reversible, but at high temperatures corrosion product ions diffuse into the oxide layer, from which they are not easily re-released. If the coolant becomes super-saturated with respect to the dissolved corrosion products, nucleation and crystallisation can occur forming a layer of deposited oxide crystals on top of the grown-on oxide layer produced by corrosion. If the oxides grow from solution, minor elemental species in the coolant, such as cobalt isotopes, will be incorporated into the bulk crystal lattice. Deposition on to, and re-release of soluble ions from, the oxides can either be kinetically or mass transfer controlled. Kinetic control occurs at temperatures below about 120°C [54], when surface absorption/desorption kinetics becomes rate controlling, whereupon deposition effectively ceases. Mass transfer control occurs above about 200°C, when the rate-controlling step is transport of the dissolved corrosion product ions across the laminar boundary layer from or to the turbulent bulk coolant. Mass transfer control exist in all the high temperature parts of the primary circuits, but not in the low temperature letdown parts of the coolant purification loops of WWER stations. Under mass transfer control the concentration at the oxide-coolant boundary layer interface is equal to the oxide solubility under the prevailing local redox conditions and, hence, will also be dependant on the temperature and coolant pH.

In addition to soluble transition metal species, the coolant contains particulate and colloidal species. Particulate are normally present in the coolant at concentrations of the order of 1 to 10 µg/kg, with a median particle size of about 1 µm. Particulate sources are nucleation in the coolant, erosion or spalling from developing oxides and wear from rubbing surfaces, but under most circumstances the main source is re-suspension of particulate that has already been deposited around the primary circuit. Nucleation occurs in the coolant if a sufficient degree of super-saturation exists at certain locations around the primary circuit. Re-suspension, erosion and spalling are sources of particulate released when the main coolant pumps are first switched on during a start up, when control assembly movement is tested during power operation and when changes are made that give rapid fuel temperature changes (e.g., spalling of loose fuel deposits during reactor trips). Transient particulate releases are rarely a problem if the amount of fuel crud present is small, but they are a significant factor in PWRs that have experiences CIPS due to the formation of thick crud deposits.

Since out-of-core radiation fields are the result of producing activated elemental corrosion products in the core, in principle, they can be controlled by minimising any of the key steps in the overall process. For soluble species the key steps are:

(1) The corrosion release rate from out-of core stainless steel surfaces,

(2) The rate of fuel crud formation,

(3) The release rate of activated corrosion products from the fuel crud, and

(4) The deposition of activated corrosion products on to the out-of-core surfaces.

For colloids and particulate the key parameter is the deposition rate on to the fuel clad surfaces. Each step depends on the coolant pH at the primary circuit temperature and, to a lesser extent, the dissolved hydrogen concentration and these two parameters are the main parameters that can be used to control radiation fields. There may also be links to the ammonia and hydrazine concentrations used to produce dissolved hydrogen, but these are second order effects, compared with the pH.

In practice, all of the methods used for radiation field control in both WWERs and PWRs are based on minimising fuel crud deposit formation from soluble iron and nickel in the coolant entering the core. Normally the assumption made is that the fuel crud deposits formed are a non-stoichiometric form of nickel ferrite, $Ni_xFe_{3-x}O_4$, phase, where x lies in the range $0.4<x<0.8$ and that, overall, the solubility is determined by the change in the thermodynamic ferrous iron solubility through the core. Although it is sometimes assumed that the optimum pH corresponds to the minimum ferrous iron solubility, the correct definition of the optimum pH if is that it corresponds to the pH above which the iron solubility increases at the temperature rises through the core (i.e., the pH above which the coefficient of solubility changes from negative to positive across the core). Originally, this pH was that defined for magnetite at PWR operating temperatures, which predicted an optimum pH of $pH_{300°C}6.9$. Later, when it was recognised that the pH should be that for nickel ferrite, the optimum pH for PWRs was increased to $pH_{300°C}7.4$. When this approach is applied to WWERs, slightly different optimum pHt are estimated, which recognise that the operating primary circuit temperatures are somewhat different from the PWRs for which the method was original developed. These revised pHt are described in more detail in Section 2.3.

2.2.4 Thick Fuel Crud Deposits

During normal WWER operation the fuel crud deposits that form are very thin and have little impact on fuel clad corrosion rates or core behaviour. Generally, part or all of the fuel crud deposit is formed by precipitation from dissolved iron and nickel from the coolant, where the precipitated crud composition is determined by the concentrations of iron and nickel circulating in the coolant. However, not all fuel crud is formed from solution and particulate in the coolant will also deposit on the fuel clad. Fuel crud is very porous and boiling ‘chimneys’ form if the crud is greater than about 20 µm thick, although deposits of this thickness do not form in operating WWERs as the amount of sub-cooled nucleate boiling even in a WWER-1000 core is smaller than in PWRs.

In early PWR operations, thicker fuel crud deposits were observed when the operating primary coolant pH was low, but after the pH was optimised and increased to at least $pH_t6.9$ in the mid-1980s fuel crud thicknesses reduced to ones that was comparable to those seen in WWERs. This situation changed in the late-1980 and 1990s, when the core duty was increased to cater for longer fuel cycles and more highly enriched fuel, both of which increased the degree of sub-cooled nucleate boiling in the core. The increased boiling resulted in the formation of thick porous fuel crud deposits in a number of U.S. 4-loop PWRs. Under these conditions a thick porous crud layer containing nickel oxide formed in the upper part of the core where boiling was greatest. Considerable efforts have been made to understand the reasons for the formation of these thick porous fuel crud layers in PWRs and on ways to prevent them forming, but for WWER operation, the main question is whether similar thick fuel crud layers will form and whether CIPS can occur.

So far CIPS has only been observed in PWRs that have Alloy 600 steam generator tubing, which are able to sustain the higher nickel release rates necessary to account for the thick nickel-rich fuel crud deposits that characterise PWRs that have experienced CIPS. In PWRs with Alloy 600 steam generator tubing, fuel crud contains a non-stoichiometric nickel ferrite under non-boiling conditions also probably contains metallic nickel. In a high duty core, when there is a larger amount of sub-cooled nucleate boiling nickel oxide forms instead of metallic nickel. Under these conditions a thick porous nickel-rich crud layer forms in the upper part of the core where boiling is greatest, within which lithium metaborate precipitates producing a crud-induced power shift (CIPS, otherwise called an Axial Offset Anomaly).

CIPS has not been observed in PWRs that have steam generator tubing with a lower nickel content (and lower corrosion release rates, e.g., Alloy 690 or Alloy 800) or in WWERs. In WWER units, the coolant contains much lower concentrations of nickel and it is not clear whether the nickel-rich fuel crud deposits that are responsible for CIPS can form, even if fuel duty is increased and sub-cooled nucleate boiling occurs on the upper parts of some fuel assemblies increases. Instead of these thick nickel-rich deposits, the fuel crud layer normally present in WWER is normally composed of an iron-rich non-stoichiometric nickel ferrite.

However, under some circumstances thick fuel crud deposits have been formed in some WWERs. These are a nickel-substituted form of magnetite and have been observed when high release rates exist following primary circuit decontaminations, as at Loviisa 2, Paks 2, etc. However, these deposits do not correspond to the porous deposits formed in high duty PWRs and not only form in a different location in the core (at the bottom of the fuel assemblies), but they are not associated with the type of sub-cooled nucleate boiling that is responsible for lithium borate precipitation and the onset of CIPS.

Since fuel crud formation from solution also depends on the coolant pH_t, and particulate deposition is linked to suspended solid concentrations, both must be controlled to limit the formation of thick layers of fuel crud. Both aspects are, however, linked to radiation field control and the selection of the optimum pH Chemistry regime and are considered in more detail in Section 2.2.3.

2.2.5 Shutdown and Start-up

For WWER-440 and WWER-1000 reactors, the available methods of chemistry control during shutdowns are determined by the lack of a separate residual heat removal systems, the use of nitrogen to pressurise the primary circuit during cool down and the loss of the main SVO-1 coolant purification loops when the main coolant pumps are stopped. In addition, ‘soft decontamination’ procedures are used before shutdown [10] at many stations to solubilise corrosion product radionuclides, so that they can be removed by the ion exchange beds in the coolant purification systems during the shutdown. In the WWER-1000 and WWER-440 V-213 units coolant purification can be transferred to SVO-2 when the main coolant pumps are halted, but there is no further clean up in WWER-440 V-230 units. Drain down of the primary circuit is carried out under nitrogen pressure (0.3 to 0.5 MPa) and oxygenation of the circuit only occurs when the reactor pressure vessel head is removed.

In WWER-440 and WWER-1000 units, acid-reducing conditions exist at the end of boration, but the dissolved hydrogen concentration is relatively low. Acidic reducing conditions are generally maintained throughout the cool down, until the reactor pressure vessel is opened allowing oxygen ingress into the circuit. Although oxygen normally enters the primary circuit by air ingress, forced oxidations using hydrogen peroxide at 140/150°C were carried out at Loviisa on two occasions to remove antimony as part of the steps taken to combat the increasing radiation fields at this unit, but this approach has not been used at other stations.

During start-up the circuit is pressurised with nitrogen. The ion exchange resin beds are borated before or during the start-up and are saturated with potassium and ammonia shortly after reactor start-up. Hydrazine is added to deoxygenate the primary coolant at about 80°C (100°C at Loviisa) and oxygen must be <10 ppb oxygen before the temperature can be raised to >120°C (although lower temperatures are defined at some stations because of transition temperature from ductile failure to brittle fracture), but hydrogen is only produced by radiolysis once the reactor is at power.

Considerable scope exists for optimising both the shutdown and start-up procedures in WWERs, but these are outside the scope of this NER.

2.2.6 Radwaste Optimisation

Most WWER-440 units in current operation were either designed in the late 1960s or adopt similar operating philosophies, and these philosophies also apply to most WWER-1000 units. The basic principles include:

- Very low liquid radwaste releases to the environment,

- Treatment of liquid wastes by concentration and the storage of the concentrate at each plant, and

- Final treatment of wet (evaporator concentrates, spent ion exchange resins and filter cartridges) and dry solid radwaste during decommissioning [55].

Although, in principle, radwaste philosophies should be similar to those in PWRs, in practice the quantities of both solid and liquid radwaste produced in WWERs are significantly greater [62]. In part, the greater amount of solid radwaste produced is due to the greater number of components present in WWER designs and conservative inspection frequencies, but for liquid radwaste it is also due to the generally greater leakage flows and regeneration of ion exchange resin. For ion exchange resins, larger volumes are used in the various auxiliary circuits of WWER units and, typically, the volume of resin used in WWER systems is about three times greater that used in PWRs. In the absence of further treatment this will result in larger amounts of spent resin radwaste [55].

One consequence of these differences is that the volume of evaporator concentrate produced is greater in a WWER and, since no processing capability was included in the original design concept, either additional storage capacity has had to be constructed at individual sites or additional evaporation capacity has had to be installed to further concentrate lower level boric acid concentrates. A second consequence is that most ion exchange beds are designed to be regenerated, so that the spent resin volumes produced can be reduced from several times that produced in a PWR to a similar volume. However, similar amounts of other wet radwaste streams (sludges, liquid organic wastes) are produced in both WWERs and PWRs.

In most WWERs, there are programmes in place to reduce the amount of liquid and wet solid radwaste produced, where the most common approaches used are:

- Recycling of purified water,
- Recycling of boric acid,
- Recycling of decontamination solutions,
- Regeneration and reuse of ion exchange resins, and
- Leak reduction for sources other than seals designed to flow partly to waste.

In addition, other volume reduction techniques, such as reverse osmosis, higher capacity ion exchange resins and ultrafiltration may also be used.

Similar programmes are in place to reduce the volume of dry solid wastes produced, which now includes segregation of the different radwaste forms and techniques such as super-compaction of the drums that contain the solid radwaste.

In addition to these general principles, and as noted in Section 2.3.3, the addition of hydrogen gas to the primary coolant instead of ammonia to form hydrogen by radiolysis is a specific method of liquid radwaste minimisation is currently under consideration at some stations. Here, the volume of liquid radwaste produced can potentially be reduced via the reduced frequency of the SVO-3 cation resin regeneration.

Although radwaste programmes are normally concerned with minimising radwaste containing the main radionuclides produced in WWER units, which are the fission product and corrosion product radionuclides, in some countries the discharge of other radionuclides is becoming of increasing importance. These include the activation products ^{3}H ($t_{½}$ 12.4 years), which cannot easily be separated and stored, and ^{14}C ($t_{½}$ 5730 years), which is not normally removed from gaseous discharges.

Of these two radionuclides, ^{14}C is of particular importance as it is responsible for the highest general population dose due to its very long half-life and dispersal in the gaseous discharges. At Temelin, for example, ^{14}C is the largest contributor to the effective dose commitment for the site. In addition, ^{14}C is one of the critical nuclides identified for the long-term storage of Intermediate Level Waste (ILW). A similar position is being taken in other European countries. Methods for removing these radionuclides are limited, but for ^{14}C at least the amount formed can be minimised the by eliminating the use of aerated primary coolant make-up water and aerated boric acid, since ^{14}C is produced from both ^{14}N and ^{17}O. If degassed make-up is used only ~2% of the total ^{14}C production arises from ^{14}N, but this increases to ~45% if aerated make-up is used (so that the total amount produced approximately doubles) The amount formed is even greater if nitrogen blanketed tanks are used and the ammonia added to the coolant is also a major addition source.

2.3 Chemistry Control Options

The primary coolant chemistry regimes used in WWER units are similar to those used in PWRs and are based on the high temperature solubility of iron in magnetite or nickel ferrite. They differ, however, in that different pH control bands are recommended for WWER-440 and WWER-1000 units to reflect the different operating temperatures (265-295ºC v. 289-322ºC).

2.3.1 Historical Development of Primary Coolant pH Regimes

From the late 1970s until 1991-92 all WWER-440 and WWER-1000 units operated to a primary coolant pH specifications, developed by Russian Institutes, known as the ‘Standard Water Chemistry’ regimes [1 and 40]. Different specifications existed for WWER-440 and WWER-1000 units. For WWER-440 units this regime gave a constant high temperature pH of $pH_{260°C}7.3$ (where 260°C was the original WWER core inlet temperature) and the control band was defined as:

$$[K_{equ}] = 4 + 4/3[H_3BO_3] \pm 2$$

with $[K_{equ}]$ (the total alkali metal ($K^+ + Li^+ + Na^+$) concentration expressed as an equivalent potassium concentration) defined in mg/kg and $[H_3BO_3]$ in g/kg (maximum 8 g/kg). An upper limit of 16.5 mg/kg K_{equ} (equivalent to 2.96 mg/kg ^{7}Li) was set to limit fuel clad corrosion.

For WWER-1000 stations two equivalent specifications were defined in 1982 and 1988. These were similar, but had lower $[K_{equ}]$ values at all boric acid concentrations reflecting the Russian view that the solubility minimum occurs at a lower pH at the higher operating temperatures of WWER-1000 stations. The 1988 specification incorporated an end-of-cycle equivalent potassium plateau, but was not adopted. The two variants were defined as:

1982 Specification $[K_{equ}] = 0.1 + 0.0148[H_3BO_3] \pm 0.05$

1988 Specification $[K_{equ}] = 0.1 \pm 0.05$ $([H_3BO_3] < 1.5)$
$[K_{equ}] = 0.065 + 0.0235[H_3BO_3] \pm 0.05$ $([H_3BO_3] > 1.5)$

where $[K_{equ}]$ is in mmol/kg and $[H_3BO_3]$ in g/kg (maximum 10 g/kg). The WWER-440 and 1000 regimes are shown in Fig. 2.4.

Although these regimes were intended to be constant pH regimes, the pHt were calculated used a method developed by Meek in the early 1960s [56], but when calculated using updated methods, the pH actually increases continuously throughout the fuel cycle. For example, the calculated pH for an operating WWER-440s calculated using the EPRI method increases from about $pH_{300°C}7.0$ to $pH_{300°C}7.5$ during the cycle. Most WWER operators moved away from the ‘Standard Water Chemistry’ regimes to the newer constant pH regimes in the early 1990s, but it remained in use at Loviisa until 2006 and currently it is still used in a modified form at Paks [52], Mochovce and Bohunice [57] (where at Paks the initial pH is low and only increases to reach the target control band in mid-cycle as lithium grows-in).

The non-constant pHs obtained with the "Standard Water Chemistry” regime were recognised by a number of the WWER operators in the late 1980s, leading to revised primary coolant specifications based on the new methods of calculating pH [57 to 69]. In the Czech Republic, the Nuclear Research Institute at Řež used its DISER code (incorporating the EPRI method of calculating pH_t) to predict the optimum pH for WWER-440 and WWER-1000 units [62 to 64]. These calculated values for minimum solubility and minimum corrosion product formation for WWER-440 and WWER-1000 units are $pH_{300°C}7.2$ and 7.1, respectively. This regime was initially used at Dukovany 3 in 1991 (when the co-ordination band was $pH_{300°C}7.2 \pm 0.05$ at <4.5 g/kg boric acid and there was an upper equivalent potassium limit of 14.5 ± 1.7 mg/kg K_{equ}) and corresponded to the “Modified Chemistry” regimes used in PWRs [1]. In 1992, the upper limit was raised to 20 mg/kg K_{equ} (≡ 3.59 mg/kg ^7Li) [67 to 69] and the control band redefined as $pH_{300°C}7.2 \pm 0.1$, where the higher K_{equ} limit was based on new Russian work on Zr-1%Nb fuel clad and stainless steel corrosion. This specification has been used at Dukovany (Czech Republic) since 1992. An equivalent WWER-1000 primary coolant regime was defined for use at Temelin with the co-ordination band set at $pH_{300°C}7.1 \pm 0.1$ and has been used at Temelin since commissioning. These regimes are shown in Fig. 2.5. A feature of the new Czech specifications was that EPRI-style action levels were introduced.

The Russian Institutes issued revised specifications in 1992-1993, based on new boron-alkaline metal calculations [70 to 72]. Although these regimes had apparently identical optimum pH bands calculated using the Russian code, they gave slightly higher optimum co-ordination pHt of approximately $pH_{300°C}7.25 \pm 0.1$ for WWER-440 units and $pH_{300°C}7.15 \pm 0.1$ for WWER-1000 units when calculated using the EPRI method, due to slight differences between the Russian and EPRI pH codes. The new specifications increased the upper K_{equ} limit to 0.5 mmol/litre (19.5 mg/kg K_{equ}), which was agreed with the Russian fuel manufacturer. Otherwise it was very similar to the Czech specification. This variant is also included in Figure 2.5 and was used in both the Russian and Ukrainian units until 2001.

New Russian specifications developed in response to new chemistry guidelines issued by the Russian Regulators in 1998 were introduced in 2001 by Russian research and design organisations [73 and 74]. These required that the water chemistry should maintain the integrity of the barriers against radioactive releases, minimise corrosion, minimise deposition on heat transfer surfaces, reduce primary circuit radiation fields and limit the consequences of radioactive releases following an accident. The new standards followed the practice of separating the parameters into control and diagnostic parameters and introduced action levels for control parameters, but more importantly introduced pH action level zones for the first time. These new specifications are currently used in Russia, the Ukraine, Bulgaria and Loviisa.

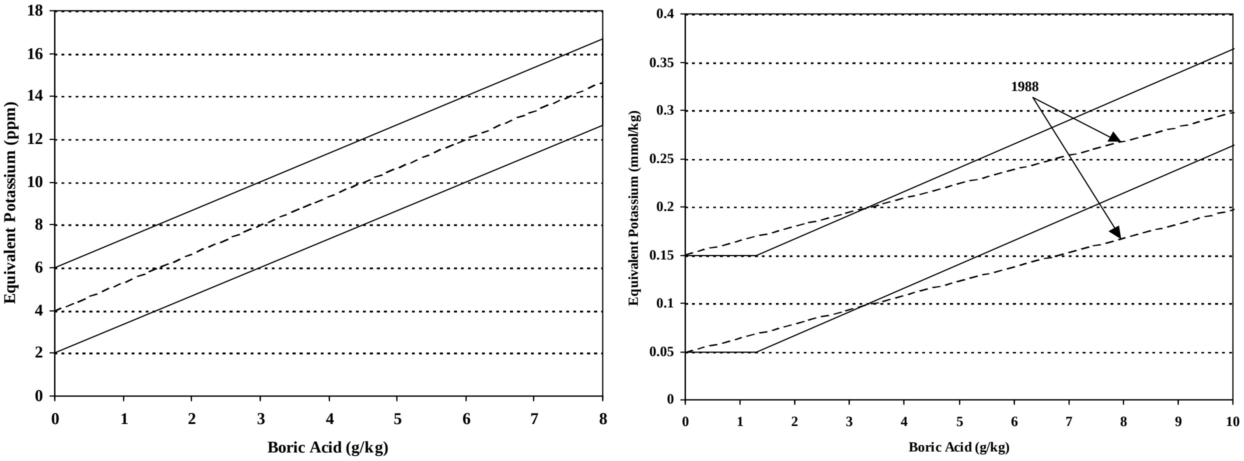


Figure 2.4 **Original “Standard Water Chemistry” Specifications for WWER-440 (left)**

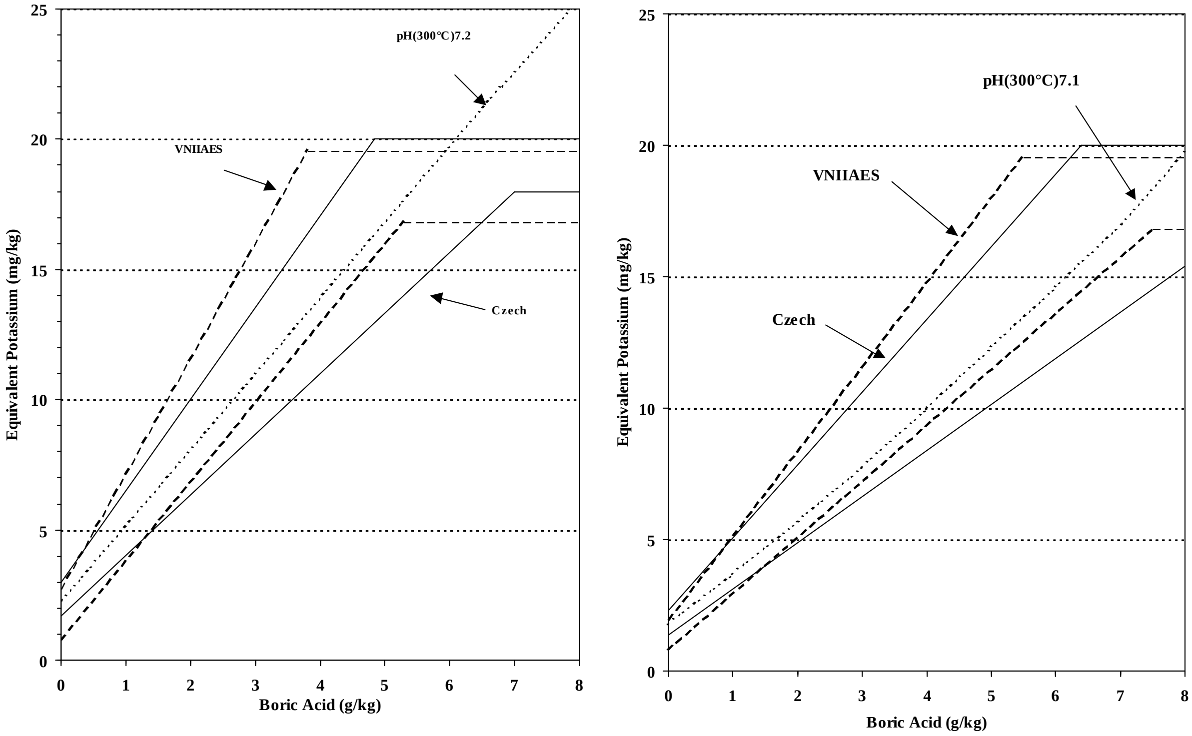


Figure 2.5 **1992 Czech and Russian Specifications for the WWER-440 (left) and WWER-1000 (right) Units (Russian specifications were actually defined in**

terms of total alkali metals (K^+ + Li^+ +Na^+) or equivalent potassium in mmol kg^{-1} (0.5 mmol kg^{-1} = 19.5 mg/kg)) [1]

2.3.2 Boric Acid and pH control

In all WWER-440 and 1000 units, boric acid control is carried out by discharging boric acid to radwaste and diluting the coolant with make-up water, or by adding concentrated boric acid. Most of the boric acid discharged is recovered by evaporation in the boron recycle system and is reused. Make-up water is added upstream of the thermal deaerator, but boric acid and other chemicals (potassium hydroxide, ammonia and hydrazine) are added upstream of the charging pumps. WWER-440 units have boric acid concentrate tanks containing 40 g/kg boric acid and boric acid tanks used for borating the primary circuit containing 12 g/kg. When large quantities of make-up water are added, the make-up system has a second thermal deaerator to remove oxygen before the water is added to the charging pump suction line, but otherwise the make-up water is fully aerated. Removal of alkali metals (except at Paks which mainly uses one of the SVO-1 loops) is carried out using the SVO-2 system, but at Loviisa, Bohunice and Mochovce alkali metal control is also effected by reducing the standing ammonia concentration in the primary circuit during the cycle, which increases the SVO-1 cation resin capacity for potassium and lithium.

2.3.3 Hydrogen

In WWER-440 and WWER-1000 stations, ammonia (or hydrazine decomposed into ammonia) is added to generate hydrogen *in situ*. In WWER-440 V-213 and WWER-1000 units, ammonia is added either intermittently (typically once or twice per shift) or continuously (depending on the letdown flow rate) to the make-up water, as all the letdown flow passes through the thermal deaerator where any hydrogen, nitrogen, fission gases and some ammonia is removed. In stations that operate with a higher letdown flow rate, higher steady state primary coolant ammonia concentrations are required to maintain the target hydrogen levels and more frequent ammonia additions must be made to the feedwater, or ammonia must be added continuously. The earlier WWER-440 V179 and V230 units do not have shaft seal pumps and do not require a continuous seal water injection flow. Consequently they only add small amounts of ammonia and lower ammonia concentrations exist in the coolant. Steady-state ammonia concentrations in stations with shaft-seal MCPs are typically 12-25 mg/kg, but are lower at 5-10 mg/kg in WWER-440 V-230 units with canned rotor pumps. They are also lower at Novovoronezh 5, which has a hydrogen recovery system (5-8 mg/kg).

When hydrazine is added instead of ammonia, the steady-state ammonia concentrations are higher that at station that add ammonia directly. Steady-state concentrations are 31-36 mg/kg (range 9-58) at Kola 3 and 4 and 40-60 mg/kg at Paks, whilst the steady-state hydrazine concentrations are very low (5-15 μg/kg).

At Dukovany and Temelin there were plans to inject hydrogen gas instead of adding ammonia, using an injection system in the high pressure charging pump discharge line of the Make-up Water System. However, the proposed changes have not yet been agreed. Similar plans have been developed at Kalinin and South Ukraine and it is expected that those at South Ukraine [75] will be implemented within the next few years.

The advantages of changing to direct hydrogen additions at Temelin and Dukovany were reported to be:

(1) improved start-up and shutdown redox control, including the formation of nitrate ion,

(2) simplified hydrogen concentration and corrosion control, which is independent of reactor power,

(3) improved coolant purification system ion exchange resin performance and resin life, absence of interference and release of cation from ion exchange resins due to the presence of ammonia,

(4) simplified pH control, as the cation resin only operates in the potassium/lithium form, and

(5) radwaste optimisation, due to the lower regeneration frequency of the boron recycle system distillate demineraliser when ammonia is absent and, therefore, a reduction in the amount of active regenerant solution radwaste produced (although this can be offset to some extent by operating past ammonia exhaustion).

At South Ukraine similar advantages were reported [75], plus:

(6) better alkali metal concentration and gross coolant activity control, particularly at the end of a fuel cycle when the boric acid concentration was low (<1 g/dm^3),

(7) lower silica concentrations due to the addition of higher amounts of lower quality make-up water, and

(8) the absence of on-line monitors and the ability to calculate high temperature pH to enable corrective actions to be taken.

To underwrite the planned changes at South Ukraine, corrosion tests were carried out to confirm that the planned change would have no effect on fuel clad corrosion rates or primary circuit stainless steel general and localised corrosion rates [2].

However, there are also disadvantages to the direct addition of hydrogen gas instead of ammonia, which are mainly concerned with safety issues due to the presence of hydrogen gas and the greater ease of operating at lower hydrogen concentrations when ammonia additions are used. Consequently, before changing from ammonia to hydrogen additions, a thorough study must be carried out.

2.3.4 Impurities

As discussed in Section 2.2 there are a number of impurities that are associated with degradation mechanisms that either cause stress corrosion cracking of the primary circuit, or enhanced corrosion of the fuel clad alloys. The former can cause loss of coolant accidents (LOCA) and the latter the release of fission product radionuclides into the primary coolant. The species primarily associated with these degradation mechanisms are oxygen (but only at primary coolant temperatures of >80-100°C), chloride, sulphate and fluoride. Each must be controlled in the primary circuit and chloride, sulphate and fluoride must also be controlled in any auxiliary system that can be connected to the primary circuit.

During power operation radiolytic reactions in the core ensure that oxygen and hydrogen cannot coexist and the latest work shows that <5 Nml/kg dissolved hydrogen will be sufficient to suppress radiolysis of water, so that reducing condition exist in the primary coolant [35].

Chloride, sulphate and fluoride are normally controlled by ensuring that the make-up water and any chemical added to the primary coolant contains very low levels of impurities, but there are other ways that these impurities that can enter the primary circuit. For sulphate, the most important route is cation resin degradation, which releases sulphate into the system. For fluoride, the most obvious route in WWERs is the HF etch solution used during Є-110 clad manufacture, but a second well known source is the weld flux used when welding work is carried out on primary system components. There are fewer routes for chloride to enter the primary coolant, but examples have occurred when organo-chlorides have been released into the coolant from a fresh weak-anion ion exchange resin charge, whilst the use of materials containing chlorine during maintenance work can be a source of chloride (and sulphate and fluoride) when the reactor returns to power. In the latter case, strict Foreign Materials Exclusion (FME) controls are normally applied to prevent this type of problem.

It is due to importance of these anionic impurities, that they are all rigorously controlled in the primary coolant and there is a consensus view amongst both WWER and PWR operators that the limit for each impurity that can be allowed in the primary circuit and any of the related auxiliary circuits is 0.15 mg/kg, although in most WWER units the limit is set somewhat lower at 0.1 mg/kg. If the concentration rises above this value, corrective actions are required that include reactor shutdown if the concentrations rise to unacceptable levels.

As was discussed Sections 2.2, there are a number of other impurities that affect the integrity of the primary circuit or the fuel clad. However, these do not pose the same degree of threat to circuit and fuel clad integrity and for this reason they are normally only defined as diagnostic parameters.

2.3.5 Zinc

Zinc is added at a number of PWRs [76] because:

(1) At 5 µg/kg zinc it reduces out-of-core radiation fields by blocking the uptake of ^{58}Co and ^{60}Co into the inner iron chromite layer on the out-of-core oxide films. However, it is not incorporated into the outer nickel ferrite oxide film or nickel ferrite-based fuel crud and does not prevent the formation of ^{58}Co and ^{60}Co in the core.

(2) At 10-40 µg/kg it displaces some ^{58}Co and ^{60}Co from the inner iron chromite layer in the out-of-core oxide films, but more importantly for PWRs it is also used to reduce PWSCC cracking initiation and possibly crack propagation rates.

(3) At 10-20 µg/kg it reduces the corrosion and corrosion release rates from new replacement steam generator tube surfaces.

In WWERs, radiation field reduction alone may not be a significant reason for adding zinc in the short-term, as radiation fields are already low due to the absence of cobalt-containing Stellite-type alloys and the use of stainless steel loop pipework and steam generator tubing with a low nickel content. However, adding zinc may be evaluated on a plant basis if there is a long-term benefit for dose rates reduction (ALARA principle).

2.3.6 Shutdown Chemistry

Refuelling shutdowns in WWER-440 and WWER-1000 units are carried out in similar ways and most stages during a shutdown are similar to those in PWRs. However, there are a number of significant differences, which are the result of to the different systems installed in the two reactor types. The main differences from PWRs are the absence of separate residual heat removal systems in WWER units, the use of high pressure nitrogen to pressurise the pressuriser steam/gas space during cool down rather than transferring to a water-solid system and the fact that the SVO-1 main coolant purification loops can no longer be operated when the reactor coolant pumps are stopped. As the SVO-1 coolant purification system is progressively during a shutdown, coolant purification is transferred to the SVO-2 system when the main coolant pumps are halted in WWER-1000 and WWER-440 V-213 units, but there is no further clean-up in WWER-440 V-230 units.

In addition to these differences, WWER units use the SVO-2 OH^--form anion beds remove born in the final weeks of each fuel cycle when boric acid is < 0.5 g/kg and many units carry out a ‘soft decontamination’ in the final week of the fuel cycle [1]. To carry this out, fresh SVO-1 and SVO-2 resin beds are normally loaded before a shutdown. A ‘soft decontamination’ is intended to solubilise corrosion product radionuclides, so that they can be removed by the ion exchange beds in the coolant purification systems during the shutdown and it is achieved by using the SVO-1 or SVO-2 cation beds to remove potassium and lithium in the last one to two weeks before shutdown, reducing pH_t to 6.7-6.9. Experience shows that ‘soft decontaminations’ have no adverse effect on station operation [77]. ‘Soft decontaminations’ were first developed at Loviisa in 1976 and are used in Russian WWER-1000 units, where the procedure used was developed at Novovoronezh 5, Kalinin and South Ukraine from 1985 to 1993 [78 to 80].

In parallel with the ‘soft decontamination’, ammonia and potassium dosing is halted 16 to 36 hours before a shutdown. Normally, the halting ammonia dosing early enough before a shutdown and operating one or both thermal degassers in series will ensure that hydrogen concentration at shutdown is reduced to <5 Nml/kg by the time cool down commences during the shutdown. At some units one of the thermal degassers is used to degas the boric acid being added to the coolant during the shutdown, but this is not done at all units. In addition to reducing the hydrogen concentration, the thermal degassers reduced the ^{133}Xe below the head lift criterion before cool down starts. As ammonia is not removed by the thermal degassers and is in equilibrium with the SVO-1 cation resins, not all can be removed and a few mg/kg remain in the coolant throughout the shutdown. Due to the ammonia that exists in the coolant during the shut down, oxygenation of the coolant generates nitrate and nitrite ions by radiolysis.

Boration normally commences when the reactor shuts down, with the target concentration being >12 g/kg boric acid in WWER-440 units and >16 g/kg boric acid in WWER-1000 units. At WWER-1000 V-320 units, boration is carried out with the high temperature particulate coolant purification loops isolated to prevent the release of any previously absorbed radionuclides from the titanium sponge filter medium.

Cooling commences when boration is complete and at 2.5 MPa high pressure nitrogen is admitted into the pressuriser, transferring pressure control from saturated steam to nitrogen gas. At the same time the pressuriser water level is raised to the level of the sprays to limit nitrogen dissolution into the coolant. Cooling continues and at 190°C the first of the main coolant pumps is halted (to reduce core Δp, which would otherwise lift the reactor internals). At 140-150°C the steam generators are filled and decay heat cooling transferred to single-phase decay heat removal using one of the two installed decay heat loops in the secondary circuit (each using three of the steam generators). Cool down continues and at 50°C the final two or three main coolant pumps are stopped, halting all flow through the two normal primary circuit purification loops (SVO-1) and natural circulation decay heat removal is established using two of the primary coolant loops (with a third loop in reserve). Drain down of the primary circuit is carried out under nitrogen pressure (0.3 to 0.5 MPa). Finally, the circuit is depressurised and the reactor pressure vessel head removed, allowing oxygen ingress into the primary coolant.

In all WWER units, the conditions existing at the end of boration are similar to those in most PWRs, i.e. acid-reducing conditions, but with a low hydrogen concentration. Acid-reducing conditions are normally maintained throughout the cool down, although some oxygen can enter the coolant with the boric acid, until the reactor pressure vessel is opened allowing oxygen ingress into the circuit. Oxygen ingress does not occur during draining, because of the nitrogen blanket in the pressuriser. Although oxygenation by air ingress is the normal procedure at all WWERs, Loviisa have carried out forced oxidations using hydrogen peroxide on two occasions. These were at Loviisa 2 in 1993 and 1994 and were aimed at antimony removal as part of the steps taken to combat the increasing radiation fields at this unit. On both occasions hydrogen peroxide was added at the relatively high temperature of 140/150°C, during the temperature hold when the steam generators were being filled for decay heat removal duties. Before hydrogen peroxide addition, on both occasions the hydrogen concentration was already below the limit value of <5 Nml/kg.

At the Paks WWER-440 units a somewhat different shutdown strategy is followed, which followed work carried out at the station to measure Cs, Mn, Co, Ag, Sb, Zr and Cr radionuclide decontamination factors across the ion exchange beds from which it was postulated that most corrosion products were present as colloidal species [81]. This has led to the installation of an ultra-filtration system to remove colloids during the shutdown and a modified method of shutdown, which is designed extend resin bed lifetimes (to reduce radwaste) by minimising oxide solubility during the shutdown. To minimise the solubility, an alkaline pH is maintained during the shutdown, with a target of $pH_{140°C}$6.8-6.9, although the calculated pHt quoted [82] are approximately 0.3 pH high when compared with values calculated using the EPRI method. This higher alkaline pH achieved by not removing the potassium or ammonia from the coolant and maintaining hydrazine dosing until boration is complete (when potassium is <2 mg/kg). As part of this different strategy, purification is carried out using all three the SVO-1 resin beds, the borate form anion bed in the SVO-2 system and the ultrafilter and coolant purification is continued until the coolant temperature falls to 70°C.

In WWER reactors residual ammonia in the coolant during refuelling can result in the radiolytic production of nitrate and nitrite ions and a reduction in the coolant pH, which can be countered by adding hydrazine to the coolant [61 82 and 83].

2.3.7 Start-Up Chemistry.

Start-up of WWER reactors is also very similar to that for PWR reactors, but the main differences are that the circuit is pressurised with nitrogen up to 240°C, the ion exchange resin beds are boric saturated with potassium, ammonia and borate during the start-up and that hydrogen is only produced by radiolysis once the reactor is taken critical. There are also detailed differences between different plants.

Before start-up the coolant contains >12 g/kg boric acid (WWER-440 units) or >16 g/kg boric acid (WWER-1000 units) [>12.4 at some plants because of burnable poisons] and is fully oxygenated. The pressuriser is filled to high water level and nitrogen gas admitted to pressurise the primary circuit to 2.5 MPa (3.0 MPa at Loviisa). Two or three main coolant pumps are started to increase coolant temperature to ~80°C. During the shutdown there is no coolant purification and the SVO-2 system is only placed in service just before start-up. Clean-up using the primary circuit purification loops (SVO-1) is re-established once the main coolant pumps are started and SVO-2 is isolated for the remainder of the start-up. However, at Paks, SVO-1, SVO-2 and the ultra-filtration system are all used and continue in service until the minimum controlled power level is reached.

Ammonia (Loviisa) is added to the charging line as soon as the main coolant pumps are started and SVO-2 is isolated. Below 80°C oxygen removal is carried out using the thermal degassers, but hydrazine is added to deoxygenate the primary coolant at >80°C (100°C at Loviisa) and oxygen must be <10 µg/kg before the temperature can be raised to >100°C (>80°C at Dukovany) At Paks hydrazine dosing is started at .80°C and potassium dosing at 120°C; at Paks oxygen must be <10 µg/kg before the temperature is >150°C. After the coolant is deoxygenated, heat-up continues to ~160°C, when there is a temperature hold for the steam generators to be drained down to their nominal water levels and cooling switched from the single phase decay heat loops to the normal steam/water circuit. Heat-up then continues using five of the main coolant pumps (the sixth pump cannot be used at lower temperatures to avoid creating too high a Δp across the core). Some heat is also supplied via auxiliary steam to the steam headers of the steam generators.

At 200-220°C ammonia and potassium hydroxide dosing is started at Loviisa to saturate the ion exchange resins in the SVO-1 loops so that concentrations of 10-14 mg/kg potassium and 55 Nml/kg hydrogen (from the ammonia) will be present at start-of-cycle (120°C at Paks). The SVO-1 resins at Loviisa must be re-saturated as they are replaced with resins in the H^+ and OH^- forms immediately before a shutdown. At Dukovany ammonia dosing is started during heat-up, but potassium hydroxide is not added until 30% power is achieved, but at Loviisa, the SVO-1 resins must be saturated during the start-up. At 200°C the final main coolant pump is started and at 240°C the nitrogen is vented from the pressuriser and pressure control is transferred from nitrogen gas to saturated steam. Heat-up continues to the hot zero power temperature of 260°C, 12.3 MPa, the boric acid is diluted to the start-of-cycle concentration of ~8 g/kg and the reactor taken critical. Since hydrogen is only formed by radiolysis, it is not formed until the reactor is critical and then builds up to its normal operating level as power is raised. At Dukovany 72 hours are allowed from criticality for coolant potassium, ammonia and hydrogen concentrations to reach normal operating levels.

In WWER-1000 stations the start-up is essentially identical to that for WWER-440 units, except that the initial boric acid concentration is >16 g/kg^{-1} (diluted to ~8 g/kg for start-of-cycle) and the oxygen limit is <20 µg/kg before heat-up above 80°C. Coolant purification using the ion exchange beds is only carried out using the SVO-2 primary coolant purification system in the letdown and make-up system. The SVO-1 loops in V-320 units, which contain high temperature titanium sponge filters, are only placed in service once the coolant temperature reaches 200°C.

2.3.8 Surface Preconditioning

WWER primary circuit surfaces are preconditioned before first start-up. Currently, there are two sets of cold and hot functional tests (HFT) in use.

The basic Russian WWER-1000 specifications specifies the following:

(1) Circulation tests with the RCS >100ºC	pH 6.5-10.5, oxygen <0.02 mg/kg.
(2) Hydro-test with RCS >100ºC (circulation flushing)	Iron <0.2 mg/kg, oil <0.1 mg/kg, chloride <0.05 mg/kg, oxygen <0.2 mg/kg, transparency >95%.
(3) Hot functional test (HFT)	pH 10.0-11.0, chloride plus fluoride <0.1 mg/kg, total alkalinity (K+ Na) 0.02-0.07 mmol/kg, oxygen <0.02 mg/kg, ammonia 10-100 mg/kg, iron <0.2 mg/kg.

SVO-1 and SVO-2 must be fully operational for preconditioning, with one mixed bed filter filled to a depth of 0.5 m, and make-up water must conform to the normal operational standard. To maintain oxygen free conditions in the primary circuit, the letdown and make-up systems, and the water fed to the main coolant pump seals must also be deaerated.

The newer Czech specification was used at Mochovce (Slovakia) and Temelin (Czech Republic). This is a modified form of HFT chemistry, which was designed to give fully reducing conditions to produce a better initial chromium rich passive layer. The revised recommendations [84 to 86] were:

HFT chemistry	$pH_{25^\circ C}$ 5.6-7.5 (before dosing), 9-10.5 (after KOH dosing), $pH_{300^\circ C}$6.9-7.5, chloride plus fluoride <0.1 mg/kg, potassium 2-5 mg/kg, oxygen <0.02 mg/kg, silica <0.2 mg/kg, suspended solids <0.2 mg/kg, hydrogen 2-5 Nml/kg.

Ammonia and boric acid were not added, but oxygen was reduced by adding a stoichiometric amount of hydrazine to the make-up water above 60ºC. Potassium hydroxide dosing starts above 170ºC and dissolved hydrogen concentrations are maximised by minimising the operation of the thermal degasser in the letdown system. Corrosion products are removed by operating the primary coolant purification loops. The target HFT temperature was 260ºC at Mochovce and 285ºC at Temelin. Mochovce 1 and 2 and Temelin 1 and 2 were commissioned using this method and samples indicated that duplex oxide layers up to 20 µm thick were produced. These were mainly magnetite substituted with nickel and chromium (e.g. 60-65% Fe, 18-28% Cr, 9-12% Ni, <1% Mn and 1-2% Si on a stainless steel primary circuit sample.

Following the Full System Decontamination carried out at Loviisa 2, a short ~8 hour passivation stage was carried by adding hydrogen peroxide as the circuit was heated up from ~100 to ~150ºC. This, however, did not prevent the formation of fuel crud deposits in the subsequent fuel cycle. An alternative method of surface pre-treatment using a hydrothermally produced chromium rich layer produced by pre-oxidation with a solution containing potassium dichromate at temperatures up to 260ºC has also been developed for WWER reactors, but has not yet been used operationally.

2.4 Proposed Control Parameters and Limits for the Primary Coolant and Associated Primary Auxiliary Systems

2.4.1 Definition of Terms Used for the Control of the Primary Circuit Systems

2.4.1.1 Plant Status

Four basic primary circuit plant states can be defined for the plant start-up, power operation and shutdown, which are defined relative to the thermal and hydraulic conditions existing in the primary coolant system as these determine the chemistry environment. These states are as follows:

Cold Shutdown
This covers cold shutdown of the primary coolant, when the temperature is low and the circuit is borated to cold shutdown boric acid concentrations (>12 or >16 g/kg boric acid). It covers two regimes: cold shutdown with the primary circuit intact (coolant temperature <150°C to ≥60°C), or cold shutdown with the primary circuit opened, or the reactor pressure vessel head closure bolts de-tensioned or refuelling (coolant temperature <60°C). It also includes the primary coolant state during a refuelling shutdown when the reactor is defuelled and the reactor circuit is open for maintenance, when the refuelling cavity may also be is filled.

Start-up and Hot and Intermediate Shutdown
This state covers that period of the start-up of the reactor when the temperature is being raised to that for normal operation, but the reactor is not critical. (≥260°C for WWER-1000 units or ≥190°C for WWER-440 units) and Intermediate Shutdown (coolant temperature <260°C or 190°C to ≥150°C). It also applies to hot shutdown, when the reactor is shutdown, but normal operating temperature and pressure is maintained, and to the condition defined as intermediate shutdown, when the primary circuit is being cooled towards cold shutdown.

Power Operation
This covers the states when the coolant temperature is >190°C (WWER-440 units) or >260°C (WWER-1000 units) and the reactor is critical. It covers power operation when the power is in excess of the minimum sustainable level of power operation (≥2% power) and operation with the reactor critical but power less than the minimum sustainable level (≤2% power).

Shutdown
At the end of each fuel cycle each reactor shuts down for refuelling and during the fuel cycle a reactor may need to be shut down for repairs (a mid-cycle shutdown). In a mid-cycle shutdown the coolant is borated to hot shutdown boric acid concentrations, but the temperature and pressure is maintained at normal operating temperature and pressure (hot shutdown or hot stand-by). In a refuelling shutdown the pressure and temperature is also reduced and the coolant boric acid concentration is raised to cold shutdown levels. In WWERs the primary coolant temperature during hot shutdown and hot stand-by corresponds to a temperature of >190°C (WWER-440) or >260°C (WWER-1000).

2.4.1.2 Definitions of Control Parameters, Diagnostic Parameters, Action Level Ranges and Zones

The definitions of the various parameters (control, expected, diagnosis) are given in the Glossary, which are applicable throughout this entire NER document. The definitions given below are those that apply specifically to Chapter 2.

In the description given below, the terms Action Level 'Range' and 'Zone' are used to define the corrective actions required to return a control parameter (or parameters) to a value (values) that are within the limit values. These are also defined in the glossary

For Chapter 2, Ranges are used in all cases except for Primary coolant Boron-Total Alkali curves (Fig 2.6 and 2.7) that use various Zones.

Expected Values
The **expected** values represent the range of values that should be met during normal power operation with the correct treatment and in absence of significant amount of impurities.

Limit Value and pH Zone A
This range represents the admissible values for long term operation. The definition of the **limit** value is given in the glossary.

For primary coolant pH control, the maximum and minimum allowable pHt are defined by the upper and lower limit lines on the total alkali metal-boric acid diagram (Figures 2.6 and 2.7), which then defines an area within which power operation can continue indefinitely. This zone is defined as pH **Zone A**.

Action Level 1 (AL1) and pH Zones B and C
If the value is outside the limit range, then the **range** defined in this NER as **Action Level 1** is entered and corrective action should be implemented on a medium-term basis. The allowed maximum time limit is 7 days without it having any significant effect on safety or other important considerations, such as component lifetimes, dose rates or radioactive discharges. If the corrective action is not able to allow the unit to come back below the Limit value within the allowed time of 7 days, the power of the unit should be decreased to hot stand by or a lower state (such as hot shutdown or cold shutdown).

For primary coolant pH control, the upper and lower Action Level 1 zones are defined, which are defined as **pH Zones B and C**. For these pH zones, if the total alkali-boric acid concentrations cannot be returned to values within zones B or C within 7 days power should not be reduced, but the reason for the problem must be investigated.

For **primary circuit auxiliary systems** only an Action Level 1 range is defined in this NER. For these systems the allowed duration is also 7 days, but if corrective actions cannot be made in this time power does not have to be reduced.

Action Level 2 (AL2) and pH Zones D and E
If **Action Level 2** is entered, corrective action should be implemented on a short-term basis. The allowed maximum time is 24 hours without it having any significant effect on safety or other important considerations. If this time limit is exceeded, the power of the unit should be decreased to hot stand by or a lower state (such as hot shutdown or cold shutdown).

If the value of the parameter can be reduced to a value within Action Level 1 within 24 hours, then the 7 day time limit for Action Level 1 should apply, but with the 7 day limit starting from when the parameter first entered Action Level 1.

For primary coolant pH control, the upper and lower Action Level 2 zones are defined, which are defined as **pH Zones D and E**.

For **primary circuit auxiliary systems** only an Action Level 1 range is defined and Action Level 2 corrective actions do not apply (unless required by the plant operating instructions).

Action Level 3 (AL1) and pH Zone F

If the Action Level 2 range is exceeded, **Action Level 3** is entered and the power should be decreased immediately. The allowed time limit of 1 hour (unless plant operating procedures for a normal shutdown dictate a different time) is intended to allow a normal shutdown procedure in order to avoid a detrimental emergency shutdown and to give time to confirm that the parameter has effectively entered AL 3.

However, if the value then falls to within the Action Level 2 range before power reduction and shutdown is complete, power operation may resume and the allowed corrective action time reverts to 24 hours, but with the time defined from the original time that the parameter entered Action Level 3.

For primary coolant pH control, the equivalent Action Level 3 zone in Figures 2.6 and 2.7 is defined on the basis of a total alkali metal concentration, above which value there is a risk of severe fuel clad corrosion. This zone is defined as **pH Zone F**.

Measurement Units

In this NER, all units (other than mmol/litre which is retained for consistency with normal Russian practice) are expressed on a mass/mass basis, rather than a mass/volume basis (e.g., mg/kg or mg/kg, rather than mg/dm^3 or mg/litre, where the sample volume (or its mass) is always that of the solution being analysed). This is because it removes any uncertainty over the measurement temperature and the composition of the sample analysed and, therefore, the density of the sample. Mass/mass measurement units are used in most counties that operate nuclear and fossil power stations.

For dilute solutions, such as those from the make-up water tank the differences between the two approaches is small, but they become more significant in concentrated boric acid solution. Changes in sample composition and density are a significant factor in the analysis of the primary coolant, as the sample composition falls from ~8% to 0% boric acid during a fuel cycle.

2.4.2 Primary Coolant Specifications

Control of a WWER primary coolant during power operation can be separated into two main aspects. These are:

- The choice of the calculated optimum high temperature primary coolant $pH_{300°C}$ for each type of reactor to select the recommended pH zones, and

- The definition of the appropriate expected values and action levels for the individual control and diagnostic parameters.

The specifications for the primary coolant are normally sub-divided into three operational conditions. These are Cold shutdown (Table 2.7), Start-up (Reactor sub-critical and coolant temperature >150°C) (Table 2.8) and Power Operation (Reactor critical at full operating temperature) (Table 2.9). The pH control bands for power operation are shown in Figures 2.6 and 2.7. These specifications are based on the measurements made at the inlets of the SVO-1 or SVO-2 primary coolant purification loops, normally after the coolant temperature has been reduced, but before the coolant is purified by the ion-exchange resin beds.

The parameters defined are separated into control and diagnostic parameters. Of the anions defined as control parameters, the need to include chloride is normally accepted in all WWER and PWR units, but sulphate and fluoride are sometimes only considered to be diagnostic parameters. However, sulphate has been shown to promote IGSCC under a number of operating conditions, as for example the spent fuel pool, and it is one of the few impurities where a clear ingress route from the coolant purification resins is well established. It is, therefore, included as a control parameter in this NER with similar limits to chloride, as is now mormal in PWR guidelines. Fluoride is also normally included as a control parameter in PWRs because of its effect on fuel clad corrosion, and it is a required control parameter in WWER units using Westinghouse fuel. Although it is expected to be equally detrimental towards Zr-1%Nb fuel clad, it is normally only included as a diagnostic parameter when TVEL fuel is loaded. In this NER it is also defined as a control parameter for consistency with other anionic impurities.

Since the high temperature pH effectively only depends on the boric acid and the total alkali metal concentration it is unaffected by changes in any other primary coolant parameter. In addition, the high temperature pH is not measured directly and must be calculated. For all WWER units it has been agreed that the high temperature pH should be calculated using a reference temperature of 300°C, as is used by most PWR operators outside the U.S.A. In this NER the pH control band is defined as approximately ±0.1 pH units. Calculations indicate that slightly different optimum pHt should be applied for the two groups of reactor. For WWER-440 units the calculated optimum pH is $pH_{300°C}$7.2, whilst for WWER-1000 units the calculated optimum pH is $pH_{300°C}$7.1.

In many WWER operating counties, actual $pH_{300°C}$ values are not normally calculated to control the operating $pH_{300°C}$ values. Instead, they are inferred from total alkali metal-boric acid diagrams of the types shown in Figures 2.7 and 2.8. However, calculated pH_t may also be used as the control parameter, either calculated on a daily basis (as is used in most PWRs), or calculated semi-continuously on-line. Control based on-line pH_t calculations is used at Temelin, where pH_t is calculated at 5-10 minute intervals, based on the data from on-line boron, ammonia, potassium and lithium monitors. Automatic alarms are included in the software package to identify if the calculated pH_t value moves into one of the action level ranges. Plant data shows that good pH control can be achieved by this approach and that pH_t is kept between 7.0 and 7.2 throughout each fuel cycle. It must be noted, however, that using this method of calculating pH_t requires that all alkali metal ions must be measured, although the use of high purity potassium hydroxide at Temelin means that sodium concentrations are not required.

Methods for calculating the high temperature pH have been developed by a number of organizations. The method developed by EPRI is used as the basis of the calculations used for the Czech and Slovak pH specifications and is used in this NER to calculate to the $pH_{300^\circ C}$ values corresponding to the latest Russian and Ukrainian pH zones (see Appendix A2, Figures A.1 to A.4). From these it is apparent that the pH bands are not strictly constant, since the curvature actually present in boric acid-alkali metal plots at constant $pH_{300^\circ C}$ values was omitted when defining the pH specifications. In this respect they differ from the Czech and EPRI PWR specifications, which are based on the calculated pH values.

As noted above, many WWER operating countries do not normally control to the operating $pH_{300^\circ C}$ values, but instead infer the high temperature pH from alkali metal-boric acid diagrams of the types shown in Appendix A2, Figures A.1 and A.2. In this NER, these diagrams are also used to define the action limits, but they give a relatively low lower Action Level 2 pH limit (pH <6.7 (WWER-440) or pH <6.6 (WWER-1000)). At Czech stations, where $pH_{300^\circ C}$ values are calculated routinely, a tighter lower Action Level 2 limits are applied, namely pH <6.9 at Temelin (WWER-1000) and <7.0 at Dukovany (WWER-440), which are significantly higher than those given in Tables 2.7 and 2.8.

Table 2.7 WWER Reactor Coolant Specifications during Cold Shutdown

Parameter	Range of Expected Value	Range for Limit values	Action Level 1 Range
Control Parameters			
Boric Acid (g/kg)	Actual values may vary at individual plants dependent of the core fuel loading and as defined in the Technical Specifications for each individual plant		<Limit Value and as defined in the plant operating instructions (a)
Chloride (mg/kg)	< 0.05	< 0.10	Not Applicable
Fluoride (mg/kg)	< 0.05	< 0.10	
Sulphate (mg/kg)	< 0.05	< 0.15	
Hydrogen (Nml/kg or (mg/kg)) (c)	< 5 (<0.45 mg/kg) (b)	< 5 (0.45 mg/kg) (b)	
Diagnostic Parameters			
pH(25°C), Silica (mg/kg), TOC or oil (mg/kg), Transparency (%)			

Notes: (a) Individual plants will generally define what actions must be taken if the boric acid concentration falls below the limit value, e.g., in the plant Technical Specifications.

(b) During shutdown, as determined from calculations carried out for each unit before opening the RCS.

The hydrogen limit only applies when there is a risk that oxygen may be present (particularly when vessels are to be opened) and, therefore, that there is a risk of forming an inflammable or explosive mixture.

Table 2.8 WWER Reactor Coolant Specifications during Start-up

Parameter	Range of Expected Value	Range for Limit values	Value Before Criticality (a)	Action Level 1 Range (AL1) ≤7 days	Action Level 2 Range (AL2) ≤24 hours (b)
Control Parameters					
Chloride (mg/kg)	< 0.02	< 0.10	≤ 0.10	Not applicable during start-up	> 0.15
Fluoride (mg/kg) (c)	< 0.02	< 0.10	≤ 0.10		> 0.15
Sulphate (mg/kg)	< 0.02	< 0.15	≤ 0.15		> 0.15
Oxygen (mg/kg) (c)	< 0.02	< 0.1	≤ 0.1		> 0. 1
Ammonia (mg/kg)	> 3	Not Applicable	> 3	Not Applicable	
Hydrogen (Nml/kg)	***Not Applicable***		***> 15 (d)***	***Not Applicable***	
Diagnostic Parameters					
Boric Acid (g/kg), pH(25°C), Total Alkali Metal Concentration (mmol/kg), Iron (mg/kg), Copper (mg/kg), Nitrate (mg/kg), Silica (mg/kg), TOC (mg/kg)					

Notes: (a) Before the reactor is taken critical.
(b) If the Action Level 2 range time limit of 24 hours is exceeded, start-up should be halted.
(c) Oxygen must be < 0.1 mg/kg before the primary coolant temperature is >120°C
(d) Only if hydrogen is added as hydrogen gas.

Table 2.9 WWER Reactor Coolant Specifications during Power Operation

Parameter	Range of Expected Value	Range for Limit values	Action Level 1 Range (AL1)	Action Level 2 Range (AL2)	Action Level 3 Range (AL3)
Time Allowed	Unlimited	Unlimited	≤ 7 days	≤ 24 hours	≤ 6 to 12 h for a controlled shutdown to hot stand-by
Control Parameters					
Boric acid (g/kg),	Actual values at individual plants dependent on reactivity during the cycle				
Chloride (mg/kg)	< 0.05	< 0.10	Not Applicable	0.10 to 1.0	> 1.0
Sulphate (mg/kg)	< 0.05	< 0.15		0.15 to 1.0	> 1.0
Fluoride (mg/kg)	< 0.05	< 0.10		0.10 to 1.0	> 1.0
Dissolved Oxygen (µg/kg) (a)	< 5	< 5	5 to 20	20 to 100	> 100
Dissolved Hydrogen (mg/kg) (b)	2.2 to 4.4	2.2 or 4.4	1.3 to 2.2 and 4.4 to 7.2	0.5 to 1.3 and 7.2 to 9.0	< 0.5 and > 9.0
Total Alkali Metal Σ K + Na + Li	Zone A (c)	Zone A (c)	Zones B & C (c)	Zones D & E (c)	Zone F (c)
pH(300°C) alternative control parameter instead of Alkali (d)	7.1 to 7.3 (WWER-440) 7.0 to 7.2 (WWER-1000)	7.1 to 7.3 or 7.0 to 7.2	7.0 to 7.1 and 7.3 to 7.6 or 6.9 to 7.0 and 7.2 to 7.5	< 6.8 and > 7.6 or < 6.6 and > 7.5	-
Diagnostic Parameters (e)					
pH(25°C), Ammonia (mg/kg), Iron (mg/kg), Copper (mg/kg), Silica (mg/kg), Nitrate (Mg/kg), TOC (mg/kg) (f), Conductivity (µS/cm), Aluminium (mg/kg), Calcium (mg/kg), Magnesium (mg/kg)					

Notes to Table 2.9

(a) Oxygen and hydrogen cannot co-exist during power operation and when hydrogen is present at >0.5 mg/kg the oxygen concentration can be taken to be essentially zero.

(b) A number of units define these values in Nml/kg hydrogen, where 1 mg/kg hydrogen = 11 Nml/kg hydrogen.

(c) The various pH zones of total alkali versus boric acid are defined in Figures 2.6 and 2.7, respectively, for WWER-440 and WWER-1000 units.

(d) The control of calculated pH $_{300°C}$ is an acceptable alternative approach to controlling the primary coolant pH.

(e) Fuel vendors may require that some diagnostic parameters are treated as control parameters.

(f) Oil may be measured instead of total organic carbon (TOC). Not all diagnostic parameters are measured at all units.

Figure 2.6 **Specifications for WWER-440 Units**
(Values are calculated for 15 mg/kg ammonia, but ammonia has a negligible effect on pH at 300°C from 0 to 30 mg/kg; alkali metal/boric acid concentrations for the start of each plateau are marked on the figure.)

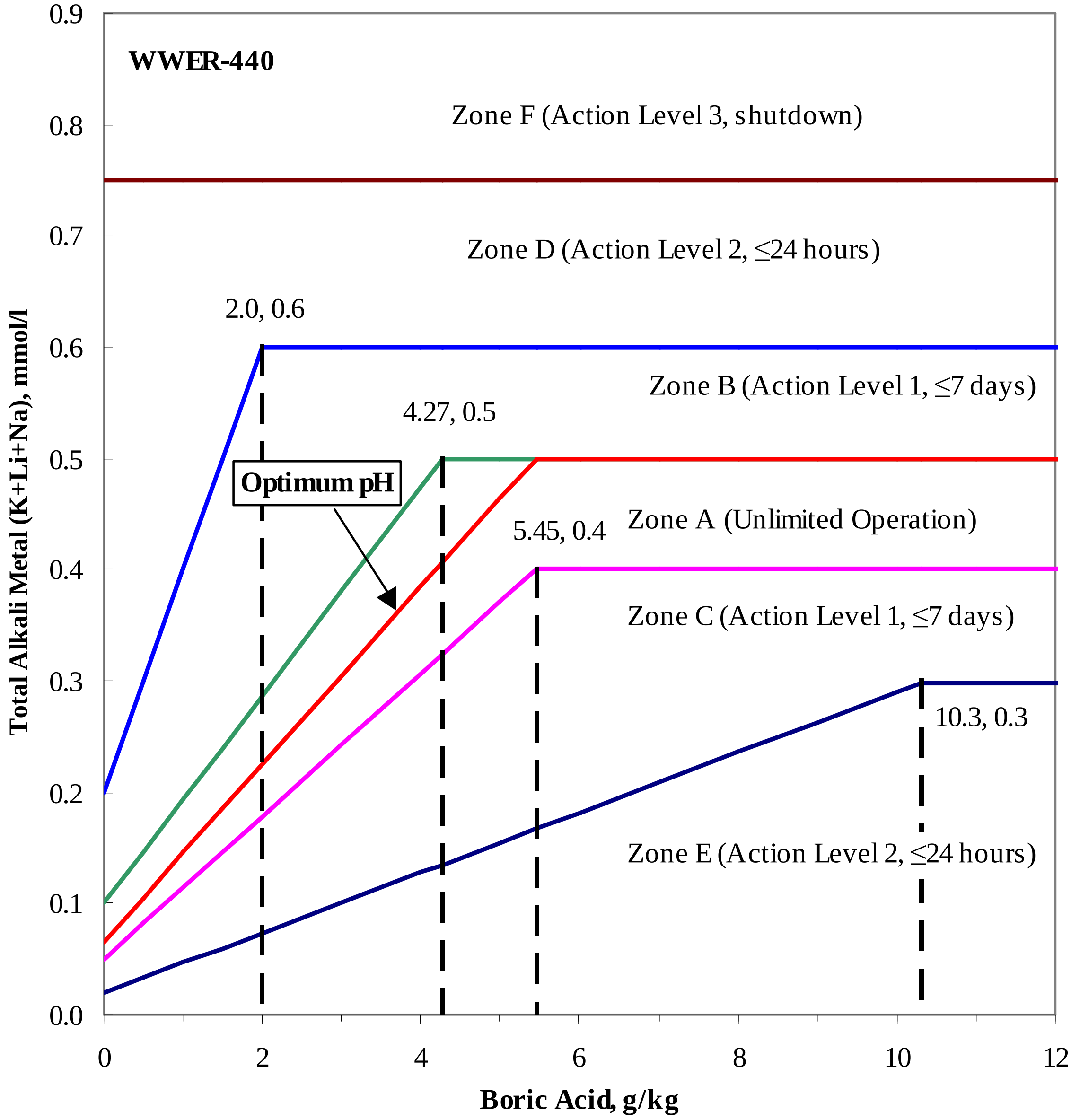
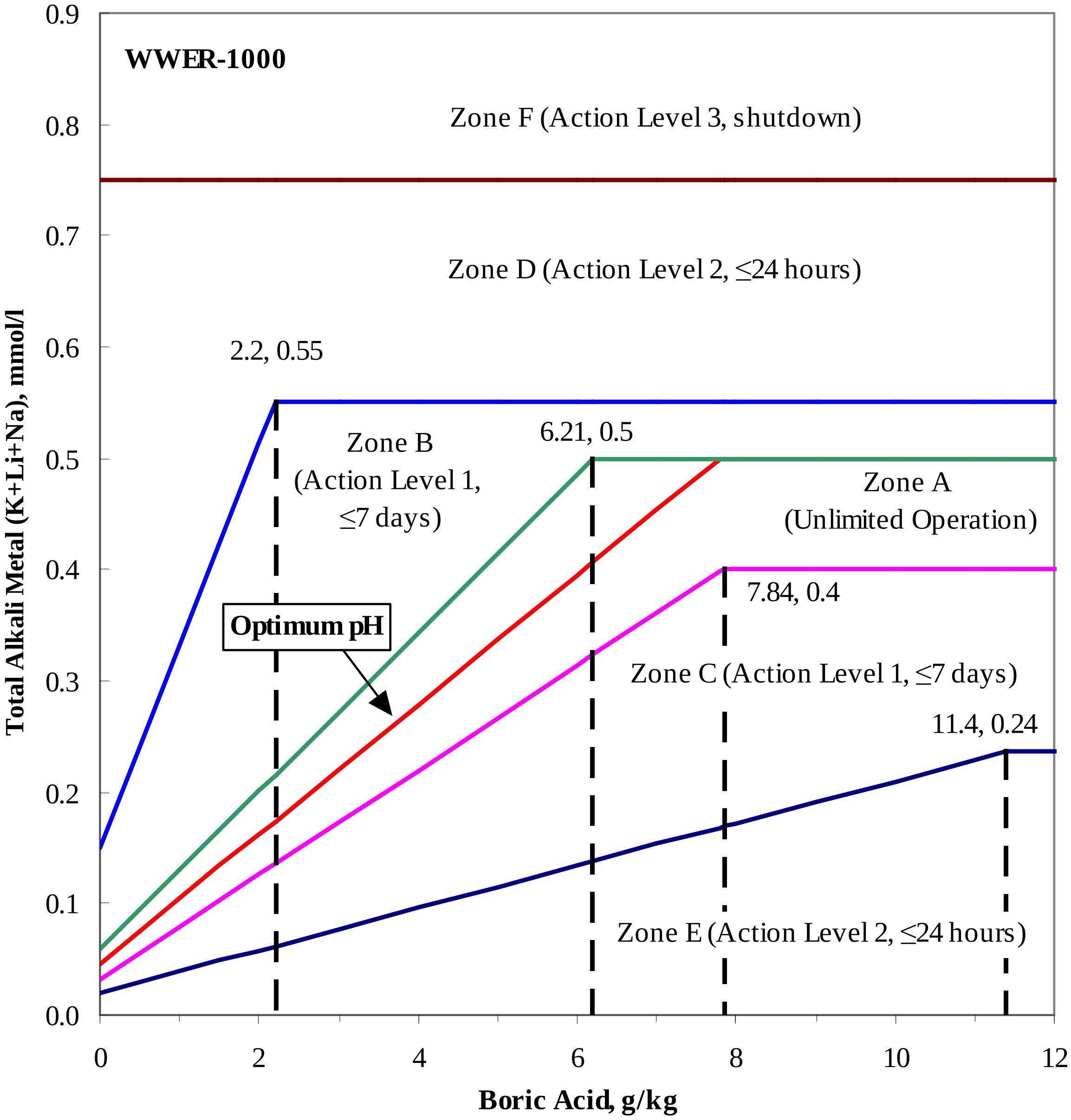


Figure 2.7 **Specifications for WWER-1000 Units (Values are calculated for 15 mg/kg ammonia, but ammonia has a negligible effect on pH at 300°C from 0 to 30 mg/kg; alkali metal/boric acid concentrations for the start of each plateau are marked on the figure)**



In addition to the measurements made on the primary coolant itself, there is a requirement to measure the effectiveness of the purification carried out by the ion exchange beds in the coolant purification circuits. This is determined by measuring the decontamination factors (DFs) across each bed for a variety of gamma emitting radionuclides (including ^{131}I, ^{133}I, ^{134}Cs, ^{137}Cs, ^{58}Co and ^{60}Co) and both chloride and fluoride.

The requirements for these beds are summarised in Table 2.10. Very similar specifications are placed on the ion exchange beds in the SVO-3 system, which is used as one of the sources of make-up water for the primary circuit.

Table 2.10 SVO-1 and SVO-2 Purification Loops Downstream of the Ion Exchange Beds

There are no control parameters, only the diagnostic parameters given below.

- Chloride (mg/kg) and Sulphate (mg/kg) measured after mixed beds and after anion beds (on both the borate or hydroxide-form beds, dependent on the system).

- Decontamination Factors: All beds, gamma-emitting radionuclide decontamination factors should be measured periodically to measure the performance of the individual beds.

Table 2.11 SVO-3 Purification System After the Ion Exchange Beds

There are no control parameters, only the diagnostic parameters given below.

- Boric Acid (g/kg) after anion bed,

- Chloride (mg/kg) and Sulphate (mg/kg) measured after cation and anion bed,

- Alkali Metals (mg/kg) after Cation bed,

- Transparency (%) after mechanical filter.

2.4.3 Specifications for Other System

2.4.3.1 Make-up Water (Clean Condensate)

WWER make-up water is either supplied from the Make-up Water plant, which is supplied to the ‘clean’ distillate tank, from which the water is supplied on demand to the letdown and make-up water system.

Since the make-up water is one of the simplest routes for impurities to enter the primary coolant (and its auxiliary systems), the purity of the make-up water must be strictly controlled. This can be achieved by making critical impurities such as chloride, sulphate and fluoride control parameters (as at Temelin), and by measuring each impurity independently, but the approach used in most WWERs is only to specify conductivity as a control parameter and to treat all other impurities as diagnostic parameters. This leads to a simpler method of control, which relies on the conductivity value to show that the concentrations of all impurity species are low.

As noted in Section 2.2.6, the make-up water is the main source of the ^{14}C produced during each fuel cycle, either from ^{17}O in the water (plus a small amount from dissolved oxygen) or from ^{14}N from dissolved nitrogen from dissolved air. Using deaerated make-up water will reduce the amount of ^{14}C produced.

The specification for the primary make-up water tank is given in Table 2.12.

Table 2.12 Primary Coolant Make-up Water

	Range of Expected Value	Range for Limit values	Action Level 1 Range (AL1) ≤7 Days
Control Parameters			
Chloride (mg/kg)	< 0.02	< 0.10	> 0.10
Oxygen (mg/kg)	< 0.1	< 0.1	> 0.1
Diagnostic Parameters			
pH(25°C), Silica (mg/kg), Magnesium (mg/kg), Aluminium (mg/kg), Calcium (mg/kg) (c)			

2.4.3.2 Boric Acid Tanks

WWERs have a number of boric acid storage tanks containing either ~12 g/kg or ~40 g/kg boric acid, which is either recovered from the evaporators or made up from fresh solid boric acid. These tanks are used for both primary coolant make-up and to supply the emergency core cooling system during a LOCA.

For these boric acid solutions it is normal to define the boric acid concentration as a control parameter, together with chloride and fluoride concentration (where the latter are normally set at the same values as are used in the primary coolant). Other impurities may be normally defined as diagnostic parameters. In this NER sulphate is also treated as a control parameter.

The specification for these tanks is given in Tables 2.12.

Table 2.13 Boric Acid Tanks (12 and 40 g/kg Boric Acid Tanks)

Parameter	Range of Expected Value	Range for Limit values	Action Level 1 Range (AL1) ≤7 Days
Control Parameters			
Boric acid (g/kg)	Actual values may vary at individual plants dependent of the core fuel loading and as defined in the Technical Specifications for each individual plant		
Chloride (mg/kg)	-	< 0.10	> 0.10
Fluoride (mg/kg) (a)	-	< 0.10	> 0.10
Sulphate (mg/kg)	-	< 0.15	> 0.15

Diagnostic Parameters			
pH at 25°C	> 4.2 or > 3.8 (b)	-	-

Notes: (a) Individual plants will generally define what actions must be taken if the boric acid concentration falls below the limit value, e.g., in the plant Technical Specifications, in tanks that form part of the emergency core cooling system.

(b) Depending on the boric acid concentration

2.4.3.3 Spent Fuel Pool and Refuelling Pool

In WWERs the spent fuel pool operates at a boric acid concentration that corresponds to a concentration that ensures that the spent fuel stored in the pool cannot go critical. In addition, as it interconnects with the refueling pool and the open primary circuit, it is normal for the boric acid concentration to be set at the value corresponding to the cold shutdown concentration, including a shutdown margin to prevent any risk that the core can become critical during defuelling and refuelling.

Since its function is to prevent criticality either during fuel storage or refuelling, the boric acid concentration is defined as a control parameter in this NER. For WWER-440 units the typical boric acid concentration is >12 g/kg boric acid, whilst for WWER-1000 units it is >16 g/kg boric acid. However, these values may be revised if the core characteristics change, e.g., following uprating or if the cycle length increases to 18-months.

In addition to these limits, the concentrations of chloride, sulphate and fluoride in the spent fuel pool are also defined as control parameters, with the limits set at the same values as those specified for the primary coolant.

The spent fuel pool specification is given in Table 2.14.

Table 2.14 Spent Fuel Pool

Parameter	Range of Expected Value	Range for Limit values	Action Level 1 Range (AL1) ≤7 Days (b)
Control Parameters			
Boric acid (g/kg)	Actual values may vary at individual plants dependent of the core fuel loading and as defined in the Technical Specifications for each individual plant (a)		
Chloride (mg/kg)	< 0.10	< 0.10	> 0.10
Fluoride (mg/kg)	< 0.10	< 0.10	> 0.10
Sulphate (mg/kg)	< 0.15	< 0.15	> 0.15
Diagnostic Parameters (c)			
pH(25°C), Iron (mg/kg), TOC (mg/kg), Transparency (%)			

Notes:

(a) Although the boric acid levels are determined by the amount required to ensure that a critical fuel mass cannot be achieved in the spent fuel pool, in practice the same concentrations are always used as those for cold shutdown used during refuelling as the spent fuel pool and refuelling cavity are interconnected.

(b) Operating in Action Level 1 does not require shutting down the plant, but the reason for the drop in concentration must be investigated and corrected.
(c) Other impurities, such as silica, may be included as diagnostic parameters.

2.4.5.4 Safety Systems

The primary circuit safety systems include a number of different tanks and systems that serve different safety functions. Of these the high and low pressure core cooling injection/recirculation trains take their flows from the high pressure borated water storage tanks containing ~40 g/kg boric acid and the low pressure borated water storage tanks containing ~12 g/kg boric acid.

The boric acid concentration is considered to be a control parameter for all tanks associated with the emergency core cooling system. The specifications of these tanks are included in the general specifications for the boric acid tanks given in Table 2.13.

In addition to these tanks there are the accumulators fitted to flood the core if there is a LOCA, the reactor building spray system tanks and in WWER-440 V-213 units the spray suppression trays fitted in the 'bubble condenser' tower. The latter are also filled with boric acid at a concentration of ~12 g/kg and are also covered by the specification given in Table 2.13.

The accumulators at most WWER units are filled with boric acid, to which potassium hydroxide is added to raise the pH to approximately neutral, but at Loviisa the accumulators only contain boric acid. As with other boric acid systems in stainless steel pipework or tanks, chloride (and sulphate) impurity concentrations should be limited to prevent SCC of the stainless steel vessels. The accumulator specification is given in Table 2.15

The smaller reactor building spray additive tanks of WWER-440 V-213 and WWER-1000 units contain similar amounts of boric acid and potassium hydroxide to that present in the accumulators, but they are also dosed with hydrazine. The latter ensures that the confinement area sprays or containment sprays provide a reducing medium, which will prevent any fission product iodine released in a LOCA from oxidising and becoming volatile. Any iodine will, therefore, remain in solution as iodide ion and collect in the coolant that collects in the base of the confinement area or containment building, rather that escaping to the environment. As in other boric acid systems, chloride (and sulphate) impurity concentrations should be limited to prevent SCC of the stainless steel vessels. at Loviisa the spray additive tanks only contain 18-22 g/kg potassium hydroxide and 4-6 g/kg hydrazine. The spray tank specification is given in Table 2.16.

Table 2.15 Accumulators

Parameter	Range of Expected Value	Range for Limit values	Action Level 1 Range (AL1) 7 Days
Control Parameters			
Boric acid (g/kg)	The actual values for each plant will be defined in the plant Technical Specifications and the values quoted are typical of those currently used in WWER units, but may change if the core duty changes		
Chloride	< 0.10	< 0.10	-

(mg/kg)			
Diagnostic Parameters			
Sulphate (mg/kg), Potassium (mg/kg), pH(25°C)			

Table 2.16 Reactor Building Spray System (Low Pressure Emergency Injection)

WWER-440 Building and WWER-1000 Containment Spray Additive Tanks

Parameter	Range of Expected Value	Range for Limit values	Action Level 1 Range (AL1) ≤7 Days
Control Parameters			
Boric acid (g/kg)	The actual values for each plant will be defined in the plant Technical Specifications and the values quoted are typical of those currently used in WWER units, but may change if the core duty changes		
Hydrazine (g/kg)	10 to15 (WWER-440) or >10 (WWER-1000)	< 10	< 10
Potassium (g/kg)	140 to150 (WWER-440) or > 100 (WWER-1000)	< 140	< 140
Chloride (mg/kg)	< 0.15	< 0.15	-
Diagnostic Parameters			
Sulphate (mg/kg)			

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3 SECONDARY SYSTEM

3.1 Main Design characteristics of WWER secondary system

The main characteristic difference between the secondary systems of WWER and PWR Nuclear Power Plants is the Steam Generator (**SG**) design, which is horizontal in WWER designs instead of being vertical in western PWR designs. Amongst commercial reactors, the overall design of WWER SGs, which are horizontal (except in the 70 MW prototype Rheinsberg, Eastern Germany) and have collectors, is unique. A second difference between WWER and PWR SGs is the tube material, which is made from an austenitic stainless steel (18% Cr, 10 % Ni stabilized with titanium) in WWERs, instead of the nickel-based alloys (Alloy 600 and 690) and higher chromium-containing alloys (Alloy 800) used in PWR SGs. The WWER alloy is equivalent to AISI 321.

The overall lay out of horizontal SG is shown on Appendix A1, Figures A1-8 to A1-10.

The steam generator tubing material is a stabilized austenitic stainless steel 08Cr18Ni10Ti with the following composition in mass % of elements [1].

Table 3.1. WWER Steam Generator Tubing material composition: 08Cr18Ni10Ti

C	Cr	Ni	Ti	Mn	Si	Co	Cu	S	N	P
<0.08	17 to 19	10 to 11,5	>5 × C to 0,6	<1,5	<0.8	<0.05	<0.3	<0.02	<0,05	<0.035

Table 3.2. Mechanical properties of stainless steel 08Cr18Ni10Ti

Ultimate tensile strength Rm in MPa at 20 °C	Relative elongation A_5 in % at 20 °C	Yield strength $R_{p0.2}$ in MPa at 350 °C
549	35	196-343

The main characteristics of WWER440 and WWER-1000 steam generators are shown below: [2]

Table 3.3. Characteristics of WWER Steam Generators (SG)

WWER Type (MWe)	**Unit**	**V-440**	**V-1000**
Number of SG per unit		6	4
Thermal Power per SG	MW	229	750
Pressure of steam at SG outlet	MPa	4.61	6.27
Temperature of steam at SG outlet	°C	259	279
Primary coolant temperature at SG inlet	°C	297	320
Primary coolant temperature at SG outlet	°C	270	289
Heat Flux	kW/m^2	90	123
Heat transfer coefficient	$kW/m^2°C$	4.7	6.1
Number of Tube per SG	-	5 536	11 000
Tube diameter (internal)	mm	16	16
Tube thickness	mm	1.4	1.5
Total Tube surface for all the SGs	m^2	15 060	24 460
Recirculation number	-	4-6	1.5-1.9

There are respectively 6 and 4 steam generators in WWER 400 and 1000 MW units.

WWER steam generators have a horizontal tube bundle, which is located in a shell with elliptical heads. The moisture separating equipment, steam collectors, steam nozzles and steam lines are located in the upper part of the SG shell above the tube bundle. Due to the single-stage moisture separators used in WWER SGs, the steam has a higher moisture content than that in PWR SGs. Feedwater enters the SG through a side penetration above the tube bundle and then flows down to feedwater headers located within the tube bundle. There is also an emergency feedwater line. Blowdown is taken from a number of locations along the bottom of the shell, where the drainage nozzles are also located. More design details are given in reference [1].

The SG heat exchanger tubing is attached to the wall of two vertical cylindrical headers called collectors, the inlet “hot” collector and the outlet “cold” collector. Primary coolant from the core enters through the inlet collector, passes through the SG tubes and leaves via the outlet collector. In WWER-440 units the temperature of hot and cold collectors are 297°C and 270°C, respectively, while in WWER-1000 units they are 320°C and 289°C, comparable with those in a PWR steam generator of western design [3].

In WWER-440 units, the collector material is 08Cr18Ni10Ti austenitic stainless steel, while in WWER-1000 units, the header material is the perlitic low alloy steel 10GN2MFA with a 08Cr18Ni10Ti stainless steel clad layer on the primary circuit side. In the first Russian-made WWER-1000 SG, the manufacturing method of expanding the tubing into the drilled walls of the collectors was by explosive expansion, which left a crevice and introduced significant stresses into the collector walls. In addition, the process of drilling deep holes in the collector walls and the subsequent method of explosively expanding the SG tubes led to the formation of a layer of embrittled cold-worked metal in the collector wall ligaments near the holes. In later Russian and all Czech WWER-1000, the SG tubing is hydraulically rolled into the collectors and these problems are avoided. The composition of the 10GN2MFA steel is given in Table 3.4 [3].

Table 3.4. WWER Steam Generator collectors material composition: 10GN2MFA

C	Cr	Ni	Mn	Mo	Si	V	Cu	S	P
0.08 to 0.12	<0.3	1.8 to 2.3	0.8 to 1.1	0.4 to 0.7	0.17 to 0.37	0.03 to 0.07	<0.23	<0.02	<0.02

In addition to the tube material, another important characteristic of WWER SGs is the temperature, significantly lower in WWER-400 than in WWER-1000 where it is comparable to that of PWRs and with a direct influence on corrosion behaviour.

All WWER-440 units and the first WWER-1000 unit (Novovoronezh 5) have two turbines and two condensers. All the other WWER-1000 units have one turbine and one condenser. In the early plants, the low-pressure heaters had copper alloys or carbon steel tubes, while the high-pressure heaters had carbon steel tubes. In some units, the carbon steel of high pressure heater tubing has been replaced by stainless steel. As an exception, high pressure heater tubing at the first WWER-1000 unit (Novovoronezh 5) was made of austenitic stainless steel.

For Low Pressure and High Pressure heaters, materials are replaced by stainless steel, when not initially in stainless steel as it is the case at of Bohunice, Dukovany, Mochovce (WWER 440) and Temelin (WWER-1000) where the secondary circuit was designed by Skoda manufacturer. The MSR (Moisture Separator Reheaters) have carbon steel tubes that were replaced by stainless steel in some units.

In Temelin, the original material for MSR was a low alloyed steel CSN 15 313 steel, with 2 to 2,5% of Cr and 0,9 to 1,1% of Mo. Later on, MSR was replaced by stainless steel material, but operational experience showed that this was not a good solution because chloride and other anions may be present in a crevice of reheater in which the last part of liquid phase after MSR is evaporated (although no condenser leak occurred). According to the Czech expert in charge of the evaluation, this may have been the cause of stainless steel cracking. Consequently, low alloyed carbon steel tubes, resistant enough to FAC, will be selected back again.

Originally, as in many other plants, the WWER condensers had copper alloy tubing. Now, due to the disadvantages of this material, copper alloys (LP heaters and condensers) are more and more eliminated. For condenser tubing, they are replaced by stainless steel or titanium, but in some cases (Bohunice), they are being replaced by brass condenser tubing for economical reasons [4].

The advantages are (i) the possibility to increase the pH value of the secondary system, which gives lower carbon steel corrosion rates, lower steam generator tube fouling, lower corrosion of carbon steel, lower fouling and (ii) a higher integrity of condenser tubes, with less impurity ingress and consequently a lower risk of SG tubing corrosion.

Appendix A1, Figure A1-5 shows the Primary system component layout at WWER-1000 plant . In Figure A1-9, can be seen the inside view of the horizontal Steam Generator of a WWER.

3.2 Important issues to be addressed

There are five important issues to be addressed in the secondary system:

- The first and most important issue is corrosion mitigation. This impacts on the safety and lifetimes of components, their operational reliability and availability, on operating costs and maintenance activities. These aspects are discussed in Section 3.2.1 for the steam generator, Section 3.2.3 for the carbon steel components of the feedwater train and Section 3.2.4 for the copper alloys used for some condenser tubing and feedwater heater tubing (and the Moisture Separator Reheaters).
- The second and most important issue, which is directly connected to the previous one, is safety, due to the primary coolant integrity. It is not only linked to material integrity related to secondary side corrosion of SG tubing, but also to primary side corrosion of the tubes. This explains why primary to secondary leak control is described in Section 3.2.6, in addition to the associated safety aspects in Section 3.2.1.
- The third issue, of growing importance, is the heat transfer capacity with a direct impact on plant performances. It has however impacts on maintenance activities that may be required to recover the pressure. In addition, it has also an almost direct impact on SG tubing integrity since fouling, at the origin of heat transfer decrease, is

one of the main contributor to corrosion associated with the concentration of impurities in the deposits. This is detailed in Section 3.2.2.

- The fourth issue, which is also of growing importance, is detailed in Section 3.2.5 and is concerning environmental and economic aspects which may be opposite to other objectives, such as corrosion resistance or proper maintenance.
- The fifth issue is a combination of the first and fourth issues, and is related to corrosion mitigation and the associated environmental constraints that occur during the lay-up of components. Possible options include: dry or wet lay up, and the use of octadecylamine to insure a better protection against air and corrosion of carbon steel.

3.2.1 Steam Generator (SG) Corrosion and Integrity

As explained above, there are two main characteristics of WWER SGs: the horizontal design and the use of the austenitic stainless steel 08Cr18Ni10Ti for the tubing. This is of great importance for degradation mechanisms.

Historically, the very first of western PWRs had SG tubing made of non-stabilised austenitic stainless steel type (18% Cr – 10 % Ni) similar to what is used in many components in the nuclear power plant and commonly used in nuclear industry. However, in western design, this alloy was not selected anymore after the 60’s and was unfortunately replaced in most cases by a nickel base alloy, very sensitive to Stress Corrosion Cracking.

The reason for this change in PWRs was the high sensitivity of the non-stabilised austenitic stainless steel (type 304) to localised corrosion (stress corrosion cracking) by chloride and oxygen at high temperature. Unfortunately, the replacement material, Alloy 600, with a high nickel content, is even more sensitive to stress corrosion cracking in pure water or alkaline environments [5 - 6].

For WWER SG tubes, the austenitic stainless steel 08Cr18Ni10Ti has been selected with a better resistance than non-stabilised austenitic stainless steel type (18% Cr – 10 % Ni).

While the pressure all over the primary system prevents from significant risk of impurity ingress by other systems during power operation, the same situation does not apply to the secondary system where the condenser operates under reduced pressure (below atmospheric pressure). Thus, in case of leak in any condenser tube or at the tubesheet, there will be impurities ingress into the secondary system by raw cooling water.

The ions contained in the cooling water will concentrate by two processes:

- Evaporation, which will concentrate the salts in the liquid phase, as the steam solubility and concentration is very low (about 10^{-4} the bulk SG concentration);
- Local concentration in areas where the flow velocity is restricted, such as in oxides deposits in some locations or crevices, according to the law describing the elevation of the boiling point of a solution as a function of the concentration of a dissolved salt (ebullioscopic law). According to this law, in regions of low flow, the temperature at the heat transfer surface of the SG tube is higher than that in the bulk SG water, which corresponds to the pressure and boiling point of pure water. Soluble ions will concentrate to a point corresponding to the ΔT, which is the difference between the

temperature in the deposit and that in the bulk SG water. The higher ΔT becomes, the higher will be the concentration of the soluble compounds while the low solubility species will precipitate. As an example, the sodium hydroxide concentration may reach 280 g/l for a ΔT of 20°C and 450 g/l for a ΔT of 40°C. When soluble impurities are concentrated in areas of restricted flow (instead of being removed by the SG blowdown), this is the hide-out, depending on the amount of heat transfer. During a shutdown, the reverse process occurs, and part of the compounds that had hidden-out, are released into the bulk SG water. This reverse process is called hide-out return. However, the reverse process is rarely complete and some of the chemicals, trapped in the oxides deposits, will remain and may re-start the corrosion process when further operation at high temperature resumes [7].

Impurities of low or retrograde solubility will mainly precipitate in the steam generator. They rarely induce direct corrosion but may result in the formation of an environment in which soluble and corrosive species may concentrate. Finally, in most cases, volatile species have a lower impact on corrosion except if after having been transported by steam they may deposit on the turbine and induce corrosion or undesirable deposits. However, in most cases, the purity required for the SG water is such that no additional constraints are required to meet turbine corrosion requirements. The case of silica is of concern for fossil fired or other units operating at higher temperature as compared with PWR or WWER, since silica volatility increases with temperature. Organic acid and carbon dioxide are also volatile but did not cause any significant degradation in WWER units.

- In addition, there is a specificity of WWER. The feeding system and SG blowdown system were reconstructed in WWER 1000 so that the salts concentrate in a location outside the collectors and are blown down from there. Temelin measurements in 32 sampling points confirmed that the feedwater reconstruction during manufacturing enabled concentrated species to be eliminated efficiently by the blowdown system, with a concentration 10 times higher than in the bulk water (the content outside of specific areas) of the SG.

Cold Header cracking- Steam Generator replacement in WWER-1000

As described in Section 3.1, crevices existed in the cold collectors of the early WWER-1000 SGs. Salts concentrated in these crevices, causing cracking and pitting corrosion in the stressed areas. The collector cold work layer was very sensitive to cracking, especially under acidic conditions [8]. The later Russian and the Czech SGs have been manufactured with a modified hydraulic expansion process with a lower stress level and do not have the same problem.

Cold collector cracking was the reason for many WWER-1000 SG replacements between 1986 and 1991 and further modification to the design, as well as the repair of the SGs at other stations. However, no SG has been replaced in WWER-440 units.

The first WWER-1000 replacement for other reasons was the replacement of the four SGs at Balakovo 2 in 1991, where 10% of the SG tubing was damaged at locations that were mainly in the lower rows near the hot collectors [9].

Temperature influence.

As mentioned in Section 3.1, the operating temperature in WWER-440 is lower than in WWER-1000. Both the stress corrosion cracking propagation rate and initiation threshold are strongly dependant on the temperature (thermally activated). In addition to the design influence of collectors, this is explaining the difference in corrosion behaviour between WWER-440 and WWER-1000 steam generators, the last ones being much more affected.

In western reactors, SG degradation problems on the secondary side have mainly been associated with high concentrations of impurities in flow-starved regions where locally aggressive solutions formed. For the WWER-440 design, a study was carried out at Loviisa unit 2, in Finland, on the influence of new feedwater distributor design and the start of the hydrazine dosing on concentration process and the distribution of impurities in the SG. [10]. This has also been done in other units, like Bohunice V-2 and Dukovany, but with other designs of feedwater distributor. In Paks NPP, the feedwater distributors have been changed in all the SGs.

Figure A1-10 in Appendix A1 shows the position of the old and new feedwater distributors in horizontal SG in Loviisa unit 2. The continuous blowdown is carried out from the primary collector pockets and periodic blowdown from both SG ends [10].

The study gave the following conclusions:

- The new feedwater distributor did not change the impurity distribution in the steam generator significantly. Measured sodium and iron concentrations were the highest in the “cold” end of the tube bundle and ammonia concentrations were the highest in the “hot” end. However, acetate was evenly distributed throughout both SGs.

- A small difference was observed in sodium concentrations in the two different designs at successive measurement points. Sodium levels were a little higher in the SG with the old design, but due to the small concentrations, a clear difference is difficult to verify.

- Due to the low impurity concentrations in the feedwater, the new design did not result in an increase in impurity levels as has been observed at some other plants with horizontal SGs. This clearly indicated that good secondary side water quality allowed component designs to be used that could cause problems in plants with higher impurity concentrations in the feedwater.

- The new location of the feedwater distributor was such that it could be easily inspected and repaired, thus resulting in shorter maintenance times during outages.

Steam Generator Blowdown (SVO-5)

The blowdown of each SG in WWER-440 is designed to operate at a continuous flow rate of 0,5% of steam generation, i.e. 2,2 5 m^3/hour, but the actual flow is ranging from 2.2 to 5 m^3/hour. There is also a periodic blowdown of 12 to 25 m^3/hour, with a frequency which differs from plant to plant (twice a day for about ½ hour in some units, permanently in others). This “periodic” higher blowdown is designed to allow a better elimination of sludge and impurities from crevices without the disadvantage (loss of heat, increased treatment) of a permanent high blowdown flow rate.

As mentioned in Section 3.2.1, the feeding system and SG blowdown system were reconstructed in WWER-1000 so that the salts concentrate at the end of the SG shell in a location outside the collectors and are blown down from there.

In WWER-1000, the blowdown of each SG is designed to operate at a continuous flow rate of 7.5 to 10 m^3/hour and a periodic blowdown of 20 to 28 m^3/hour, with a frequency which differs from plant to plant (twice or three times per day for about 2 hours) during which the continuous blowdown flow is reduced by a factor of about 3. This “periodic” higher blowdown has the same objective as for WWER-440.

Degradation mechanisms

The main degradation process that occurs in a steam generator is localised corrosion of the tubing, which depends on several parameters:

- the material characteristics (composition and mechanical characteristics, and therefore the relative sensitivity or immunity to various types of corrosion;
- the temperature which has an influence in many types of corrosion, all those which are thermally activated, but not all of them, some being able to appear at room temperature;
- the stress level for the most frequent type of corrosion, which is stress corrosion cracking;
- the environment, which can vary with time and which is the main parameter that can be controlled once the plant is operating.

The great variability in the corrosion behaviour of SG tubing throughout the world depends on these parameters.

Initially, (before 1960) a non-stabilised austenitic stainless steel (type 18 % Cr – 10 % Ni) was selected for first few western-designed low power PWR steam generators. No significant degradation occurred, but for the next generation of higher temperature, higher powered Nuclear Power Plants, a different alloy was selected by the American industry. The selected alloy, Inconel 600 which has a high nickel content (>72%), was chosen to give high corrosion resistance in a chloride environment, as this type of contamination was possible if there was cooling water ingress through a condenser leak at a time when there was no method of safely operating without such leaks.

The most important type of degradation occurred in PWR SGs with Alloy 600MA tubing (where MA refers to mill annealing), as this alloy contains insufficient chromium due to its high nickel content and has a more susceptible microstructure. Alloy 600MA is highly sensitive to stress corrosion cracking, particularly in alkaline environments and even in pure water for locations with a high stress level. Alloy 600TT (where TT refers to Thermally Treated) has been used in the 1980s in many PWRs.

Although it is still sensitive to stress corrosion cracking, there is a significant improvement to corrosion resistance and no secondary side degradation has been observed except in a few cases when there had been manufacturing anomalies. Alloy 600 was replaced in the 1970s in German-designed SGs by Alloy Incoloy 800, which has a slightly higher chromium content and a much lower nickel content. This Alloy has given good operating results, with a lower sensitivity to corrosion in many environments.

However, in most other countries, new SGs put into service after the early-1990s used Alloy Inconel 690TT tubing, which is highly resistant to the corrosion in the many types of environments normally encountered as it contains sufficient amounts of both chromium and nickel. No corrosion has been observed, or is expected in SGs using this type of tubing. In addition to these alloys, Alloy 800 and Monel 400 have also been selected in some other cases.

As mentioned above, non-stabilised 18% Cr + 10% Ni austenitic stainless steel is quite sensitive to stress corrosion cracking at operating temperature in presence of chloride and/or oxygen. In the WWER design, the addition of titanium as a stabilizing element significantly decreases its sensitivity towards corrosion, compared with the American AISI 304 (or 316) stainless steel grades, but it does not provide full immunity.

The main advantage of the austenitic stainless steel 08Cr18Ni10Ti used in WWER designs is its lower sensitivity to stress corrosion cracking in pure water in presence of stress, compared with Alloy 600 in which the chromium content is insufficient. Thus, WWER SG tubes do not suffer from stress corrosion cracking on the primary or secondary side in absence of impurities, such as occurs in Alloy 600 in regions with high stress levels and high temperatures.

On the contrary, 08Cr18Ni10Ti is much more sensitive to acidic corrosion in presence of chloride and this is the main risk of corrosion of this material in operating WWER units, since chloride may easily enter the secondary system through condenser leaks.

Transgranular stress corrosion cracking (TGSCC) of 08Cr18Ni10Ti stainless steel could develop from the secondary side of the steam generators, where higher chloride concentration can occur (e.g., in steam generator tube support crevices) [17].

In summary, it needs to be emphasized on the key corrosion behaviour of various alloys when evaluating the risk of degradation and selecting the corresponding chemistry regimes and guidelines (section 3.4.4).

- Alloy AISI 304 is sensitive in chloride environment and, more generally, in presence of several types of contaminants,
- Alloy 600 is very sensitive to stress corrosion cracking in alkaline environment and even cracks in pure water in presence of high stress level,
- Alloy 800 has a much better resistance in most environments,
- Alloy 690 has the best corrosion resistance in almost all environments, except in very few ones which are not representative of normal operating conditions (e.g. extremely oxidizing environment with copper or high lead contamination),
- Stainless Steel 08Cr18Ni10Ti used in WWER SGs has a slightly lower corrosion resistance, compared to Alloy 690 or even 800 but has much better corrosion behaviour under normal operating conditions than Alloy 600 and does not require as restrictive chemistry guidelines. On the contrary to Alloy 600 which is very sensitive to stress corrosion in alkaline environments, stainless steel 08Cr18Ni10Ti is more

sensitive to acidic conditions while a slightly alkaline environment is not detrimental and should be preferred if necessary.

Laboratory tests specific to 08Cr18Ni10Ti stainless steel confirmed the high sensitivity to corrosion by chloride in acidic environment [11]. This showed that SG tubes are sensitive to transgranular environmentally assisted cracking (EAC) in the three concentrated environments, i.e. alkaline, neutral and acidic, with the most dangerous environment being the acidic one.

The initiation time to cracking was extremely short (2 hours), whereas the initiation process took a long time under neutral and alkaline laboratory conditions on C-Ring specimens at 270°C, with oxide layers covering the C-Ring surface and in presence of rarely random shallow pits. The measured EAC crack growth rates ranged from 2×10^{-9} to 2×10^{-8} m/s in the three environments, based on C-Ring extrapolation for acidic environment and on Single Edge Notch Tensile (SENT) for the two other chemistries.

The governing phenomenon for the corrosion resistance of tube in service is consequently the initiation time which is very long, if any initiation, under neutral or slightly alkaline conditions (pH 9.8) while it is very short under acidic conditions at pH 2.7. This is of great importance to evaluate the risk of degradation according to various potential impurities. These results do not mean that under strongly alkaline conditions, which may be easily formed in crevices due to the low volatility of sodium as compared to chloride, WWER SG tubing is immune. However, it is the reason why, when acidic impurities are present, a small addition of LiOH in the secondary system has been applied in several plants to try to mitigate the corrosion process.

The main difference between stainless steel AISI 304 corrosion resistance and the Czech – NRI results on WWER stainless steel equivalent to AISI 321, is the higher resistance of this last stabilized steel in alkaline environment.

A second Czech study confirmed the lower sensitivity to cracking and pitting under alkaline and neutral environments, compared with an acidic environment in presence of the identical concentrations of 100 mg/kg chloride at 275°C [12].

Some laboratory electrochemical experiments performed in Finland showed that sulphate ions are even worse than chloride for breaking the passive film at the tube surface [13] but there is no clear demonstration from these specific tests that the corrosion resistance behaviour of the SG tubes is more important in the presence of sulphate than chloride. Most experts would consider that there is no higher sensitivity of sulphate as compared to chloride and that acidity or simultaneous presence of oxygen are the key factors. An abundant and historical literature data always considered the high sensitivity of austenitic stainless steel to corrosion in environments containing chloride and oxygen at high temperature [14-15-16].

Moreover, another laboratory study on this Alloy 08Cr18Ni10T (AISI 321) allowed to conclude that the number of microcracks were lower in presence of sulphate than chloride, in two different acidic environments (100 or 500 mk/kg) of anion added as the corresponding acid). Finally, in presence of chloride + sulphate, this last anion (sulphate) was found to be an inhibitor of chloride induced SCC initiation [17].

Lack of condenser tightness can results in air ingress bringing oxygen, also very detrimental to 08Cr18Ni10Ti stainless steel. This is why it is important to maintain a low oxygen concentration and a reducing environment in the steam generators.

08Cr18Ni10Ti stainless steel is also sensitive to pitting corrosion in presence of chloride, even at low temperature. Thus, the absence of contaminants containing chloride or sulphur during manufacturing, transportation and lay-up is mandatory. It is forbidden in any type of nuclear power plant but is of even greater importance in WWER units than for any other design to prevent rapid degradation.

In addition, laboratory tests on various alloys for SG tube alloys (any of those selected in WWER or PWRs) have shown a great sensitivity to corrosion in presence of reduced sulphur or lead contamination [18].

Finally, the feedback of WWER 440, with a lower temperature as compared to WWER 1000 and PWRs of western design, did not show degradation requiring steam generator replacement and thus demonstrating a satisfactory resistance of SG tubing.

- **Lead corrosion**

Degradation associated with lead has been identified in the case of Kozloduy NPP. The steam generators low alloy perlitic steel of 10GN2MFA type of the vertical cylindrical headres suffered from corrosion which was attributed to the presence of lead observed by Scanning Electron Microscope of tube specimens. [19]. Temelin NPP experienced lead presence in the secondary system of one unit due condenser painting. Several tens of kg of lead have been introduced in the system with a concentration of lead at SG Blowdown decreasing versus time from about 90-120 µg/kg in 2005 to 20-40 µg/kg in 2007. Laboratory investigations allowed to conclude that the risk of degradation was mainly associated with lead within crevices in a acidic environment. No degradation has been seen up to 2007 in the SG, likely due to the absence of lead in the oxide film as noticed on SG tubes analyses.

- **Condenser leaks mitigation**

Whatever the type of condenser cooling water, it will contain chlorides that are deleterious to WWER SG tubing. This is why it is of utmost importance to avoid condenser leaks, particularly in sea water-cooled units where magnesium chloride hydrolysis will induce an acidic environment according to the following reaction, due to the precipitation of magnesium hydroxide, which has an extremely low solubility at high temperature.

$$MgCl_2 + H_2O \rightarrow Mg(OH)_2 \downarrow + 2\,\mathbf{HCl}$$

In contrast, most river waters have compositions that result in an alkaline environment under thermal decomposition and after carbon dioxide elimination in the steam phase.

$$NaHCO_3 \rightarrow CO_2 \nearrow + \mathbf{NaOH}$$

Thus, early replacement of condensers with copper alloys (brass) tubing is important, necessary, particularly for WWER cooled by sea water (acidic forming cooling water), if the condensate polishers is not any more able to manage the complete elimination of impurities entering the circuit from the condenser leak. Acidic forming cooling water is mainly observed for sea water and there are very few of such WWER plants. With river water cooled plants, the consequence of a condenser leak is not so detrimental since the river water is alkaline forming under heat thermal decomposition, and the concentration of ions in river water is much lower than in sea water. Nevertheless, depending on the decarbonisation method applied to the treatment of the river water in the closed cooling water system (in the presence of a cooling tower), the water may become less alkaline and even slightly acidic under steam generator condition in concentrated areas.

Whatever the cooling water, it is never desirable to continue operating with a leaking condenser and to attempt to eliminate the impurities permanently using the condensate polisher resins. In addition, the permanent use of condensate polishers has many disadvantages described in Section 3.2.5. Consequently, it is better to consider using the condensate polisher as a temporarily method of eliminating impurities, e.g., during start up, after a condenser leak, or any other source of impurity ingress, before having to shut down the unit or to decrease power to fix the leak.

- **Condensate and Feedwater oxygen control**

As described earlier, the stainless steel used for WWER SG tubing is particularly sensitive to cracking in oxygen environment. This is why air ingress in condenser should be limited to the minimum reasonably achievable value of no more than a few µg/kg (ppb). This needs to be applied even when the secondary circuit has a deaerator (deaerating feedwater tank), since the oxygen entering the condenser will react with the metal, producing oxidising oxides that will enter the steam generator and maintain an oxidising and potentially corrosive environment.

The feedwater oxygen concentration should generally be very low in order to be sure to avoid an oxidizing environment inside the steam generator where it could induce cracking of the tubes.

It is important to be aware of the fact that oxygen measurement, like suspended solids, is very sensitive to the characteristics and particularly the length of the sampling line. This is even more important for samples from a circuit at high temperatures, since oxygen may easily react with the sampling line materials. Thus, a particular care should be taken to the sampling line for the measurement of the oxygen concentration, particularly from the feedwater at high temperature.

Another way to evaluate the presence of an oxidising environment or oxygen transients, that may be detrimental for the Steam Generator, is to make a specific on-line measurement of the ECP (Electro Chemical Potential) [20].

However, the oxygen concentration in the condensate water should not be too low since it is not optimum for mitigation of Flow Accelerated Corrosion (FAC) of carbon steel in feedwater train heaters (see Section 3.2.3).

High oxygen pollutions are also to be avoided when the conditioning reagent is morpholine since oxygen will increase its thermal decomposition into organic acids that will adversely increase the cation conductivity in the whole secondary water system.

3.2.2 Steam generator fouling and heat transfer

Fouling is due to the deposition of corrosion products, mainly iron oxides on the SG tubing itself (which is different from sludge formation by gravity), with several consequences:

- A decrease in heat transfer, a reduction in the outlet steam pressure and, when these is severe fouling, a power reduction;
- The formation and transport of corrosion products into the steam generator can increase the corrosion risk, due to the concentration of chemical compounds in the deposits.

The oxides that deposit on the tube surface are essentially coming from the corrosion of large surfaces of carbon steel materials, mainly the tubes in the feedwater train, such as the feedwater heaters, the moisture separator reheaters, and potentially the condenser.

The quantity of deposited corrosion products is directly related to several parameters:

- the corrosion rate of material which is more important for carbon steels than for stainless steel or low alloy steels,
- the corrosion rate of carbon steel which is more important when the pH at the operating temperature decreases and consequently is one of the main objectives of correct chemistry selection,
- the deposition rate on the tubes, which depends on efficiency with which oxides particles are eliminated by SG blowdown,
- the deposition rate on the tubes which depends on the specific properties of the chemical reagents (zeta potential) in front of the tube material.

Oxides may deposit either on the tubes with the above consequences (thermal heat transfer reduction) or in areas of restricted flow or at the bottom of the steam generator by gravity.

Oxide deposition in restricted areas may cause flow changes with in some extreme cases the potential risk of flow and water level instability, as has occurred in some PWR steam generators of western design. Such problems have not been reported in WWER SGs, but should be taken into account as it has a direct influence on operation and safety. Any instability can increase flow-induced vibration and rapid cracking of some tubes due to cyclic fatigue. In WWER SGs, relatively large amounts of sludge can accumulate below the tube bundle, but in some extreme cases the sludge layer reached the tube bundle and had direct operational consequences. Thus, although there is no direct impact of impurity concentration in the sludge deposited on a WWER SG tube under normal conditions, as it is the case for western PWR designs, a very large amount of sludge must also be avoided.

Although the consequence of deposits on the SG tubing or in areas with restricted flow is the same in PWR and WWER designs, there is one main beneficial difference for WWER designs. This is that horizontal SGs do not normally form sludge pile around the tube bundle, which in a vertical SG is another location where the chemicals may concentrate and induce corrosion. On the contrary, in horizontal SG the sludge will deposit at the bottom of the SG away from the tubes. Sludge should be eliminated during shutdown maintenance in WWER SGs but not with the same acuity and chemical cleaning is mainly requested to recover the heat transfer due to deposit on the tubing itself.

The presence of copper has the main disadvantage for fouling of imposing an operation at a low pH (9.2 at 25°C) for avoiding ammoniacal corrosion. Such a low pH does not provide a sufficient protection to carbon steel against FAC (Section 3.2.3). The progressive replacement of copper alloys in the secondary system of some WWER units allows an increase of room temperature pH at a value depending on the reagent, which decreases the generation of corrosion products. This results in lowering the concentration of iron in feedwater, the quantity of sludge and fouling, of corrosion under deposits, and better control of the SG operation.

The use of an alternate amine treatment as described in sections 3.2.3 – 3.2.5 and 3.3 should also be considered for fouling and corrosion transport mitigation.

3.2.3 Flow Accelerated Corrosion (FAC) for Carbon Steel components

FAC in an important issue as has been demonstrated by the severe accident that occurred on a feedwater pipe at the Finish WWER-440 Loviisa, the American PWR Surry 1 and the Japanese PWR Mihama 2.

This phenomenon, an accelerated generalized corrosion of carbon steel, is depending on 3 conditions:

- a material with very low content of chromium (< 0.1%),
- a high velocity of the flow, quickly eliminating the dissolved iron,
- an insufficient alkaline environment, in absence of oxygen.

This FAC problem may be easily solved by:

- the selection of stainless or low alloyed steel (in replacement of carbon steel),
- the protection against high flow velocities,
- the selection of proper chemistry using ammonia at high $pH_{25°C}$ of 10 or an amine,
- an adequate non destructive examination program, preferably based on computer codes, taking into account the required thickness of the piping, the previous measured thickness, the applied chemistry regime and the chromium residual content of the carbon steel [21].

The higher local pH at the secondary system operating temperature that reduces carbon steel FAC rates can be obtained either by increasing the pH with the alkalising reagent concentration, or by selecting a reagent that gives a higher pH in the area to be protected. This is related to the reagent partition coefficient which induces different concentrations in various parts of the secondary system and to the reagent evolution of alkalinity versus temperature.

One option is to use ammonia at the $pH_{25°C}$ of 10, but this cannot be an universal option for all WWER plants, since many of them have copper alloys in the secondary system that would suffer from unacceptable copper corrosion at such a pH (Section 3.2.4).

Thus, the most applicable option in order to avoid FAC is to select an amine. Morpholine is mainly used in France while ethanolamine (ETA) has been widely used in USA since the early 1990s and in several other countries. Both reagents or dimethylamine (DMA) used in some cases, are generally able to give sufficiently low FAC rates.

However, reducing FAC rates under single-phase conditions (mainly in the feedwater heaters) is favoured by the use of an amine that gives as high a pH as possible at the operating temperature, which means that there should be a limited reduction of its dissociation constant versus temperature. On this basis, for the same $pH_{25°C}$, the capacity to protect carbon steel from FAC at high temperature is:

morpholine > ETA ≈ ammonia [3].

On the other hand, reducing FAC rates under two-phase conditions (SG internals, MSR) requires the use of an amine that has both a lower reduction in its dissociation constant versus temperature and a lower distribution coefficient between steam and water (which approximates to its relative volatility). Thus, in the SG internals, the moisture separator reheater blowdown and wet steam lines, the ability to protect carbon steel from FAC, for the same $pH_{25°C}$ is:

ETA > morpholine > ammonia.

Consequently, ammonia may be used only at a high concentration and $pH_{25°C}$ value.

FAC is also strongly depending on the Redox Potential. An oxidizing environment is beneficial for FAC but not acceptable for the SG tubing corrosion, particularly with the WWER austenitic stainless steel. Consequently, the oxygenated treatment is not an appropriate option. The selection of an adequate pH and reagent is the safest option to avoid FAC [22].

Consequently, the chemistry options for protecting carbon steel against FAC through chemistry selection are as follows:

- when copper alloys are absent and if the overall system is able to cope with a high ammonia concentration (see Section 3.2.5), then an ammonia treatment at a feedwater $pH_{25°C}$ close to 10 can give satisfactory results without the use of condensate polishers (or with these bypassed) if the condensers are tight (leak free). This is used in some countries such as Germany and in some WWER units such as Temelin or Paks and may be selected for other WWER if the other criteria described in other parts of this document are met. Using an amine is an alternative option which has to be used when operating at low pH due to the presence of copper alloys;

- when copper alloys are present, the feedwater $pH_{25°C}$ must be limited to about 9.2 with ammonia (or potentially at a slightly higher value with amine treatment). In presence of copper alloys, an amine must be selected to mitigate FAC, but the amine choice will depend on many of the aspects developed in other parts of this document.

3.2.4 Copper Alloys corrosion

In order to mitigate ammoniacal corrosion of copper alloys, pH 25°C in feedwater has to be limited to ≈ 9.2 to 9.3, to avoid the formation of soluble copper-ammonia complexes, but even with this low pH, corrosion of copper alloys still exists in a number of plants. A pH of 9.2 with ammonia is not acceptable to keep carbon steel corrosion at a sufficiently low level. Thus, an amine has to be used in this case.

Copper corrosion is less sensitive in the presence of some amines as compared with ammonia and plant experience have shown that the pH with some amines may be increased slightly above 9.3 while keeping an acceptable copper alloys corrosion rate. The pH limitation will also depend on the location and number of the components with copper alloys.

In addition to pH limitation, the presence of copper alloys has the inconvenient of being corroded and bringing copper to the steam generator where it may increase the risk of tubing corrosion, especially with an oxidizing environment.

Finally, an important problem of brass condensers is the abrasion on the cooling water side which may easily occur after a couple of decades or not, depending on the cooling water properties. Consequently condensers may leak and bring impurities in the condenser and finally into the steam generator.

Copper alloys are not appropriate for sea water cooled plants, where a small leak is unacceptable unless an adequate condensate polishing plant is operated. The high chloride concentration and moreover the acidic reaction under temperature are very detrimental for the WWER SG tubing, even in the absence of sea water.

But, even for units cooled by river water, the selection of design without copper alloys in the secondary system will be very beneficial for the treatment selection.

The presence of copper alloys:

- prevents from operating at a sufficient pH for carbon steel corrosion, with several impacts,
- prevents from adding a sufficient hydrazine concentration if blowdown resins are operated after exhaustion with the pH reagent and in absence of condensate polishers,
- induces the presence of copper in the steam generators, deleterious for the tubing.

This is why more and more WWER units are replacing their brass condensers, although there is still copper alloy tubing, either in original condensers, or in a few cases, in replaced condensers

Thus, for hydrazine-ammonium water chemistry regime, scheduling a replacement of copper condensers reheaters or other components made of copper alloys, is a good decision which should be taken as soon as possible, according to maintenance and costs possibilities.

3.2.5 Economic and environmental aspects

With the sustainable development required for nuclear energy, environmental aspects should be considered in addition to economical ones, independently of other constraints such as safety and long-term behaviour of materials, which are the core of the objectives in chemistry options.

These economic and environmental aspects are not only linked to the limitation of reagents concentration but particularly to

- the selected resin, length of working cycle of resin between regeneration if any;
- the release of chemicals into the environment, depending on recycling of the chemical, operating mode of the resin;

- the reagent selection, composition and corresponding concentration.

Each point is specifically discussed below.

- **Blowdown operating mode, resins selection**

As detailed in Section 3.1.2.1. the blowdown design in WWER is optimized for minimizing heat loss and water use while keeping a sufficient efficiency of impurity removal by SG blowdown purification system.

In presence of copper alloys, an amine treatment should be selected for mitigating Flow Accelerated Corrosion of carbon steels (Section 3.2.3). On the units without copper alloy, an amine treatment may be also preferred. Ethanolamine or morpholine are the most commonly used amines although some other amines are also selected in PWR units. For the operation of steam generator blowdown resins, morpholine, as applied in French units, allows the operation of SG blowdown resins in morpholine form and with a sufficient duration without high sodium at resins outlet. This is due to the comparative affinity of sodium, which is higher than the one of morpholine on cation resins while ammonia affinity is more comparable to sodium one. The advantage of such an operating mode is the possibility to operate with resin saturated by morpholine, during around one year, without regeneration. After about one year, the resin is replaced by a new resin. Selecting a Nuclear Grade Resin will increase the guarantee of a high quality resin, with fewer impurities during in service use, and potentially longer duration before reaching the replacement criteria.

All the advantages of such a design and options are:

- Lower investment costs,
- Absence of risk of pollution by regeneration reagents and resin fines,
- Less liquid wastes into the environment, for 2 reasons: no regeneration reagents releases and less addition of amine or ammonia in the system since the resins are operated after exhaustion by the alkaline reagent.

Ethanolamine having a higher affinity than morpholine with resin, the cation resin duration in saturated form is theoretically shorter but the practical feedback shows that this option should not be eliminated.

Consequently, if operation of the cation resin without regeneration and in saturated form is possible, morpholine treatment is an interesting option while if the resin must be regenerated, ethanolamine, with a lower molar concentration is a better option.

Ammonia at high pH (close to 10 at 25°C) may be used if there is not constraint on regeneration and release of chemicals.

In Temelin, when hydro ejectors for vacuum are used, hydrazine is not sufficient for reaching the pH of 10 and ammonia addition is necessary. Loss of ammonia from secondary side via ejectors might cause pollution of cooling systems and affect discharges of ammonia and/or nitrates. In this plant, blow-down resin are regenerated once per 3 - 4 months because of Si release.

Other amines or mixing of amines may also be considered.

- **Reagents type selection and concentration,**

All Volatile treatment (AVT) is based on the addition of an alkaline volatile reagent for obtaining the selected pH and hydrazine as a reducing chemical.

Two main types of AVT reagent may be used:

- Either ammonia, frequently obtained directly by thermal decomposition of hydrazine, with, in this case, the small advantage of adding only one chemical for the two purposes,
- Or an amine, as the main reagent for the required pH, in addition to hydrazine which is producing some ammonia in lower quantities.

The organic amine used is chemically similar to ammonia, in which one or several atoms of hydrogen are replaced by an hydrocarbon chains. These amines have alkalinity generally higher than ammonia and better characteristics.

The selection of the reagent is strongly depending on the materials in the secondary system and the subsequent risks of corrosion, such as FAC (see Section 3.2.3) or copper corrosion (see Section 3.2.4).

Presence of copper alloys in the secondary system

It has been explained that in presence of copper, an amine selection is mandatory since the pH at high temperature cannot sufficiently be raised with ammonia.

In this case, the only reliable option is an amine of which the most widely used reagents are morpholine or ethanolamine (ETA) that have already successfully tested in WWER, at a $pH_{25°C}$ of ≈ 9.2. This pH could be increased slightly on a plant specific basis if it has been demonstrated that the copper alloys corrosion rate remains acceptable.

Absence of copper alloys in the secondary system

When copper alloys are absent, two types of secondary water treatment are possible:

- Ammonia at a feedwater $pH_{25°C}$ of about 10 (9.8 -10), which corresponds to an ammonia concentration of about 10 mg/kg, as used in some PWR and WWER,

- An amine, used at the highest possible feedwater pH compatible with other constraints (blowdown ion exchange resin lifetimes or regeneration, presence or absence of condensate polishers, operating costs, waste releases). Typically, a feedwater $pH_{25°C}$ of about 9.5 - 9.7 is a good compromise, with a minimum pH value of 9.4 to minimise FAC, corrosion product transport and SG fouling sufficiently. The corresponding reagent concentrations depend on the amine selected and the contribution of ammonia to the feedwater pH.

Table 3.5. Example of pH values with ammonia plus morpholine or ethanolamine

$pH_{25°C}$	Ammonia (mg/kg)	Morpholine (mg/kg)	Ethanolamine (mg/kg)
9.2	0.3	3.7	0
9.2	0.3	0	0.63

9.3	0.5	4.3	0
9.3	0.5	0	0.65
9.3	0.3	7.8	0
9.3	0.3	0	1.2
9.4	0.8	5	0
9.4	0.8	0	0.7
9.4	0.3	0	2.0
9.5	1.3	5.3	0
9.5	1.3	0	0.7
9.5	0.8	14.4	0
9.5	0.8	0	1.9
9.5	0.3	0	3.1
9.5	0.3	25	0
9.6	2	6	0
9.6	2	0	0.7
9.6	0.8	30.4	0
9.6	0.8	0	3.6
9.96	10	0	0

There are general advantages and disadvantages of the various amines potentially used, mainly morpholine or ethanolamine. Table 3.6 give a general overview on the two most commonly used amines in presence of copper alloys in the secondary system. Table 3.7 gives the same comparison but also including ammonia in absence of copper alloys. Ammonia is not considered a viable option at low pH in presence of copper alloys. Detailed information is given in section 3.3.

From an environmental point of view, the main advantage of ethanolamine (ETA) over morpholine is the potentially smaller amount of nitrogen compounds released to the environment because of the higher basic nature (dissociation and alkalinity) of ETA. However, all parameters have to be compared, including the blowdown resin duration, the quantity of sludge and the protection of the various parts of the secondary system against FAC.

Table 3.6. Advantages and inconveniences of 2 amines in the presence of copper alloys [22].

	Morpholine	Ethanolamine
Advantages	Distribution coefficient of 1 ➔ constant concentration throughout the secondary system ➔ good protection of many parts of the system against carbon steel FAC.	High alkalinity ➔ lower concentration ➔ more favourable for the environment and good compatibility with the use of condensate polishers
	Good feedback experience for SG fouling and corrosion	Very low concentration of organic acids produced by thermal decomposition
	Compatibility with the operation of blowdown resin beyond breakthrough in its exhausted form (after saturation): ~1 year for the cation resin	Good protection against FAC in some parts of the system, where the pH is higher than with morpholine

Disdvantages	Low alkalinity ➔ high molar content not always compatible with the use of condensate polishers	Partition coefficient <1 ➔ non-homogeneous protection for the various parts of the secondary system
	Limited stability ➔presence of some organic acids, increasing the cation conductivity in the SG blowdown and decreasing the detection sensitivity of other impurities	Lower possibility of blowdown resin operation beyond breakthrough in the exhausted form, due to the higher affinity of ETA for cation resins compared with morpholine ➔ lower Na elimination

Table 3.7. Advantages and disadvantages of morpholine, ETA and ammonia in the absence of copper alloys in the secondary system.

	Morpholine	Ethanolamine	Ammonia
Advantages	Coefficient distribution of 1 ➔ constant concentration all over the secondary system.	High alkalinity ➔ lower concentration ➔ more favourable for the environment.	Easy treatment and monitoring, with potentially only hydrazine added if the ammonia is recycled.
	Good protection against FAC and corrosion transport throughout the system at high pH	Good protection against FAC and corrosion transport throughout the system at high pH	No organic acids produced as by products. Thus, no impact on cation conductivity and impurity detection.
	Compatibility with the operation of blowdown resin in exhausted (saturated) form	Low concentration of organic acids produced by thermal decomposition	
Disdvantages	Low alkalinity ➔ very high molar content hardly compatible with condensate polishers	Partition coefficient < 1 ➔ non-homogeneous protection for the various parts of the secondary system	Requires a high $\text{pH}_{25^\circ\text{C}}$ (almost 10) to give sufficient protection against FAC and for corrosion product transport. High nitrogen release into the environment.
	Limited stability ➔presence of some organic acids, increasing the cation conductivity in the SG blowdown.	Lower possibility of blow down resins operation in exhausted form (relative affinity) ➔ lower Na elimination or more frequent regeneration or replacement.	Limited possibility of blow down resins operation in exhausted form (relative affinity) and high frequency of regeneration required. Not compatible with condensate polishers.

- **Condensate polisher operation.**

The first environmental advantage of having tight (leak-free) condensers is the possibility of deciding not to install a condensate polishing plant or to bypass it for most or part of the time.

In addition, a condensate polisher system has many adverse effects [21].

- Investment costs,

- Operating costs for chemicals, resins and the time spent for regenerations and monitoring,
- Risks of contaminating the secondary system by regeneration reagents,
- Risk of contaminating the secondary system by resin fines,
- Difficulty to operating with the optimum pH and amine concentrations in the feedwater, thus causing adverse effects as described above (fouling and FAC),
- Release of important liquid waste streams into the environment, which is one of the most important concerns for the future, sustainable development.

The only advantages of condensate polishing plants are:

- Possibility of continuing the operation in presence of condenser leak, although the operation with large sea water leaks is not feasible,
- Eliminating the impurities by the time the plant is shutdown in case of large leak,
- Shorter time during start up.

Nevertheless, if condensate polishers must be permanently used to mitigate condenser leaks, the reagent selection may be different.

The high molar concentration required with morpholine treatment has, as with a high pH ammonia regime, an impact on the condensate or blowdown polishers. This is why only a few plants with condensate polishers have selected morpholine.

Ethanolamine has the advantage over morpholine, of a lower molar concentration for the same pH, due to a higher dissociation, and will be a good option if condensate polishing plants are used regularly.

3.2.6 Primary to secondary leak control

Primary to secondary leak control is an important safety issue. Monitoring for the presence of activity in the steam and SG blowdown to determine the leak tightness of the SG tubing has a number of objectives:

- to avoid any sudden large leak (burst) of a steam generator tube,
- to trend small leaks due to the presence of a through-wall defect to see if there is any risk that it will develop into a tube rupture (burst).

The consequences of leaks are:

- dissemination of radioactive compounds out of the primary system and into the environment;
- the loss of primary coolant for keeping the reactor at its nominal temperature.

A small amount of primary to secondary side leakage may be tolerated and steam generator tubes with small cracks can be allowed to remain in operation provided that they have been evaluated as not susceptible to evolve toward an unacceptable leak during the following period of operation up to the next inspection and maintenance shutdown.

As a safety measure, the primary to secondary leaks rate must be measured during operation. The main method of on-line monitoring is to measure each steam generator blowdown stream for total gamma activity, or to make laboratory measurements of ^{24}Na or ^{42}K (or any other suitable radionuclide). In addition, other activity measurements are carried out on samples taken from the main steam line and the condenser vacuum off-gas extraction line.

Finally, a sudden primary to secondary leak may generally be avoided by a quick reaction in case of significant increase of ^{16}N on-line monitored and immediately detected in the steam line going out of each steam generator. This method is to be used for quick and safe detection of large leaks but is not accurate for monitoring small leaks, due to the large steam generator water volume and the time taken for radionuclides from leaking primary coolant to appear in the steam when there are small cracks in the collectors.

Other methods of avoiding tube burst should rely on critical length of defect which is acceptable and which is determined according to the tubing, considered degradation and plant specificity. Burst tests and corresponding primary to secondary leaks for different identified types and sizes of defects contribute to such an evaluation which must include some safety margin.

For example, at Temelin, such a Leak Before Break evaluation showed that applying a limit of primary to secondary leak of 8 l/h per SG is able to prevent from uncontrolled situation of SG tube burst.

3.2.7 Make-up Water Options for Good Water Quality

Good make-up water quality is a key factor for maintaining good chemistry control in the various systems, since it is normally the main source of impurities, i.e. in the absence of condenser leaks and of impurities released from condensate polishers.

In addition to economical and environmental reasons, it is a good reason to minimise steam and water losses from the secondary system and, therefore, the make-up water flow rate and corresponding impurities introduction in the secondary system by the make-up water. Temelin tried to reduce this flow below 15 m3/h per 1000 MW unit.

The make-up water to the secondary system is demineralised water, which may or may not contain the alkalising reagent used for the AVT treatment of the secondary system.

Demineralised water is generally produced in two steps:

- the first pre-treatment stage is aimed at eliminating non or slightly-ionised compounds, i.e. suspended solids, colloids, silica, organic compounds and some of the calcium and magnesium bicarbonate present in the source water;

- the second stage normally uses ion exchange resins beds to produce demineralised water and includes cation, anion and mixed-bed resin in a number of configurations. The oldest systems have weak and strong cation and anion beds for regeneration optimization while the more recent systems have a more limited number of resin beds. For a good water quality, it is necessary to have a mixed-bed in the final demineralisation step in order to eliminate the final traces of ions more efficiently in a neutral environment. This is the only resin bed option, because if the final bed is a separate cation or anion bed it would operate in a slightly acidic or alkaline environment and consequently would give a lower purity.

There are now new processes of producing demineralised water with physical methods such as reverse osmosis or electrodesionisation that may alternatively be selected, particularly for new stations.

Any solution is acceptable, provided it meets the specifications recommended in Section 3.4.6.

3.3 Chemistry Regimes Options

The challenges described above for selecting the best secondary water chemistry for the secondary system of PWR plants include:

- avoiding ammoniacal corrosion of copper alloys if they are present in the system,
- minimising flow accelerated corrosion of carbon steel (FAC),
- mitigating stress corrosion cracking (SCC) of steam generator (SG) tubing,
- reducing steam generator fouling,
- decreasing operating costs,
- reducing the amount of chemical waste produced, as well as their effect on the environment, through the use of acceptable reagents and concentrations and their impact on the ion exchange resins of the SG blowdown and condensate polishers.

- **History of Regimes**

The two Loviisa Power Plant WWER-440 units started operation by using neutral water chemistry in the secondary side. The oxygen free feedwater (reducing environment) and low impurity concentrations resulted the steam generator stainless steel tubes remaining in good condition and therefore no tube leakages have occurred during the operation.

Also, the horizontal position of the SG and the lack of tube sheet have prevented the formation of alkaline cracks, which are typically found in vertical steam generators. The drawback of the applied water chemistry has been the FAC in other parts of the secondary circuit. Due to the feedwater line breaks in units 1 and 2, as well as the observed erosion corrosion damage in the SG blowdown system, a decision was made to re-evaluate the applied water chemistry and the possibilities of increasing the pH value of the feedwater. As a result, a change to hydrazine water chemistry took place in 1994 at Loviisa unit 2 and in 1995 at unit 1. In both units, the hydrazine concentration was increased until a pH value between 9.1 and 9.2 in the feedwater was achieved.

The following main conclusions were reached as a result of the extensive water chemistry measurements in Loviisa unit 2:

- Iron concentrations in the feedwater were higher during neutral water chemistry operation than after the hydrazine water chemistry was introduced. This is a clear indication of the reduced corrosion product release rates from the carbon steel feedwater lines.

- Electrochemical corrosion potential measurements of typical construction materials and Pt showed that a reducing environment exists on the top of the tube bundle in both studied SGs. This means that concentrations of oxidising species (oxygen, copper, etc.) in feedwater are low enough. This is important because hydrazine/ammonia water chemistry is used mainly to increase the pH of the feedwater to the target value of 9.1 -9.2 [10].

The hydrazine-ammonia treatment with potential later addition of lithium hydroxide had been traditionally used for the secondary system of WWER plants.

Increasing ammonia content at new WWER Units (Tianwan, Paks, Dukovany or Volgodonsk Unit 2, Balakovo Unit 5, Kalinin Unit 4, Temelin), which do not use copper alloys in the secondary systems, can inhibit flow-accelerated corrosion (FAC). On the contrary, this countermeasure cannot be used at operating WWER plants with copper alloys.

HAVT (High All Volatile Treatment with ammonia), as applied in Temelin NPP, is a high $pH_{25°C}$ associated with a flow of ammonia of:

- ≈ 37200 g/h in the final feedwater,
- ≈ 22.3 g/h at SG blowdown,
- ≈ 9.7 g/h in demineraliser cationic ion exchange resin bed.

Morpholine chemical treatment was proposed by experts for the South Ukraine (SU) NPP under a European Community TACIS programme.

Morpholine and the alternative amine ethanolamine (ETA) have been tested at a number of WWER plants that have copper alloys in their secondary systems and have been more widely adopted since 1998 and particularly since the beginning of years 2000:

- Morpholine at the South Ukraine NPP since 1998, at Zaporozhe NPP since 2001, and at Volgodonsk NPP since June 2005
- ETA at Bohunice V-2, Rovno-3, Balakovo 2 since September 2006.[24]

The beneficial results of using morpholine in WWER units are:

- corrosion mitigation, as an increased SG sludge removal efficiency by “washing effect” has been observed in Ukrainian NPP,

- compliance with the chemistry specification applied in Ukrainian NPP,

- a reduction in the FAC rate and wall thickness losses of carbon steel piping,

- a significant and permanent decrease of the iron corrosion products concentration in feedwater, which has been reduced by a factor of about two from ~12 µg/kg to ~5 µg/kg. A much lower limit can be readily achieved when copper alloys are absent and the secondary system feedwater pH is higher,

- a large reduction in the primary to secondary leak rate of the SG tubing due to corrosion mitigation, which is probably the most important result as it has a direct beneficial impact on safety issues.

The morpholine treatment required a higher culture of proper chemistry operation in order to produce its maximal benefit. These were:

- decreasing the oxygen concentration in the secondary system to an acceptable level,

- eliminating leaks and the ingress of impurities from the condensers and other components of the steam-water system,

- adequately controlling oxygen, organic acids, corrosion products and sulphates concentrations in the circuit [25].

Ethanolamine has been selected at Bohunice V-2 (Slovakia) after a theoretical study and mainly for a cost/benefit comparison and gave the following results [4-26-27].

A concentration of 1.5 - 2 mg/kg ETA in feedwater has been shown to be efficient at decreasing the iron corrosion product content by a factor of about 10 in MSR and by 30 to 50 % in feedwater. This enabled achieving a satisfactory concentration of 3 ppb in feedwater.

The main benefits of ETA were to be able to mitigate FAC of carbon steel in presence of copper alloys (condenser tubing) and to minimize corrosion product transport, while keeping the same duration of condensate polishers (present in units 3 and 4) between 2 regenerations. The iron concentration in SG respectively decreased (25 - 18.8 - 15.6 - 9.4 µg/kg) when ETA was increased in feedwater (0 - 0.5 - 1 - 1.8 mg/kg). SG heat transfer coefficient measurements showed an improvement when using ETA as compared to ammonia.

Organic acids concentration remained at low values (< 20 µg/kg) of formate and acetate.
Based on AECL results, morpholine is supposed to provide a lower fouling rate of SG tubing, as compared to ETA, but the Bohunice results did not show any fouling issues with ETA [4].

- **Ammonia - Low and High pH Operation**

In most early nuclear power plants, ammonia was used as it is easy to implement, there is a large amount of experience with its use, it has known characteristics, there are no decomposition products, it has a low cost and it has no adverse effects except for corrosion by ammonia of copper alloys due to the formation of soluble copper-ammonia complexes if feedwater pH is above 9.2 at room temperature. In addition, its use is even easier as it is the main decomposition product of the hydrazine generally added as a reducing agent. This allows the use of a higher hydrazine content, than is required just to obtain a reducing environment.

In Temelin, the addition of hydrazine is not sufficient to reach the $pH_{25°C}$ of 9.8 - 9.9 when hydro ejectors for vacuum are used and in this case, additional ammonia additions are required to give a concentration of ~5 mg/kg.

However, ammonia has one disadvantage, which is that a high molar concentration is required to give a high enough feedwater $pH_{25°C}$ to minimise corrosion product transport along the feed water train due to general carbon steel corrosion and to protect carbon steel components from single-phase FAC. This will increase the amount of either the liquid or solid chemical waste released into the environment. When copper alloys are present, the maximum $pH_{25°C}$ of 9.2 – 9.3 that can be tolerated leads to an unacceptable FAC rate.

When copper alloys are absent, the feedwater $pH_{25°C}$ can be increased to 9.9 to 10 to avoid FAC and to minimise corrosion product transport. However, when condensate polishers are always in operation and only operate in the hydrogen-hydroxide ion form, the regeneration frequency will be too high. However, when there are no installed condensate polishers or if the condensate polisher is bypassed as at Temelin, operating at a feedwater $pH_{25°C}$ of 10 will minimise corrosion product transport, but requires either (i) frequent regeneration of the blowdown demineraliser resins or (ii) operation of resins past exhaustion by ammonia with the associated risk of reduction in their efficiency for sodium elimination at such a high ammonia molar concentration.

High pH ammonia treatment has been successfully applied in some WWER and is considered to have resulted in a significant decrease of SG tubing degradation at Paks NPP [28].

In summary, ammonia is a viable option for operation at $pH_{25°C}$ of 9.9 – 10 and is easy to implement and monitor, but can only be used in plants without copper alloys and normally without condensate polishers in service and if the blowdown resins are regenerated.

- **Amines : Morpholine, Ethanolamine, other amines**

Morpholine

The main advantage of morpholine is its ability to protect all of the secondary system against FAC efficiently (see Section 3.2.3), even in presence of copper alloys and at a $pH_{25°C}$ of 9.2.

With morpholine, a $pH_{175°C}$ of 6.8 in two phases flow conditions can be obtained with a $pH_{25°C}$ of 9.3 while the same high temperature pH would require a room temperature pH of 10 with ammonia. This can be explained by two advantages of morpholine over ammonia:

- The change in the morpholine dissociation constant as a function of temperature, which does not fall as rapidly as the temperature increases as does that of ammonia. Therefore, for a same feedwater $pH_{25°C}$ value with each reagent, the alkalinity reduces more rapidly for ammonia than for morpholine as the temperature increases.
- The morpholine steam/water distribution coefficient (which in this case is approximately the same as the relative volatility) is close to 1, which gives an approximately constant concentration throughout the steam/water system, while with ammonia, liquid drains have a lower concentration and, therefore, a lower pH.

The main disadvantage of morpholine is the relatively high molar concentration that is required for give the desired feedwater pH, particularly if $pH_{25°C} > 9.5$ is selected.

The consequence of the higher molar concentration is that, as with ammonia at high pH, it reduces the lifetimes of the condensate polisher or blowdown resins beds. This is why plants with condensate polisher should not normally use morpholine or should bypass the condensate polishers the most part of the time, unless they can be operated in the morpholinium form.

The second main consequence of this higher molar concentration is an increase of nitrogen in liquid effluents, particularly if the ion exchange resins are regenerated.

The third main consequence of morpholine is an increase in the concentrations of the organic acid anions, acetate and formate, that is observed in some cases. Depending on the unit, the blank cation conductivity in the SG blowdown water typically increases by 0 to 0.15 µS/cm with morpholine treatment, compared with ammonia. Higher values would be considered to indicate significant organic contamination and/or air ingress, which should be avoided. Even though laboratory studies and operating experience feedback have never indicated any steam generator tube corrosion due to pure organic acid contamination, their concentrations should be kept as low as possible to minimize their contribution to the cation conductivity, as a low value is the key on-line monitoring of the secondary system overall purity.

An economical inconveniency of morpholine may be its price, particularly for countries where it is not produced and where it is much more expensive than ammonia or ethanolamine.

In summary, morpholine is a good selection when the blowdown resins are not regenerated to avoid any risk of chemical contamination, to limit liquid chemical wastes, when the condensate polishers are not permanently in operation or to give uniform protection to all parts of the secondary system against FAC.

It has been also successfully tested in several WWER units, with an important reduction of corrosion transport and of the number of corroded SG tubes (see above, history of regimes).

Ethanolamine

Ethanolamine (ETA) is an alternate amine, largely used in the USA and an increasing number of countries with PWR units (50 % of Japanese plants and some plants in other countries).

It has also been tested in some WWER, mainly Bohunice and Rovno

The relative volatility of ETA is about 0.6, compared with about 1 for morpholine, which will not give a constant concentration in the different parts of the steam-water system. This results in the possibility that the various portions of the system are not exposed to the optimum ETA concentration and, therefore, less protection may exist in some parts of the secondary system if ETA concentration is adjusted for other parts of the system. However, in the two-phase parts of the secondary system, the liquid phase may have a higher ETA concentration so that carbon steel components that may be affected by FAC will be more efficiently protected.

It has been noted that the main advantage of ETA is the lower molar concentration that is required, compared to morpholine, to achieve the target pH at operating temperature. Consequently, the load on the condensate polisher or the blowdown resins will be lower, with a beneficial effect on one or several of the following parameters (see Section 3.2.5):

- operating cost, especially with a potentially lower cost than morpholine,

- run length of cation resin in hydrogen form,

- reduced frequency of resin regeneration,

In addition, the nitrogen compounds released into the environment, which is now always of increased concern, will be lower (see Section 3.2.5). Another important advantage of ETA is its higher thermal stability, which in some cases gives a lower organic acid concentration than morpholine, although it is not a key issue against the use of morpholine.

In summary, ETA is a good selection when condensate polisher are in continuous service or if specific parts of the secondary system must be protected against FAC or if nitrogen release into the environment must be decreased or finally, if the reagent cost is in favour of ETA.

Other amines

In addition to morpholine or ethanolamine (ETA), other reagents may be used, each of which has its own advantages and disadvantages. However, only the two main reagents used in PWRs and already tested in WWER are discussed in detail in this report, but this does not mean that other amines should not be considered.

Moreover, some utilities with PWR made the interesting approach of using a mixing of amines with each one its own purpose, such as protecting different part of the steam/water circuit against FAC or more efficiently reducing the corrosion products transport and deposition. The main considered amines are DMA (dimethylamine) and MPA (methyl-propanolamine). The only disadvantage of such a mixing of amines is the higher complexity of reagents dosing and monitoring.

- **Hydrazine**

A reducing environment in the secondary side of SG is of utmost importance for minimising the initiation and growth of steam generator tube cracks, which are sensitive to oxidising compounds. Although hydrazine is a hazardous chemical, it can be added using a sealed dosing system and no suitably efficient reagent is known that does not have a similar health hazard.

Hydrazine (N_2H_4) reacts stoichiometrically with oxygen and has the added advantage of the excess reagent thermally decomposing into ammonia. It is, therefore, an acceptable reagent for the steam/water system and is mainly used at a hydrazine concentration of about 100 µg/kg, as recommended by many organisations. However, hydrazine additions should not be used to solve problems due to air ingress into the condenser, which must be identified and eliminated by the plant staff.

Hydrazine should not be used only to produce the large quantities of ammonia required to achieve a selected pH using ammonia, due to the hazards associated with hydrazine handling and its higher cost compared with ammonia, unless the overall method of operation does not require the addition of increased amounts of hydrazine to produce the ammonia.

Moreover, the presence of very large concentrations of hydrazine in the feedwater would increase the risk that sulphate would be reduced to sulphide, which is very detrimental for steam generator tube cracking.

Several laboratories have studied the effect of feedwater hydrazine concentrations on the composition of suspended iron oxides (magnetite versus haematite) and on the redox potential to optimise the feedwater hydrazine concentration. From these tests, it was shown that increasing the hydrazine concentration above 100 µg/kg, or 8 times the oxygen concentration in condensate water was not relevant.

Another potential issue of high concentration of hydrazine on FAC rate has been recently demonstrated as not having any measurable negative impact. Consequently, the main reasons for limiting the hydrazine concentration are the environmental and economical impacts and, for extreme concentrations, the risk of producing corrosive reduced sulphur compounds.

Thus, the required concentration of hydrazine defined in Section 3.4.2 should be selected without unnecessary excess.

- **ODA, lay up option**

Octadecylamine ($C_{18}H_{37}NH_2$) has been used in some WWER units to give some benefits. It forms a good protective film and, therefore, may be used during lay-up to protect wetted metal surfaces. It has the great advantage that the film produced is hydrophobic, which forms a barrier against carbon steel corrosion by oxygen contained in the air and mitigates against the difficulty of achieving an air-free environment. Octadecylamine is removed by flushing and during power operation, without it producing unacceptable thermal decomposition products.

The corrosion rate of Carbon Steel 20 was reduced by a factor of ~20 in presence of ODA under wet atmospheric condition. [29].

However, no specific recommendation to use ODA or not during lay-up is made in this report and for normal power operation it is not the best alkalinising reagent because of its poor thermal stability at operating temperature.

- **LiOH or $LiBO_2$**

As described in Section 3.2.1, the most corrosive environment for WWER steam generator tubing is an acidic environment. For condenser seawater leaks than cannot be eliminated fully by the condensate polishers or any other remedy, adding lithium hydroxide has been used as a temporarily method of preventing cracking in some WWER units. This is not the best permanent way of combating impurity ingress, but the slightly alkaline environment produced is less detrimental than an acidic one. However, there is some risk that lithium hydroxide will concentrate in some areas of the steam generators, due its high solubility and low volatility.

The selection of lithium instead on sodium is based on the fact that the lithium hydroxide (LiOH) solubility is slightly lower than that of the sodium hydroxide (NaOH), limiting the risk of formation of an extremely high alkaline environment. In addition, LiOH reacts with iron according to the following reaction, which also prevents the formation of highly alkaline environment [30].

$$LiOH + Fe + H_2O \rightarrow LiFeO_2 + 3/2\ H_2$$

If an alkaline environment has also to be avoided (such as the risk of impurities leaking from condensate polisher resins or river water ingress), limited borate ion additions may be used at the same time as a lithium addition. Thus, adding lithium borate will act as a buffer against the formation of an acidic environment without any risk of forming a strongly acidic or alkaline environment, since boric acid is a weak, slightly volatile acid, whose steam concentration is ~1/10 of that in the liquid phase under steam generator conditions. Lithium borate additions have been used since the 1990s in the six WWER-1000 units at Zaporozhe [9].

3.4 Proposed Control Parameters and Limits for the Various Systems During Operation

The control parameters and limits below may be considered for all WWER types.

3.4.1 Definitions

The definition of the various parameters (control, expected, diagnosis) are given in the Glossary and are applicable to this entire NER document. Below are only added specificities to Chapter 3.

For Chapter 3, Ranges are used in all cases except for Steam generator Blowdown (Fig 3.3) that uses various Zones.

Zone A or Range A corresponds to the Expected Values
The **expected** values represent the range of values that should be met during normal power operation with the correct treatment and in absence of significant amount of impurities.

Zone B or Range B corresponds to the values up to the Limit Value.
This range represents the admissible values for long term operation. This is defined in more details in the Glossary.

Zone C or Range C corresponds in this NER document to the **Action Level 1 (AL1).**
When the value is outside Zone B/Range B, **the Action Level** is entered and a corrective action should be implemented on a medium term basis. The allowed duration in zone/range C is two weeks without there being a significant effect on safety or other important considerations, such as component lifetimes, operating costs or the release of chemical waste to the environment.

If the corrective action is not able to allow the unit to come back below the Limit value within the allowed time of 2 weeks, the power of the unit should be decreased to hot stand by or a lower state (such as hot shutdown or cold shutdown).

If AL1 is not applicable, there will be no need to reduce power if the value of a parameter exceeds the limit value.

Zone D or Range D corresponds to the **Action Level 2 (AL2), when it exists.**
In zone/range D, **the Action Level 2** is entered and a corrective action should be implemented on a short term basis. The allowed time is 24 hours with the same basis and requirements as above, and if the time allowance is to be exceeded, the power should be decreased. If the value of the parameter can be reduced to a value that is within zone C/range

C values within 24 hours, then the two week time limit for zone C/range C should apply, but with the two week limit starting from the time when the parameter first entered zone C/range C.

Zone E or Range E corresponds to the **Action Level 3 (AL3), when it exists.**
In zone/range E, **the Action Level 3** is entered and the power should be decreased immediately. The allowed time limit of 1 hour (unless plant operating procedures for a normal shutdown dictate a different time) is intended to allow a normal shutdown procedure in order to avoid a detrimental emergency shutdown and to give time to confirm that the parameter has effectively entered AL 3.

However, if the value then falls to within the Action Level 2 range before power reduction and shutdown is complete, power operation may resume and the allowed corrective action time reverts to 24 hours, but with the time defined from the original time that the parameter entered Action Level 3.

Diagnostic parameters are not included in the tables and are only mentioned in the text. However, they are useful for further evaluation either when a control parameter is outside its limit value, under abnormal situations or if an evaluation is being made to optimise the water chemistry. In addition, for some specific cases, diagnostic parameters are included in the tables, where only an expected value is defined.

3.4.2 Feedwater.

Table 3.8. Control parameters for the Feedwater

Parameter	**Unit**	**Range A** Expected value	**Range B** Limit for normal operation	**Range C (AL1) Action Level 1**
Duration	-	unlimited	**Unlimited**	**2 weeks**
pH [a] with copper	at 25°C	9.3	8.8 – 9.4	< **8.8** and > **9.4** [c]
pH [a] without copper	at 25°C	9.4 – 10.0	9.2 – 10.1	< **9.2** and > **10.1** [c]
Oxygen	µg/kg	< 5	< 10 or 20 [b]	Not applicable
Hydrazine	µg/kg	20 to 100 (w/o Cu) 10 to 50 (with Cu)	> 10 (w/o Cu) > 5 (with Cu)	Not applicable
Iron (with Cu in system)	µg/kg	< 10	None	Not applicable
Iron (w/o Cu in system)	µg/kg	< 3	None	Not applicable
Copper	µg/kg	< 3	None	Not applicable

[a,b] Some parameters may be monitored in the condensate water instead of final feedwater. This is mainly the case for pH and oxygen.

[c] For plants with copper alloy, the upper pH limit may be higher when an amine is used and if it has been shown that copper transport remains acceptable. For plants without copper, the lower pH limit is defined as an appropriate limit for mitigating FAC and iron corrosion product transport, but it must be recognised that there is no short term risk if the lower pH limit corresponding to the one defined for units with copper is applied.

Hydrazine may also be monitored in the condensate water instead of feedwater in absence of condensate polishers and if the control is performed downstream of the injection point. However, it must be recognized that if oxygen is measured in the feedwater it will not be possible to detect a small or even an average air ingress leak into the condenser, since reaction with the feedwater line materials and elimination in the deaerating tank will remove almost all the dissolved oxygen, but may keep an oxidizing environment.

It may be the plant preference and decision to on-line monitor total conductivity and use it as the control parameter instead of pH, if this provides more reliable data. Corresponding curves in Appendix 1 should be used to define the conductivity for the pH values given above.

[b] The oxygen limit may depend on the location: 10 should be the maximum value at least for the final feedwater. There is no oxygen limit for short term operation since the air ingress cannot be localized if the plant is shut down.

pH, amine

Amine concentrations should be directly inferred from the various $pH_{25°C}$ values and Appendix 1.

Diagnostics parameters in the final feedwater are iron, copper, total and cation conductivity, reagent (ammonia, amines).

Iron, copper

The detrimental impact of corrosion product transport to the steam generator has been widely explained in Sections 3.2 and 3.3. It creates a potential zone of contaminants concentration, a sludge pile that may need to be eliminated and a risk of decreasing the heat transfer of the SG tubing due to fouling effect.

Thus, it is of high importance to try to keep this transport as low as possible. But obviously, it depends as much on the materials in presence in the secondary system as on the right chemical treatment selection.

As explained above, the best treatment selection (reagent and pH) depends on many parameters and will induce some corrosion product transport quantity.

It is, therefore, advisable to define the optimum chemistry regime on a plant specific basis using measurements of corrosion product transport (quantity and quality) determined in a careful diagnostic evaluation programme, and then operate at all times using this optimum treatment. The iron and copper concentration measurements should be made during stable operation using the most reliable methods of analysis, but copper measurements need only be made and expected values defined when copper alloy components are present in the secondary system. This is the reason why the control parameter in table 3.8 is the $pH_{25°C}$

value and iron and copper concentrations are only diagnostic parameters with only an expected limit.

3.4.3 Condensate water

Table 3.9. Control parameters for the Condensate water.

Parameter	**Unit**	**Range A** Expected values	**Range B** for normal operation	**Range C** **Action Level 1** **AL1**
Duration	-	unlimited	**Unlimited**	**2 weeks**
Cation Conductivity	µS/cm	< 0.2	**< 0.5**	Not applicable
Oxygen	µg/kg	See Feedwater limits. The limits are established at the feedwater location.		

The condensate **cation conductivity limits** are determined on the basis of a large condenser leak or for localisation of the section of the condenser when a leak is detected by an increase in the SG blowdown parameters. However, the limit for steam generator tubing integrity is defined at SG blowdown and, therefore, a cation conductivity AL1 value is only defined in the SG Blowdown.

Oxygen does not concentrate in the steam generator and ingress into the condenser is more efficiently controlled in the condensate, where it enters the steam/water circuit and before it reacts with the feedwater system materials. It generates oxidising species, such as copper oxides, that can enter the steam generator and may jeopardise tubes resistance to stress corrosion cracking or just increase their sensitivity in presence of other contaminants. In the case of WWER units which all have a deaerator in the feedwater train, oxygen in condensate water is not a critical parameter.

High oxygen concentrations should also be avoided when the alkalising reagent is morpholine, as oxygen will increase its thermal decomposition to organic acids that will adversely increase the cation conductivity throughout the whole secondary water system (Section 3.3).

No action level or time limit is defined for oxygen, as it is not possible to identify the location of an air ingress leak when the power is decreased.

Diagnosis parameters in Condensate water
pH should be monitored in condensate water in addition to feedwater, particularly in presence of copper alloys.

3.4.4 Steam Generator (SG) Blowdown

Start-Up, Shutdown and hide out return evaluation, Power Operation

The key parameters that may have an impact on safety during operation are those that may induce SG tubing corrosion. As explained above, those are mainly ions that can concentrate in the SG under boiling conditions, heat transfer and, particularly, when it is possible to generate higher local concentrations in specific restricted flow areas.

Table 3.10. Control parameters for SG Blowdown during power operation > 30 %

Parameter	**Unit**	**Zone A** Expected range	**Zone B** for normal operation	**Zone C** **A**ction **L**evel 1 **AL 1**	**Zone D** **A**ction **L**evel2 **AL 2**	**Zone E** **A**ction **L**evel 3 **AL3**
Duration	-	unlimited	**Unlimited**	**2 weeks**	**24 hours**	**1 hour**
Cation Conductivity	μS/cm at 25°C	< 1 [a]	**< 3**	**3 to 5**	**5 to 10**	**> 10**
Chloride	μg/kg	< 10	< 100	Limits covered by cation conductivity limit		
Sulphate	μg/kg	< 20	< 200	Limits covered by cation conductivity limit		
Sodium	μg/kg	< 30	**< 300**	**300 to 500**	**500 to 1000**	**> 1000**

[a] The Cation Conductivity expected value partly originates from organic acids due to amine thermal decomposition when amines are present, while it may also be partly due to carbon dioxide with high ammonia treatment. In all the cases, cation conductivity may partly be due to organic acids coming from many potential sources, including maintenance activities (grease, etc.) and from residual organic materials contained in demineralised water used as make up water.

The above values have been settled as a compromise between existing operational feedback including chemistry values, degradation occurrence, operating feasibility and aim of improving WWER chemistry performance to the most frequent international practices.

The Zone A and B values correspond to chemistry performances that are normally achievable and that help at keeping the long term integrity of SG components. The values in Zones C-D-E (AL 1-2-3) correspond to limits which are increasing while the allowed duration of operation is decreasing in order to keep the integrated values of impurity ingress sufficiently low to avoid rapid degradation of SG components but giving sufficient flexibility to look for the origin of the pollution (AL1 and 2) and to program a shutdown for eliminating the source of impurity if necessary. The Zone E (AL3) limit correspond to a value above which the advantage of keeping the unit in operation is not balanced by the high risk of SG components degradation by corrosion.

It should be recognized that:

(i) the older WWER-440 SGs that operate at lower temperatures have not suffered from significant corrosion, even though some have operated at higher cation conductivity values,

(ii) WWER-1000 SGs mainly suffered from tube degradation in the earlier SGs, due to the stresses introduced by the manufacturing process,

(iii) other WWER-1000 SGs have operated with a cation conductivity of 5 μS/cm, without any tube degradation,

(iv) the more recently built WWER-1000 units with tight condensers should be able to operate with lower cation conductivity values to give even more reliable long-term operation.

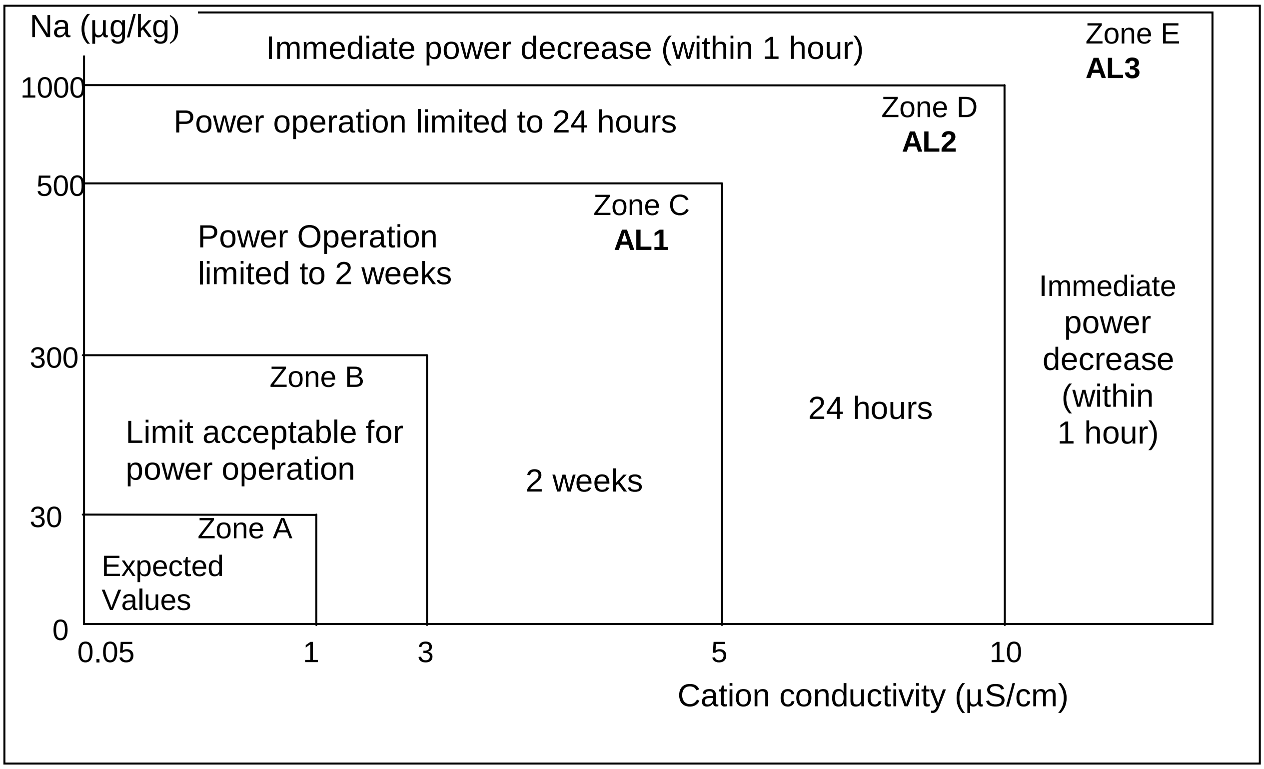

Figure 3.3. Diagram of Control Parameters for SG Blowdown during Power Operation.

Table 3.11. Control Parameters for SG Blowdown during Start-up and for the First Two Weeks of Power Operation.

Parameter	**Unit**	**Zone A** Expected value	**Zone B** Limit value	**Zone C** **A**ction **L**evel 1 **AL1**	**Zone D** **A**ction **L**evel **2** **AL2**	**Zone E** **A**ction **L**evel **3** **AL3**
Duration	-	unlimited	**Unlimited**	**2 weeks**	**24 hours**	**1 hour**
Cation Conductivity	µS/cm at 25°C	< 2	**< 5**	**5 to 7**	**7 to 10**	**> 10**
Chloride	µg/kg	< 20	< 100	Limits covered by cation conductivity limit		
Sulphate	µg/kg	< 30	< 200	Limits covered by cation conductivity limit		
Sodium	µg/kg	< 50	**< 500**	**500 to 700**	**700 to 1000**	**> 1000**

Table 3.12. Control Parameters at the SG Blowdown during Shutdown

Parameter	**Unit**	**Range A** Expected value	**Range B** Limit for normal operation	**Range C** **A**ction **L**evel **1** **AL 1**

Cation Conductivity	µS/cm at 25℃	< 2	Not applicable due to hide out return process that may occur	Not applicable due to hide out return process that may occur
Chloride	µg/kg	< 20		
Sulphate	µg/kg	< 30		
Sodium	µg/kg	< 50		

Chloride ion is particularly detrimental for WWER steam generator tubing under acidic conditions.

Sulphate ion is also detrimental for corrosion of steam generator tubes with different results according to various laboratory studies. The reduced sulphur anions are much more corrosive than sulphate, but this last anion is the most easily detected.

Besides direct sulphate contamination, laboratory experiments and the operating experience feedback show that **resin fines** constitute a very high risk of causing SG tube corrosion. This is the reason that condensate polisher regeneration processes must be carefully controlled and the use of condensate polishers should normally be limited to situations where it is necessary. In the absence of condenser leaks, except for purification of the secondary system during start-up periods, the use of condenser polishers may be a greater potential source of impurities than a remedy to avoid them. To a lesser extent, the resin regeneration chemicals may also cause a corrosion risk.

Sulphate control at Russian WWER-1000 SG blowdown water was initiated, at least as a diagnostic parameter, in 2003, considering that some sulphur sources may have induced collector failures. These sulphur potential sources include Ion Exchange Resin fines, lubricants [31].

Cation Conductivity (conductivity after cation ion exchange resin) will in many cases be easier to control and it corresponds to the total anionic concentration in the water. The advantage of using this parameter instead of chloride and/or sulphate is that it will include a larger range of potential impurities, is easily and reliably measured on-line and give an immediate indication of an impurity ingress.

The only disadvantage is that it will reflect any anionic impurity, irrespective of its impact. Thus, if the cation conductivity increases and if the source of it has not been clearly identified, it is advisable to measure the potential anions present to identify the cause and define precisely the corrosion risk.

The higher limits for cation conductivity but not for chloride and sulphate in table 3.11 (start-up) as compared to table 3.10 (normal power operation) is due to the fact that chloride and potentially sulphate are particularly detrimental while many other less detrimental anions may be present at a higher concentration in the specific operation modes of table 3.11.

In addition to **chloride** and **sulphate**, the most frequent anions that contribute to the cation conductivity are **carbon dioxide** and **organic acids**, which are weak anions, partially volatile and, therefore do not concentrate greatly and do not pose a significant corrosion risk.

The table 3.13 gives corresponding cation conductivity values at 25°C for various chloride and sulphate concentrations in the absence of any other contributing anion.

Table 3.13. Cl and SO_4 Concentrations corresponding to Cation Conductivity (CC) values

CC at 25° C (µS/cm)	0.055	0.2	0.5	1
Chloride (µg/kg)	0	14	42	85
Sulphate (µg/kg)	0	20	56	113

If the demineralised water make-up station is designed to provide good organic material elimination in its pre-treatment stage and if measurements confirm that the make-up water does not contain a significant total organic carbon (TOC) concentration, there is no need to make regular measurements TOC in any part of the secondary circuit and it may be defined as a diagnostic parameter. However, when an amine is used, TOC measurements will not reflect the presence of impurities but rather the reagent concentration, which will be more efficiently measured by other methods.

In conclusion, the choice is left to the utility, according to the various potential situations, to define what is the best way to control the risk of corrosion of the SG tubing by aggressive deleterious anions: either a cation conductivity limit or specific anions measurements, mainly chloride (and sulphate in some cases). The choice is whatever is the most feasible, accurate, practical or sensitive. But, in addition to cation conductivity, at least some regular monitoring of chloride and sulphate should be carried out.

Sodium is one of the chemical that may easily concentrate in the steam generator and induce stress corrosion cracking of the tubing under strongly alkaline conditions. However, for WWER tubing, it is less detrimental than the acidic environments associated with chloride or sulphate and, in any case, it is not as aggressive as it is in PWR steam generators that use the more sensitive Alloy 600 material.

Diagnosis parameters at the SG Blowdown

These are pH, ammonia and the amine(s) if it applies, organic acids, silica, calcium. A hide-out return evaluation is also an important diagnostic tool.

Organic acids

The organic acid concentration in the feedwater and/or in various points in the secondary system may be measured as a diagnostic parameter if there is an increase in the cation conductivity in some part of the system that cannot be explained by the only presence of the other anions which are normally present (chloride, sulphate and, potentially, borates from a boric acid treatment). In the presence of organic acid contamination, the increase of cation conductivity will be particularly high in the Moisture Separator Reheater drains, due to the liquid-vapour partition coefficient favouring the presence of these ions in the liquid phase.

The measurement of organic acids is very important for diagnosing the origin of any cation conductivity increase and to determine the reason for the increase in order to show if it is due to harmful impurities such as chloride or sulphate, or a less deleterious impurity such as some organic acids produced by amine thermal decomposition.

Calcium, Silica

Calcium is measured occasionally in some river water-cooled plants to confirm a cooling water leak when the origin of the increase of other parameters has not been clearly identified. However, calcium hides out very highly in the steam generator and the measured concentration will be much less that the value calculated from the condenser leak rate and blowdown flow rate. It is, therefore, more accurate to rely on other diagnostic parameters.

Silica is controlled in fossil fired units as it may deposit on the turbine blades, due to the high boiler water temperature which increases silica transport in the steam. For WWER units, with a high quality make-up water and a lower SG temperature, silica measurements should be a diagnostic parameter, but there is no need for it to be a control parameter.

Hide out return

Hide out return is the process that starts to occurs during power reduction below about 30% power and continues during the shutdown. This is the reverse of the hide out process that occurs when chemical species are concentrated in regions of low flow due to heat transfer (Section 3.2.1). The hide out return is a beneficial way to eliminating these chemical species, as they may be harmful for SG tube corrosion. In addition, the analysis of the chemicals returned during a shutdown is an excellent diagnostic method for evaluating the potential aggressiveness of the chemical species that had concentrated in the steam generator. It, therefore, is way of linking the conditions that existed during power operation to the hide out process, which in turn depends on the design, heat transfer conditions, tube fouling and sludge accumulation.

3.4.5 Steam

Steam limits are normally defined by the turbine manufacturer's requirements, but in practice the SG blowdown limits, together with the low volatility of most deleterious impurities, ensure that the steam limits are also satisfied. Only cation conductivity is defined as a control parameter in table 3.14. Sodium, chloride and silica can be measured as diagnostic parameters if necessary.

Table3.14. Control parameters for the Main Steam

Parameter	Unit	**Range A** Expected value	**Range B** Limit for normal operation	**Range C Action Level 1 AL1**
Cation Conductivity	μS/cm at 25°C	< 0.3	Not applicable	Not applicable

3.4.6 Blowdown Demineraliser Outlet

The purpose of the blowdown demineraliser outlet limits is to minimise the build-up of impurities in the feedwater, coming from the blowdown water returned to the steam/water circuit after purification and, consequently, to prevent SG tubing corrosion.

Table3.15. Control parameters for Steam Generator Blowdown Demineralisers Outlet

Parameter	Unit	**Range A** Expected value	**Range B** Limit for normal operation	**Range C Action Level 1 AL1**
Cation Conductivity	μS/cm at 25°C	< 0.1	< 0.5	Not applicable
Sodium	μg/kg	< 2	< 5	Not applicable
Chloride	μg/kg	< 2	< 5	Not applicable

Sulphate	µg/kg	< 2	< 10	Not applicable

3.4.6 Make Up water

Table3.16. Control parameters for Demineralized water (at station preparation outlet)

Parameter	Unit	**Range A** Expected value	**Range B** Limit for normal operation	**Range C Action Level 1 AL1**
Conductivity	µS/cm	< 0.1	< 0.3	Not applicable
Sodium	µg/kg	< 2	< 3	Not applicable
Silica	µg/kg	-	< 20	Not applicable
Chloride	µg/kg	< 2	< 3	Not applicable
Sulphate	µg/kg	< 2	< 3	Not applicable

The specific or total conductivity limit is aimed at controlling the general water quality while sodium, chloride and sulphate limits are lower than that guaranteed by the conductivity limit. These ions must be particularly avoided in the secondary system due to associated SG tubing corrosion risks.

The limits correspond to a good demineralised water quality as previously defined (3.2.7) which is easily achievable through normal systems of purification and that prevents ingress of unnecessary impurities into the secondary system and other circuits. The conductivity limit is not extremely restrictive and does not correspond to ultra pure water, in order to take into account the possible presence of weak anions that are not always easily eliminated and not as harmful as strong ions which may concentrate in the SG. Thus, the limits for ions that may easily concentrate are defined at lower levels, which correspond to that normally achievable.

3.4.7 Lay Up for various components

The lay up conditions are important for two main reasons:

- to avoid corrosion during the lay-up itself,
- to avoid contamination by compounds that could cause corrosion either during lay-up or more likely during subsequent operation.

During lay up, the most sensitive materials to corrosion in absence of impurities are the carbon steel components. These steels require a sufficiently alkaline environment and in the absence of copper, a pH $_{25^\circ C}$ of ~10 is required for secondary side of steam generator wet lay-up. In addition, reducing environment is also beneficial to prevent corrosion of any non-passive metals alloys such as carbon steel. The main difficulty is that using reducing agents such as hydrazine or using nitrogen may be hazardous for people working on the steam/water system.

For other parts of the secondary system, the wet lay up conditions will depend on the material (a high pH is not required with copper alloys or stainless steel) and the part of system (consequence of some generalized corrosion, conditioning feasibility).

In addition, it is mandatory to keep wet lay-up conditions and any maintenance products free of highly corrosive elements, such as chloride or sulphur. Finally, lead has a very detrimental effect on SG tubing and can be transported to the SG through the feedwater. Consequently, any material that contains lead should be avoided or used in such a way that it cannot contaminate the secondary system.

As explained in Section 3.3, octadecylamine (ODA) can be used as an interesting option for carbon steel during lay up, as it protects carbon steel components from corrosion by oxygen and water by forming a hydrophobic film on the metal surface.

Another option is the dry lay up with the use of dehumidifiers after completely draining the components under hot conditions. A humidity of less than 40 % should be achieved in this case.

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4. AUXILIARY SYSTEMS

There are several auxiliary systems in WWER plants, in which demineralised is used, either with or without any additional inhibitor reagent addition. The auxiliary systems are very different at older generation WWER units, compared to new units. Multiple modernisation programmes at older generation WWER plants have resulted in the upgrading of the safety and other auxiliary systems.

The auxiliary systems may be classified into several categories, depending on their function and related systems. Of these, primary circuit safety systems are covered in Chapter 2 (section 2.1.4.) and this chapter only describes the various auxiliary systems that contain either pure water, or chemically treated water that are not covered in Chapters 2 and 3.

The definitions of the various parameters (control, expected, diagnosis) given in the Glossary are also applicable to this chapter.

There is no specific power decrease associated with Action Level 1 (if any AL1), since a shutdown will not solve the reason for the deviation or eliminate the corrosion risk in these auxiliary systems.

4.1 Auxiliary Systems located in the Reactor Island

4.1.1 Annulus water tank

The annulus water tank around the Reactor Pressure Vessel of first generation WWER-440 units is used to reduce neutron flux.

The annulus tank water is dosed with chromate to provide corrosion protection of its carbon steel sections, as a stainless steel lining was only applied below the water level. Due to the radiolytic decomposition of water under irradiation, hydrogen is produced, which accumulates in the annulus. The gas phase is filled with gaseous nitrogen and the hydrogen must be removed periodically to avoid an explosion.

Table 4.1 – Specification for water and gas phase* in annulus water tank of early WWERs

Parameter	pH at 25°C	$K_2Cr_2O_7$,	Hydrogen *
Expected Value	8-9	1 to 2 g/kg as Cr_2O_7	< 3.0 %

4.2 Intermediate Cooling Systems

There are some intermediate cooling systems in WWER plants, where water is used as the coolant. These are the following system:

- primary system letdown cooling circuit
- reactor coolant pump cooling circuit (which may be the same circuit as above)
- control rod cooling circuit
- stator cooling circuit
- diesel generator cooling circuit.

These systems differ to some extent from plant to plant (design, use of various systems with various type of water characteristics), but these differences will not be described here. These systems operate with different chemical dosing regimes that are designed to provide corrosion protection, taking into account the different materials present in the circuits both in the materials in contact with the coolant and the heat exchangers.

The intermediate component cooling system (ICCS) at WWER-440 V-213 plants is designed to perform both normal and emergency functions. It is used for heat removal from several components installed in, or connected, with the reactor primary system. The ICCS is composed of three independent circuits that provide cooling for three following groups of equipment:

- emergency core cooling and reactor building spray pumps (for some WWER plants),
- reactor coolant pumps and other equipment located inside the containment envelope,
- control rod drive mechanisms (for some WWER plants).

4.2.1 Primary system letdown cooling circuits

In WWER-440 and early WWER-1000 units, the primary coolant letdown is cooled before it is purified by ion exchange resin beds (SVO-1,2). The letdown system coolers lie downstream of the regenerative heat exchanger in these systems. The pressure of coolant in primary system letdown cooling circuit is lower than the pressure in primary feedwater-letdown system at WWER plants to avoid accidental ingress of non-borated water into primary system that could cause boron dilution and safety issues. The coolant in primary system letdown cooling circuit is cooled, in most cases, by the service water system or via the intermediate cooling system. The pressure of coolant in primary system letdown cooling circuit is lower than pressure in the service water system at WWER plants to avoid accidental release of radioactive species into the environment.

These circuits are also used to cool systems such as samples from the primary coolant and the pressurizer relief tank.

In all WWER, this system is made of stainless steel, which is why only demineralised water from the plant make-up water system is used without any additional chemical additive.

Table 4.2. Parameters for Primary system letdown cooling circuits

Parameter	Unit	**Range A** Expected value	**Range B** Limit for normal operation
Total Conductivity	µS/cm	1 to 3	<6 [a]
pH at 25°C	-	6.5 to 7.5	≥ 6
Chloride	µg/kg	< 50	< 150
Iron	µg/kg	< 50	Not applicable

[a] This limit may not apply in the presence of ammonia in pure condensate which is used for filling this system.

The chloride content is specified to ensure the absence of any corrosion risk of stainless steel. The total conductivity and the pH values are aimed at demonstrating the absence of any significant impurity level in the coolant. The same parameters and activity measurements will show the presence of any in-leakage of primary coolant into this intermediate circuit.

4.2.2 Reactor coolant pump and control rod drive cooling circuits

A cooling system is used for several functions associated with the main circulating pumps (coolers of the autonomous/independent cooling circuit, fan cooling, stator and bearing cooling). The closed cooling systems for the control rod driving mechanism cooling, consisting of pumps, filters, heat exchangers and buffer tank, are cooled by the intermediate cooling system for component cooling (ICCS), but the reactor control rod drive mechanisms at some WWER units are cooled by the reactor control rod cooling circuit.

Some components in these circuits at some of the WWER plants are made of carbon steel, which is why the demineralised water from the plant make-up water system is treated in this case with chromate as a corrosion inhibitor. Phosphate is also used in some cases, due to the toxicity of chromate. The expected values of the parameters are shown in Table 4.3 a and b for chromate and phosphate treatment, respectively.

If the system only contains stainless steel, the treatment below may not be necessary and the same limits as the one of Table 4.2 are applied.

Table 4.3a. Parameters for Chromate Treatment of Reactor coolant pump and control rod drive cooling at the first generation WWER-440 plants.

Parameter	Unit	Reactor coolant pump sealing circuit	Control rod cooling circuit
$K_2Cr_2O_7$	g/L as Cr_2O_7	>0.5	>0.1
pH at 25°		>7.0	4-9

Table 4.3b . Parameters for Phosphate treatment of Reactor coolant pump and control rod drive cooling circuits at the first generation WWER-440 plants.

Parameter	Unit	Expected value
Phosphate. Na_3PO_4	mg/kg as PO_4	100 – 500
pH at 25°		10.8 – 11.5

4.2.3 Stator alternator cooling circuit

Stator alternators in WWER plants are cooled by the stator alternator cooling circuit. The hollow conductors of the stators are made of copper, but other components of the stator alternator cooling circuit are made of steels. The optimum pH value to avoid copper corrosion is pH 8.5. Ammonia and the presence of dissolved oxygen accelerate copper corrosion. The conductivity of water in the stator alternator cooling circuit is limited.

There are two alternative chemistry regimes that may be used: either a high or a low oxygen regime (but an intermediate oxygen concentration regime or cycling between low and high oxygen concentrations should be avoided), both at a pH of about 8.5 to maintain the lowest possible copper corrosion rate. Figure 4.1 [10] illustrates these two options, with either high or low oxygen in order to avoid corrosion.

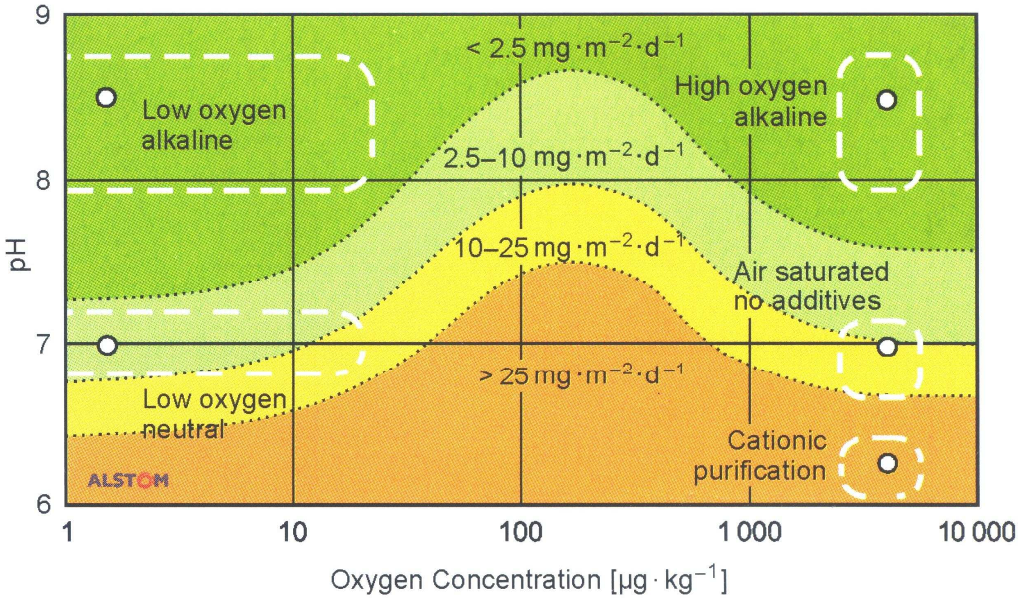

Figure 4.1 **Summary of Copper Release as a Function of Oxygen Concentration and pH showing Operating Areas of Different Stator Water Chemistry Regimes** [10].

Demineralised water from the make-up water system is saturated with air and thus contains about 8 mg/kg of dissolved oxygen. This is the reason why, in the case of the option with low oxygen content, aerated demineralised water should not be used for the make up of stator alternator cooling circuit due to the impact of dissolved oxygen on the release of copper oxide in the alternator.

If a low oxygen regime is selected, a vacuum membrane degasser unit is one easy option to install. pH control can be achieved with a microdosing system or with a mixed bed with the cation resin in Na form and the anion resin in the OH form.

The main turbine condensate in secondary system is oxygen free, but ammonia or amines are present in the absence of, or by-passing of, the condensate polishing system. From Ukrainian WWER-1000 experience, water from the main turbine condensate may be used as the coolant in the stator alternator cooling circuit.

Table 4.4. Parameters for Stator Alternator cooling circuits

Parameter		Unit	**Range A** Expected value	**Range B** Limit for normal operation
Total Conductivity at 25 °C		µS/cm	< 0.5 [a]	< 5
pH at 25°C		-	8.0 to 9.0	Not applicable
Oxygen	Oxygenated mode	mg/kg	6 to 9	Not applicable
	Deaerated mode oxygen	µg/kg	< 20	Not applicable
Copper		µg/kg	< 20	Not applicable
Iron		µg/kg	< 20	Not applicable

[a] Limit of 2 µS/cm in the case of operation with a cation resin in Na form for pH control

The pH value limit is defined at pH 8.0-9.0 to avoid too a high a corrosion rate of copper alloys. The conductivity is defined for the control of the water purity, but the limit for electrical risk is higher (5 µS/cm)

4.2.4. Diesel generator cooling circuit

For these circuits, the use of phosphates or, better, organic inhibitors are recommended instead of the toxic inhibitors chromate and nitrite, in view of new strict environmental requirements.

The diesel generators at WWER plants are cooled by internal cooling circuits. There are different designs for different manufacturers and some of the diesel generator components cooled by the cooling systems are made of carbon steel. This is why demineralised water from the plant make-up water system dosed with corrosion inhibitors is recommended, although demineralised water is not always available for diesel generator cooling water circuits.

Chromates, nitrites and phosphates and some other inhibitors have been used as chemical additives to avoid corrosion and some WWERs use a commercial inhibitor. Due to new environmental requirements, chromates or nitrates should be replaced by phosphates or organic inhibitors. Examples of chemistry specifications, with or without phosphates, are given in Tables 4.5 a and b, where the most important parameter of the cooling water is the hardness limit, to avoid scaling.

Table 4.5 a. Parameters for Diesel generator cooling circuit with phosphate treatment

Parameter	Unit	**Range A** Expected value	**Range B** Limit for normal operation
Total hardness	mmol/kg		≤ 0,175
pH at 25°C	-		8.8 to 10.2
Na_3PO_4	mg/kg of PO_4		5 to 15
Chloride	mg/kg	< 0.15[a]	< 50
Iron	mg/kg	< 0.15	< 1

[a] Chloride may have a higher limit (up to 50 mg/kg) if demineralised water is not available.

Table 4.5 b. Parameters for Diesel generator cooling circuit without phosphate treatment

Parameter	Unit	**Range A** Expected value	**Range B** Limit for normal operation
pH at 25°C	-		> 8.8
Total Conductivity at 25 °C	µS/cm	< 2	
Chloride		< 0.15	Not applicable
Copper		< 0.2	Not applicable
Iron	mg/kg	< 1	Not applicable

4.3 Essential Service Water Treatment

Service water is used for cooling of some plant systems, namely ECCS (Emergency Core Cooling System), RHR (Residual Heat Removal) and other systems in the nuclear island including intermediate circuits.

Heat removal from Essential Service Water System is achieved by either forced ventilation towers or a special spray system with open pools.

Usually, the pipework of the service water systems are made of carbon steel and its corrosion must be mitigated by the addition of appropriate corrosion inhibitors. Scaling and biofouling may also occur at some WWER plants, when anti-scaling inhibitors and chemical biocides (algaecides and bactericides) are added to some service water systems, especially the spray cooling system. The type of reagent, its quantity and when to use it is plant specific and is defined locally.

4.4 Non-essential Service Water System

This system is supplied by the filtered or clarified raw water system at the majority of WWER plants. No further treatment is applied. At new WWER-1000 plants such as Busher and Tianwan, this system is composed of several closed water circuits. Due to this, phosphate water chemistry was successfully implemented to avoid corrosion, based on some western plant experience. Phosphate water chemistry is also adequate for the new generation of WWER units that have these systems.

In many cases, there it is not possible to control the chemistry in this open (once-through) system. In these cases, some corrosion mitigation can be achieved by mixing raw river water with water from the main condenser cooling tower system.

4.5 Emergency/auxiliary Feedwater System

The emergency/auxiliary feedwater system is designed to provide an adequate supply of cooling water to the steam generators so that they can act as heat sink for decay heat removal if the main feedwater system is inoperable. The system consists of two independent sub-systems:

- subsystem supplying feedwater from the deaerator tank (auxiliary feedwater system),
- subsystem providing feedwater from demineralised water storage tanks (emergency feedwater system).

It is not necessary to define any chemistry regime, since the system is only used in an emergency.

4.6 Condenser cooling system

The condenser cooling water system is generally the plant system with the greatest water volume and has very significant influence on plant performance due the effects of scaling, fouling and corrosion processes. Depending on the water composition, open once-through systems with seawater or river water cooling do not cause major difficulties, but there can be quite complicated chemistry problems in semi-closed cooling tower circuits. The solution to such problems is very site-specific and it is often based on injection different reagents or mixtures of reagents that may be acids, anti-scalants, dispersants, biocides, or corrosion inhibitors. Thus, there can be no universally applicable specification and, consequently, none is proposed here. There are some methods for calculating scaling risks based on the use of Langelier, Ryznar, Puckorius, Larson-Skold or Pisigan-Singley indexes that use specific methods of characterising water properties and tendencies, but these calculated values must always be evaluated very carefully with regard to experimentally measured values and adapted to specific plant behaviour.

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Glossary and Acronyms for NER WWER

1. General terms.

NER	**Nuclear Energy Report.** This is the type of Document of IAEA covered here, which is a technical document, not mandatory, for technical support that may be used by Member States).
IAEA	**International Atomic Energy Agency**
NPP	**Nuclear Power Plant.** A location where Electricity is produced by a Nuclear Reactor.
WWER	**A Russian acronym for a Russian-designed pressurized water reactor design.**
PWR	**Pressurized Water Reactor.** A type of NPP where the primary system containing the reactor core is pressurized water only in liquid state (in most part of the system under normal operating conditions) and where there is a secondary system where the steam is produced, as opposed to BWR (Boiling Water Reactor or RBMK for the Russian design) where the steam is produced in the same system as the primary coolant.
EPRI	**Electric Power Research Institute.** An American Organisation in charge of R&D and editing reference documents such as guidelines to be used by American Utilities. These guidelines may be used or not by other members of EPRI. American Utilities are members of EPRI and some Utilities from other countries are also members of EPRI (www.epri.com).
VGB	**German Acronym for a German Organisation .** This organization is mainly in charge of gathering German Utilities and some Utilities form other countries (Europe) who have decided to be VGB members. VGB is editing reference guidelines for Utilities. VGB PowerTech and the committees of the department "Nuclear Power Plants" are dealing with all issues concerning a safe and economical operation of NPPs (www.vgb.org).
EDF	**Electricité de France** (the French Unility that developed its own chemistry specifications for its whole fleet).

2. Terms related to chemistry in any system.

Anions	**Negatively charged ions.** Mainly chloride, sulphate, nitrate, hydroxyl (OH$^-$)
Cation	**Positively charged ions.** Mainly sodium, potassium, lithium, ammonium and amine cations and hydrogen ions H$^+$.
Regime	**Chemical treatment or conditioning.** Regime comes from the Russian terminology and does not have the equivalent in other languages such as English but is a convenient term to define the chemical content of the water in a circuit, including compounds, chemical properties such as pH, redox potential, and operation as well. It includes all the operations carried out to perform the chemistry in the circuit.
Alkaline	**pH > neutral pH.** Also called **Caustic** (which normally refers to strongly alkaline compounds such as sodium or potassium hydroxide) or more generally **Basic**
Acidic	**pH < neutral pH.**

Redox	**Redox potential.** Represents the electrochemical potential of a solution, and can be used to show if it is oxidizing or reducing or neutral and thus some characteristics of the solution that may influence the corrosion of the materials in contact with it.
pH	**Negative Log of Hydrogen cation activity, indicating** the acidity or alkalinity of the solution
pH_T	**pH at the operating temperature of the solution** (generally high temperature, since the pH at high temperature is different from that at room temperature). This is generally a calculated pH in opposition to measured **$pH_{25°C}$**
$pH_{25°C}$	**pH at 25°C.** Also, but not so precise, is the pH at room temperature, which is the measured pH.
$pH_{300°C}$	**pH at 300°C.** This is a calculated pH, mainly used for primary water chemistry.
Conductivity	**Also termed the Specific Conductivity or Total Conductivity.** This represents the electrical conductivity of the solution depending of the type and concentration of ions in the solution. Highly dissociated ions are the main contributors to conductivity. The conductivity of small ions is higher than that of large ions, for a similar concentration.
Cation Conductivity	**Conductivity of the solution after having passed on a cationic resin** in H^+ form on which the cations have been replaced by H^+ ions which may recombine with OH^- if the cation was in alkaline form (e.g. NH_4OH). Consequently, alkaline compounds such as ammonia or the amines for the conditioning of the secondary circuit are eliminated and do not affect the cation conductivity. Only anionic impurities will be measured and the purpose is to detect such impurities by a global and easy measurement. **Degassed Cation Conductivity** refers to a solution where cation conductivity is measured after elimination of volatile acids such as carbon dioxide and organic acids for measuring only strong harmful and concentrable anions such as chloride, sulphates.
Organic acids	**Organic Compounds.** For organic acids, this refers to organic anions such as acetate, formates, glycolates, etc**.** Organic acids are mainly contained in the secondary system after thermal decomposition and degradation of organic compounds (ie., amines used for the secondary water treatment) and materials (i.e. ion exchange resins, oils, greases, etc).
TOC	**Total Organic Carbon.** Represents the concentration of all the organic compounds in the solution**.** This is mainly applies to the demineralised water produced from raw water and that may contain such compounds that may hardly eliminated by ion exchange resins and that may remain in the solution if the overall preparation process is inadequate. Then TOC will be thermally decomposed in the circuits at high temperature and produce **Organic acids**.
IER	**Ion Exchange Resins.** These are present in various systems to purify the water by eliminating ions in resin beds. Such bed may be **Cation Bed** with cationic resins for cation elimination or **Anion Bed** with anionic resins for anion elimination or **Mixed Bed** with a mixing of cationic + anionic resins cationic resins for the most efficient purification in a neutral environment
Make up water.	Demineralised water used to compensate for losses or other needs to fill any circuit.

Demineralised water. Raw Water that has been demineralised on ion exchange resins and/or other purification means

Raw Water. Water as easily obtained in large quantity in the NPP to produce Demineralised water or too cool the condenser (in this case also called **cooling water**). Cooling water may be sea water, river water, etc. Raw water for demineralised water production is generally river or other type of water but rarely sea water.

Control Parameters These are the parameters for which a range of operating values is defined in the tables of the document and that should be used to control the chemistry properly (adequate regime or presence of impurities) in the various circuits.

Diagnostic Parameters. They are not included in the tables (except in some cases) of this NER document and are only mentioned in the text. They are useful for further evaluation either when a control parameter is outside its normal operating range or as part of an evaluation to optimise the water chemistry.

Expected value. The **expected** values represent the range of values that should be met during normal power operation with the correct treatment and in absence of significant amount of impurities.

Limit value. The **limit** value represents the maximum or minimum admissible value for long term operation but does not correspond to the expected value. Any operation between the expected range and the limit value requires investigation to identify the source of the deviation from the expected value, as well as its consequences. Whether or not long-term operation can be continued should be evaluated on a plant-specific basis, depending on the origin of the situation

Zones or Ranges (Action levels). For the most important control parameters, particularly for those that may have an impact on safety, when the admissible values for long term operation are exceeded, the Ranges/Zones for operation with limited time or condition are defined. Thus, corrective action(s) should be implemented. The allowed operation duration in the corresponding zone depends on the circuit and the parameter.

3. Terms related to primary system.

CIPS	**Crud Induced Power Shift.** A deviation in the power flux along the fuel element, induced by deposits on the fuel where boron may concentrate and induce an undesired and uncontrolled variation of power. There is another term used for this phenomenon, sometimes called AOA but which literally means that the flux anomaly is axial while the CIPS is a more general definition of such an anomaly.
AOA	**Axial Offset Anomaly.** See CIPS
CILC	**Crud Induced Localized Corrosion.** Corrosion of material in the primary coolant induced by crud deposits, with the consequence of a local higher temperature and higher impurities concentrations.
Crud	**Insoluble deposits in the primary coolant, on the fuel cladding.**
RCS	**Reactor Coolant System.**
RHR	**Residual Heat Removal System.**
RPV	**Reactor Pressure Vessel.**
MCP	**Main Circulating ¨Pump**

SG **Steam Generator** (some types of steam generator tubing can be identified as either mill annealed (MA) or thermally treated (TT)).

08Cr18Ni10Ti or (08H18N10T). The most widely used stainless steel in the Russian design of WWER, including SG tubes. It approximately contains 18% chromium, 10 % nickel and some titanium as a stabilizing element. Russian denomination in roman letters is (08X18H10T. This alloy is equivalent to AISI (ANSI) 321).

ZIRLO **Zirconium based Alloy** for cladding of fuel elements, containing both tin and niobium

Stellite A material with specific mechanical properties but containing a large quantity of **cobalt** that is highly activated in the primary system, thus undesirable

Nickel base alloy. A material with high proportion of nickel. This is mainly Inconel 600 or Inconel 690 used for some components, including the SG tubes of many PWRs.

SVO **A Russian acronym for purification or regime control system.** A number is added at the end of SVO to address a specific system. The table below give the definition of the various systems according to this acronym and the equivalents in other standards.

System	Original Russian Standard	New Russian Standard (KKS)	Early VGB AKW System
Primary Coolant Letdown Purification System	SVO-1 (WWER-440)	-	TC
High Temperature filtration of primary coolant	SVO-1 (some WWER –1000)	KBE 10-40	TC
Letdown Purification System	SVO-2	KBE 50-80	TE
Leakage and Drains Water Purification System	SVO-3	KPF	TR
Fuel Cooling Pool and ECCS Tank Water Purification System	SVO-4	KBH	TM
Steam Generator Blowdown System	SVO-5	LCQ	RY
Boric Acid Concentrate Purification System	SVO-6	KBB	TD

Burn Up Characteristic of the fuel representative of its capacity and situation during its life in the core

LOCA **Loss of Coolant Accident.** Terminology used in safety for defining the accident where the primary coolant is lost.

ECCS **Emergency Core Cooling System.**

SCC **Stress Corrosion Cracking.** Type of corrosion where a crack may develop in the metal under the influence of the stress and may be aggravated by the presence of impurities or specific environment (redox potential). **IGA/SCC** (**I**nter**G**ranular **A**ttack) is the type of SCC that may occur on the secondary side of SG tubes.

IGSCC Intergranular stress corrosion cracking.

TGSCC Transgranular stress corrosion cracking.

Ammonia **NH_3 (or NH_4OH when in solution).** Reagent that is used to produce hydrogen in the primary coolant. It may also be obtained by thermal decomposition of **hydrazine**.

Total Alkali Total of elements contributing to the alkalinity in the primary system: potassium, lithium and potentially some sodium (excluding ammonia, which is very slightly dissociated at high temperature).

Zeolite Low soluble compounds containing silica and elements such as calcium, magnesium, aluminium and that may deposit on the fuel cladding

Surface preconditioning. Treatment applied on the primary circuit surfaces before start up in order to get a passive film during the hot functional tests **(HFT)** and then having a lower release of corrosion products that may be activated in the core once the plant is in operation.

ILW **Intermediate Level Waste.**

4. Terms related to secondary system.

SG **Steam Generator** (some types of steam generator tubing can be identified as either mill annealed (MA) or thermally treated (TT)).

MSR **Moisture Separator Reheater.**

AVT **All Volatile treatment.** Means the used of only volatile reagent added in the secondary circuit regime (opposed to non volatile ones like in the past sodium phosphates)

Ammonia **NH_3 (or NH_4OH when in solution).** Reagent that may be used to get the secondary circuit chemistry alkaline regime. It is also obtained by thermal decomposition of hydrazine.

Amines Ammonia where one H has been replaced by an organic part. Alkaline compounds which are volatile, not strongly alkaline and that are used alternatively to ammonia (or in addition to it) for the treatment of the secondary system in order to get a slightly basic pH in the whole circuit.

Morpholine **C_4H_9NO.** A type of **amine** widely used for the secondary circuit

ETA = EthanolamineC_2H_7NO. A type of **amine** widely used for the secondary circuit

Octadecylamine Alkaline and filming amine that may be mainly used to protect the carbon steel surface during lay up

Hydrazine **N_2H_4.** A reducing agent mainly added into the secondary system (and into the primary circuit at start up) in order to get a reducing environment and avoid **SCC.** It is also contributing to the pH through thermal decomposition into ammonia and may even be the only added pH reagent.

Partition coefficient. Ratio of concentration steam/ liquid phase

Hide out Concentration process of compounds in the secondary water of the SG under power operation**.** Impurities are concentrating or precipitating in some areas instead of being

	eliminated through the steam generator blowdown. They are not measured at the blowdown, explaining the term of “hide”
Hide out Return	**Reverse process of Hide out.** During power decrease, a part of the hidden out impurities may be released from the specific location where hide out occurred. This is called the hide out return. However, this reverse process is rarely 100 % efficient and the efficiency decreases with the operation duration after the hide out process occurred.
Lay up	State of a component during shutdown when it is not used and preferably protected form corrosion. **Dry** lay up refers to the use of dry air or inert gas to protect the component while **wet** lay up refers to the use of controlled quality water.
SCC	**Stress Corrosion Cracking.** Type of corrosion where a crack may develop in the metal under the influence of the stress and may be aggravated by the presence of impurities or specific environment (redox potential). **IGA/SCC** (**I**nter**G**ranular **A**ttack) is the type of SCC that may occur on the secondary side of SG tubes.
IGSCC	Intergranular stress corrosion cracking.
TGSCC	Transgranular stress corrosion cracking.
EAC	Environmentally assisted cracking.
Pitting	Type of corrosion where a pit or hole is formed on the metal surface, mainly due to the presence of specific impurities such as chlorides, and under oxidizing environment
FAC	**Flow Accelerated Corrosion or also called Erosion-Corrosion.** Generalized corrosion of carbon steel under specific condition (chemistry and flow velocity)
Carbon steel	A non alloyed steel, mainly containing iron some carbon and other element in very low concentrations.
Copper alloys	A material containing high quantity of copper (copper based alloy) that has been widely used for heat exchangers such as condenser and heaters. They are more and more replaced by titanium tubing for condenser tubes and stainless steels for condenser tubes or other components of the secondary circuit.
Sludge	Insoluble compounds that are depositing in the bottom part of SG (mainly metal oxides)
Deposits	Insoluble compounds that are depositing on the SG tubes (mainly metal oxides)

IAEA - NER

Water Chemistry of WWER Nuclear Power Plants

Appendices

A1. Overall WWER Design Characteristics
A2. pH and conductivity Calculations
A3. Chemicals and Ion Exchange Resins Quality.

Appendix A1. Overall WWER Design Characteristics

A1.1 WWER-440 units

All WWER-440 MWe plants except Loviisa were constructed in twin unit modules, with both reactors housed in a common reactor hall and sharing a number of frequently used operational systems. However, they have independent and separate safety systems [A1 to A6]. The primary circuit of all the WWER-440 units has six loops, all of which have two main loop isolation gate valves that enable the steam generators and main coolant pumps to be isolated from the reactor pressure vessel. The main difference between the first and second generation WWER-440 plants is that the first generation design has canned rotor main coolant pumps and does not require a continuous seal water flow, whereas the second generation WWER-440 design has main coolant pumps with shaft seals; there are also differences in the primary coolant purification systems. Nine of the earlier WWER-440s (Novovoronezh 3 and 4, Kola 1 and 2, Kozloduy 1 and 2, Armenia 1 and Greifswald 1 and 2) were built without stainless steel cladding to their reactor pressure vessels inner surfaces. In addition, in these stations and Greifswald 3 and 4 the pressurisers were not clad with stainless steel.

V-230 units were not built with full set of emergency core cooling systems, although these have being fitted to the surviving units, nor were they built with systems to ensure complete retention of any fission products that might be released in loss of coolant accidents. Additional safety systems were fitted to the four first generation WWER-440s at Kola, Novovoronezh and Bohunice 1 and 2 as part of their lifetime extension programs in the early 2000s [A7]. However, the V-213 units were fitted with enhanced safety systems as part of their original design, Figure A1-1. These include a hermetic confinement system, Figure A1-2 and A1-3, that vents to atmosphere via bubbler towers that condense steam produced in a loss of coolant accident (LOCA) to prevent pressure build-up in the confinement system. The two Loviisa units are essentially identical to the standard V-213 design, but have Western-type containments incorporating ice condensers, but due to their intermediate status between the V-230 and V-213 designs and because some components were made outside Eastern Europe, the Loviisa units have a number of minor differences from the later V-213 primary circuits [A1].

The secondary circuits of all the WWER-440 are similar and all have two separate steam/water circuits, each fed from three of the steam generators. Each circuit has a turbo-alternator rated at about 220 MWe. Originally all WWER-440 units had condensers with copper-based alloy tubes, but a number of units now have either stainless steel or titanium condenser tubing and have replaced all other copper-based alloys such as those in the low pressure (LP) heaters. Except for the WWER-440 units at Novovoronezh NPP, Kola NPP and Bohunice 1 and 2, all other WWER-440 plants have a full flow condensate polishing plant.

Some WWER-440 stations have been uprated, or have increased electrical output compared with their original designed output due to various plant improvements. The most significant changes are those at Loviisa 1 and 2, which were uprated to 510 MWe (9.7% core uprate to 1500 MWth) and Paks 1 and 4 which were uprated to 500 MWe. The remaining two Paks units increased their output to 460-470 MWe when the condensers were retubed, but have nor yet been uprated. Other plants (Bohunice 3 and 4, Dukovany 1-4) are planning to uprate within 2-3 years.

1.2.2 WWER-1000 and WWER-1200 units

All the WWER-1000 MWe units have four primary coolant loops. The initial unit Novovoronezh 5 was built as a single unit with twin 500 MWe turbo-alternators. The next four V-302 and V-338 units (South Ukraine 1 and 2 and Kalinin 1 and 2) were built as twin units, each with a single 1000 MWe turbo-alternator [A1 and A2]. These early designs were fitted with two isolation gate valves that are fitted to the hot and cold legs of each loop, one between the RPV and SG and one between the RPV and MCP (main coolant pump) and they have two ion exchange coolant purification systems analogous to those fitted to second generation WWER-440 plants. No high temperature filter loops were fitted in first generation WWER-01000 plants. In addition, the fuel at Novovoronezh 5 retained the sheathed fuel design used in the WWER-440 units, but all later WWER-1000 stations use non-sheathed fuel. All WWER-1000 units have a full containment building.

These initial designs were followed by the standard V-320 design, all of which have an individual containment, Figures A1-4 and A1-5, and a single 1000 MWe turbine. Compared with the earlier units, Figure A1-6, the standard V-320 design differs in that no isolation gate valves are fitted to the primary loops, Figures A1-6 and A1-7, and that there are four high temperature filter loops installed across each main coolant pump [A1, A2 and A6]. The later WWER-1000 sites were intended to accommodate multiple individual units, for example Balakovo, which was originally planned as a 4-unit site, and Zaporozhe, which was planned as a 6-unit site. The primary circuits of latest export version of the standard WWER-1000 design are similar, with the exception that the two V-428 units at Tianwan are not fitted with high temperature filter loops installed across each main coolant pump.

Except for Novovoronezh 5, all VWWER-1000 units have a single secondary circuit, containing a single 1000 MWe turbine. All WWER-1000 plants have a full flow condensate polishing plant. Most units were built with low pressure heater tubing made from copper-based alloys and only the Temelin and Tianwan units have titanium condenser tubing and an all-ferrous secondary circuit. The new WWER plant designs will have titanium condensers and a high efficiency SG blowdown clean-up system, but will only have a condensate polishing plant operating at one half or one quarter of the total feedwater flow rate.

At present no WWER-1000 unit has been uprated, but there are assessments underway to uprate some Russian units by 4%.

The new WWER-1200 V-491 design being developed for construction at a number of Russian nuclear stations is an evolutionary design based on the existing WWER-1000 V-320 and V-392 designs, but with increased power and with greatly enhanced active and passive safety features for both design-basis and beyond-design-basis accidents. Further details of the specific differences from the WWER-1000 design are given in Section 2.1.

1.3 Main Structural Materials in WWER Units

Primary System Components

The main components of all WWER units are constructed using similar materials. In all except the earliest WWERs, which had unclad reactor pressure vessels and pressuriser, the surfaces of the primary circuit in contact with the primary coolant are either made from stainless steel or low alloy steel and carbon steel weld clad with stainless steel. Stainless steel components are normally made from a titanium-stabilised stainless steel, whilst the reactor pressure vessels are weld clad in a niobium-stabilised stainless steel. With the exception of the Loviisa units, which have Stellite-containing in their coolant purification circuits, WWER plants do not use components or valves having Stellite™ hard facing cobalt alloys. Further details of the materials inventories are given in Section 2.

Fuel Assemblies

WWER-440 fuel mainly has zirconium-1% niobium clad and the fuel assemblies have a zirconium-2.5% niobium outer sheath. WWER-1000 fuel also has zirconium-1% niobium clad, but there is no outer sheath except at Novovoronezh 5. Most WWER-440 and WWER-1000 fuel is manufactured in Russia (MSZ and NZCK) and supplied by TVEL. Westinghouse fuel with Zircaloy-4 and ZIRLO clad is used at Temelin (but will be replaced by Russian fuel after 2010) and ZIRLO clad fuel has been loaded at South Ukraine 3. The very similar BNFL fuel has been is used in one of two Loviisa units since 1998 and there were plans to use BNFL fuel at Paks, but this will not now be loaded. The BNFL fuel at Loviisa will be replaced by Russian fuel from 2008; the other Loviisa unit always loaded Russian fuel.

Secondary System Components

WWER secondary circuits were originally mainly made from carbon steel (with the exception of the stainless steel steam generators tubing and collectors, Figures A1-8 to A1-10), high alloy steel (turbine blades) or Admiralty brass of cupronickel alloy (MSR tubing, low pressure heater tubing and condenser tubing, although Loviisa, Temelin and Tianwan [A7] have titanium condenser tubing). Due to the extensive flow assisted corrosion (FAC) damage that occurred, which particularly affected the carbon steel high pressure heater tubing, moisture separator reheater tubing, wet steam lines and feedwater heater shells, the damaged sections were replaced with stainless steel equivalents. In addition, where possible, cupronickel components were replaced by copper-free so that the feedwater pH could be raised to suppress residual FAC damage and iron transport into the steam generators.

At some stations it was found that the copper-based alloy condenser tubing suffered from numerous leaks, which increased impurity levels in the feedwater in spite of the presence of a full flow condensate polisher. To limit ingress and to permit operation at high pH the tubing at some East European WWER-440 plants have been replaced by titanium (Dukovany) or stainless steel (Paks and Kozloduy), allowing operation at high pH [A2]. Other plants (Bohunice, Zaporozhe) that still operate with brass condensers, have successfully tested and use amine based AVT chemistry regimes (like ETA or morpholine) to minimise FAC problems.

At Temelin these changes were made before the station commissioned and both units were completed with titanium condenser tubing and an all-ferrous secondary circuit. Titanium tubing and an all-ferrous circuit were also specified for the Tianwan units and similar secondary circuit materials will be specified for other new units, with the exception that the condenser tubes may be either titanium or stainless steel; no copper-based alloys will be used. The decision to use titanium tubing is expected to increase plant reliability and performance, as cooling water flow rates can be increased, compared with copper-based, which will not only improve condenser vacuum but will reduce deposition on to the condenser tubing (fouling), potential condenser leaks and permit the increase in secondary circuit pH to limit FAC damage and iron transport.

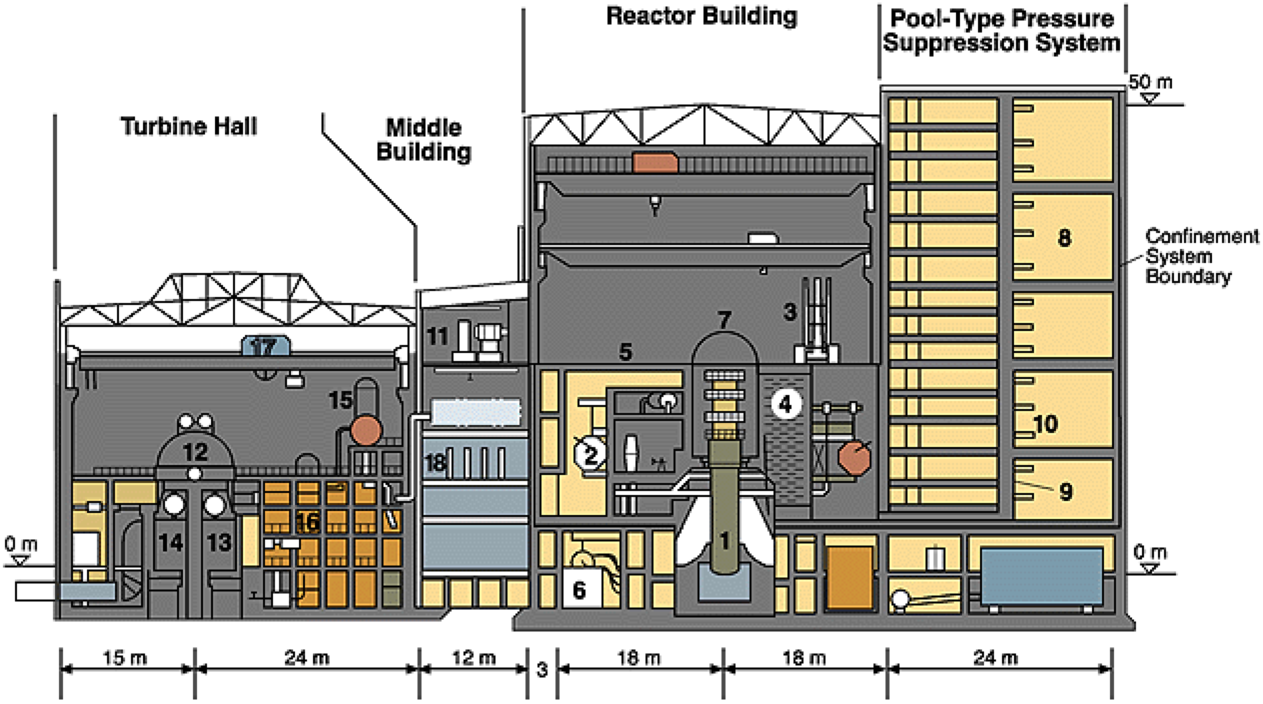


Figure A1-1 Cross Section of a WWER-440 V-213 Unit

1	Reactor pressure vessel	2	Steam generator	3	Refuelling machine
4	Cooling pond	5	Biological shield	6	Emergency feedwater system
7	Reactor	8	Localization tower	9	Bubbler trays
10	Air trap	11	Aerator	12	Turbine
13	Condenser	14	Turbine hall	15	Deaerator-feedwater tank
16	Preheater	17	Turbine Hall Extract	18	Control and instrument room

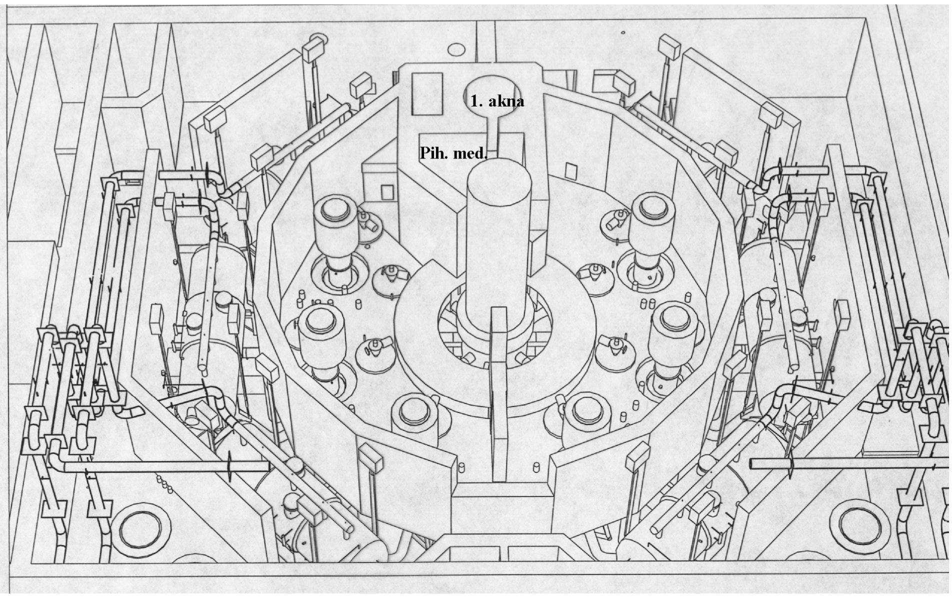


Figure A1-2 Layout of a WWER-440 V-213 Confinement Area

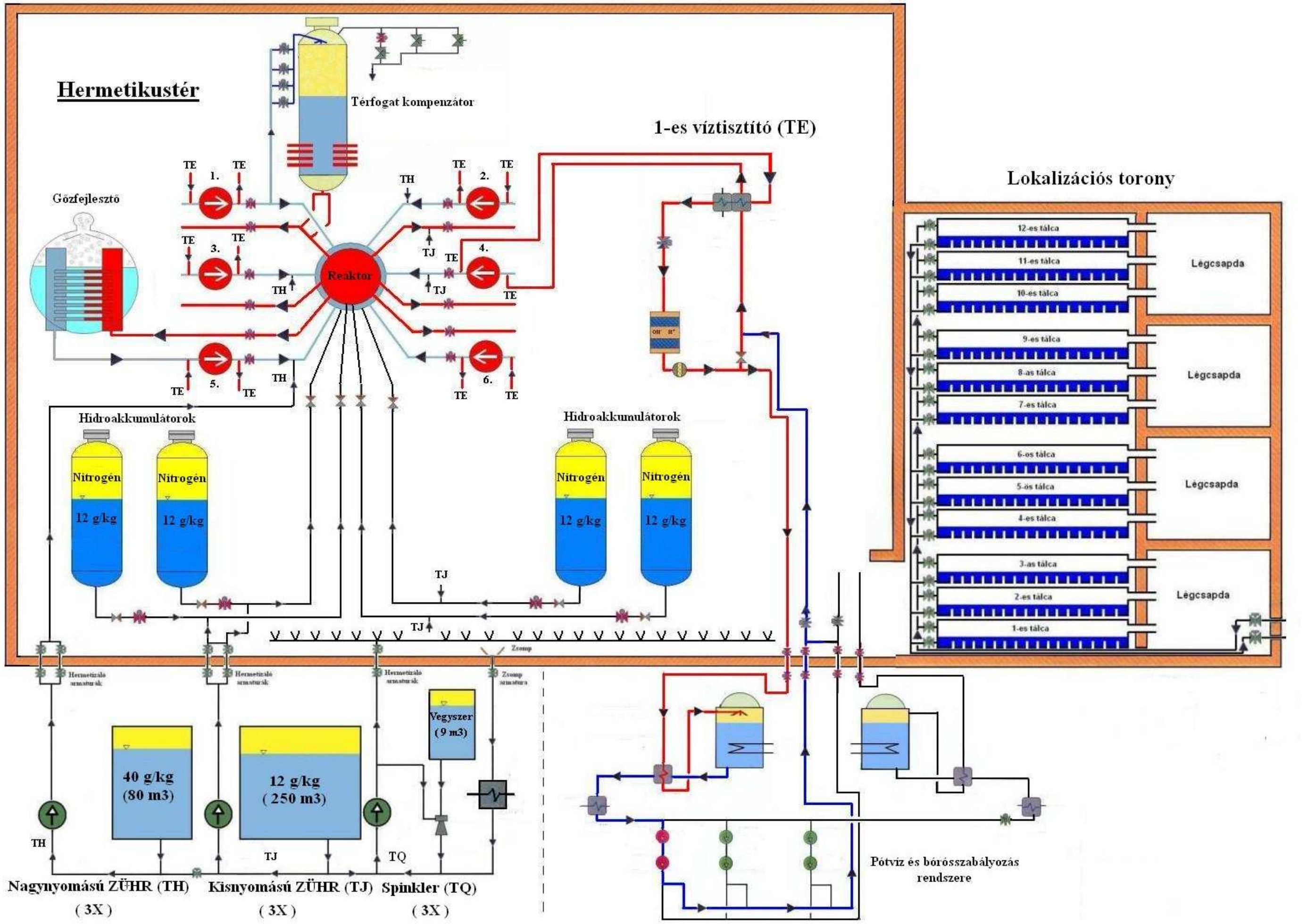


Figure A1-3 Schematic Layout of a WWER-440 V-213 Primary Circuit and Nuclear Auxiliary Circuits

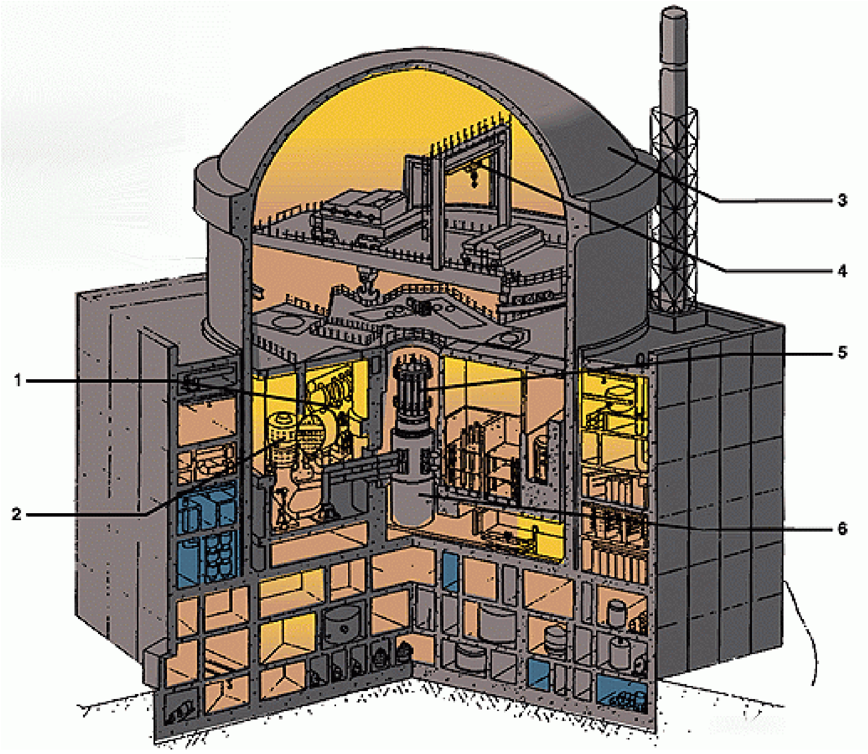


Figure A1-4 **WWER-1000 V-320 Containment Building Layout**

1	Horizontal steam generator	2	Reactor coolant pump
3	Containment building	4	Refueling crane
5	Control rod assemblies	6	Reactor vessel.

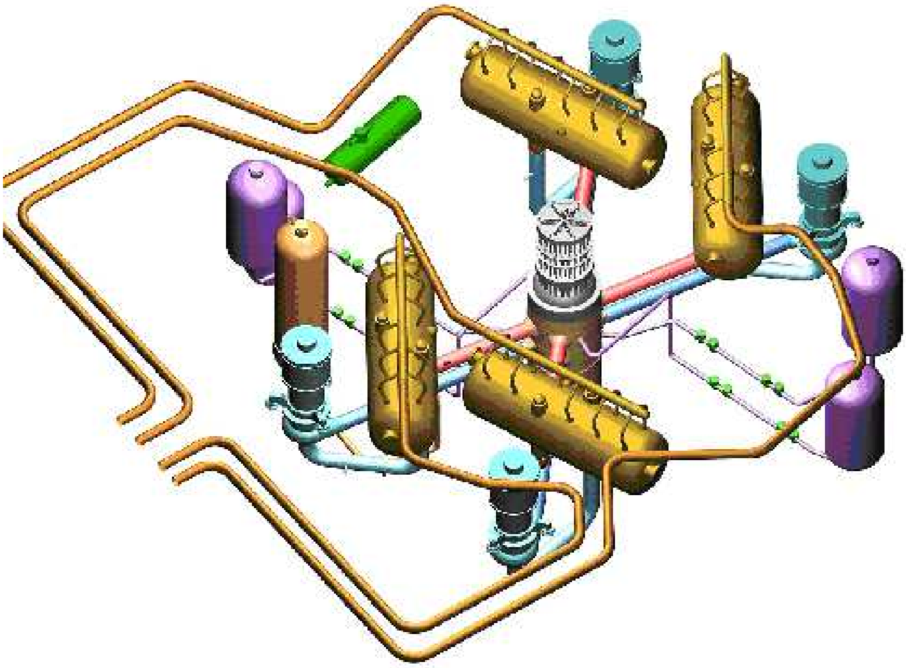
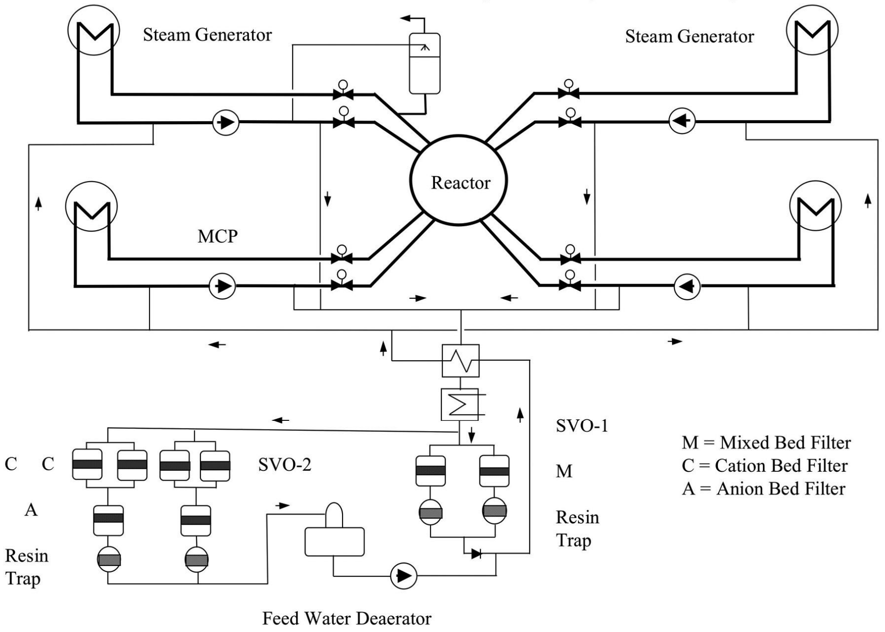


Figure A1-5 Layout of WWER-1000 V-320 Primary Circuit

WWER-1000 V-187, V-338 and V-302 Simplified Primary Water Flow Diagram



WWER-1000 V-320 Simplified Primary Water Flow Diagram

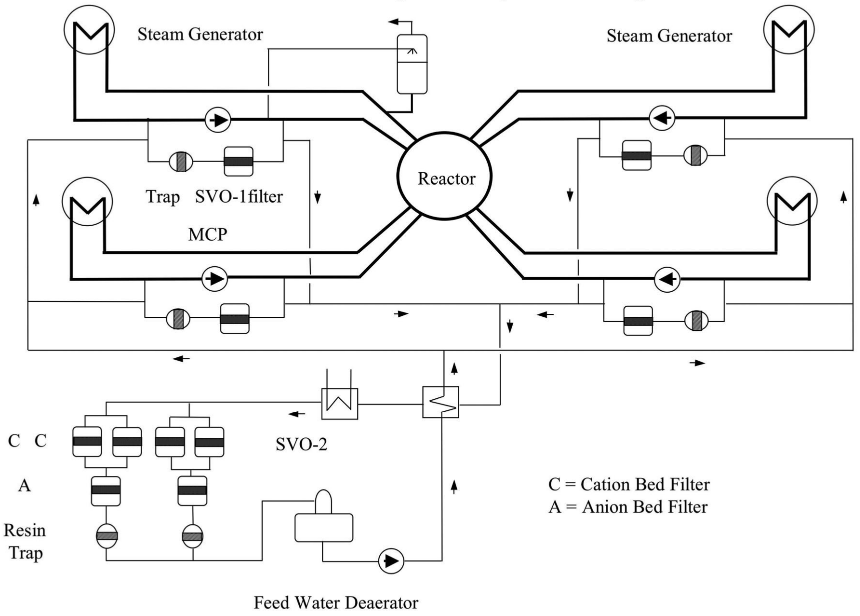


Figure A1-6 Simplified Layouts of WWER-1000 V-187, V-302, V-338 And V-320 Primary And Primary Purification Circuits

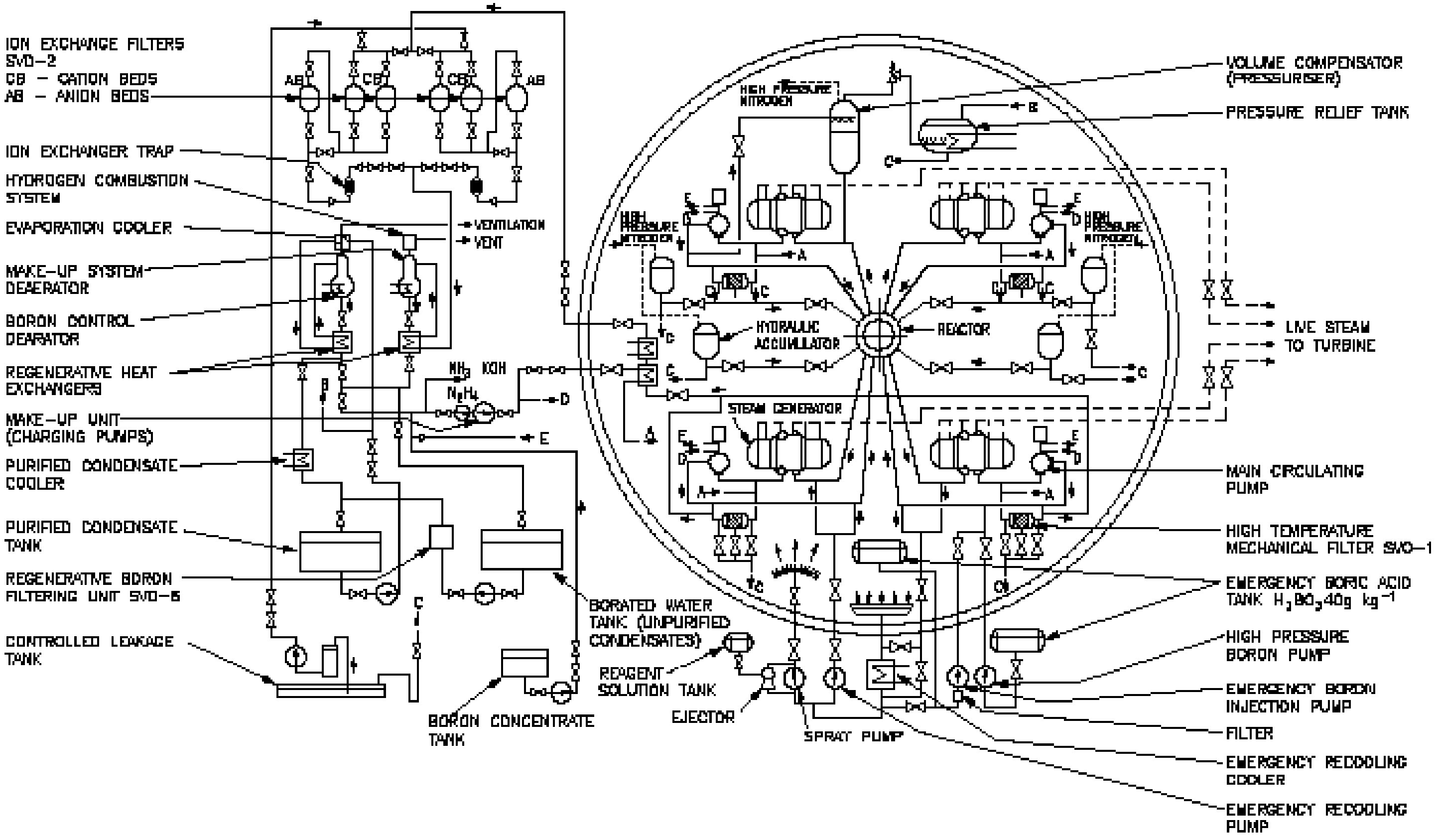


Figure A1-7 Schematic Layout of a WWER-1000 V-320 Primary Circuit and Nuclear Auxiliary Circuits

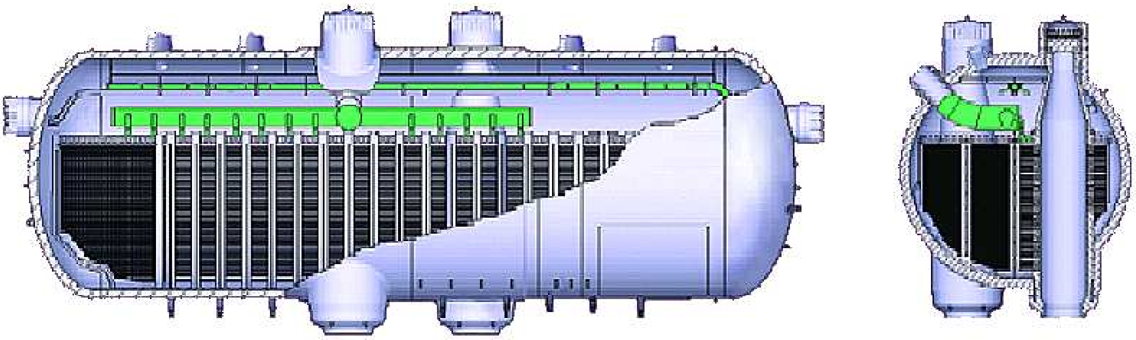


Figure A1-8 PGV-1000 Steam Generator used in WWER-1000 plants

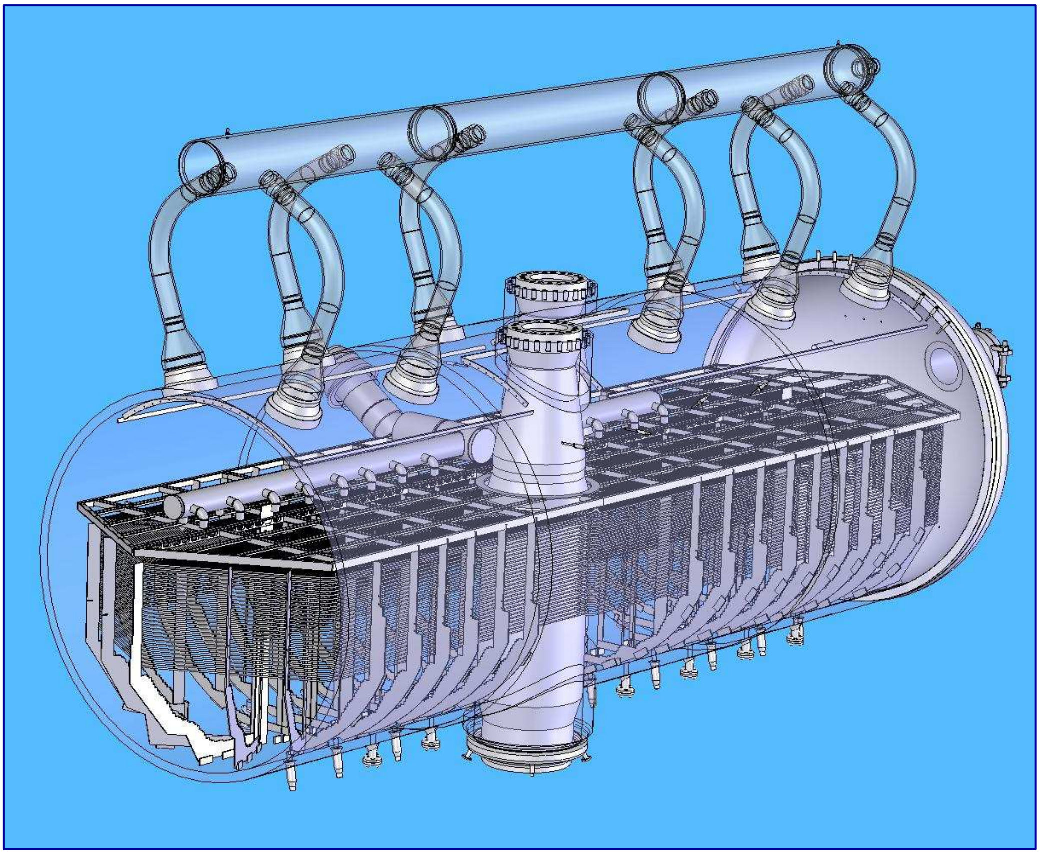


Figure A1-9 Cte-away View of a WWER PGV-1000 SG showing the Tubes and Collectors.

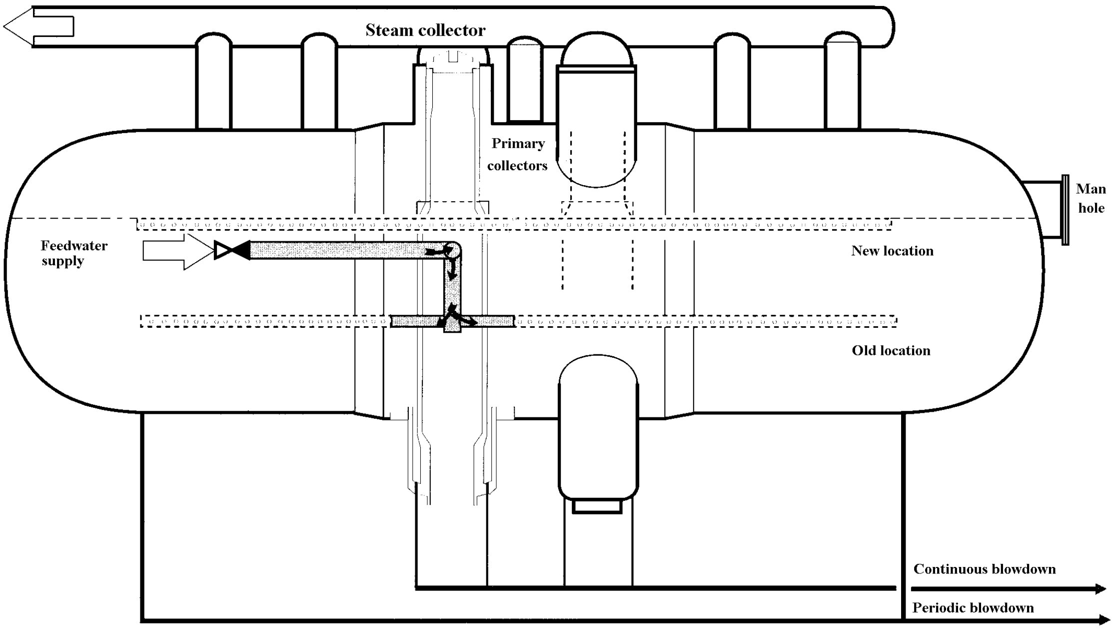


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Figure A1-10 Position of the Old and New Feedwater Distributors in the PGV-440 Horizontal Steam Generators in Loviisa Unit 2.
The continuous blowdown is carried out from the primary collector pockets and periodic blowdown from both ends of the steam generator [A9]

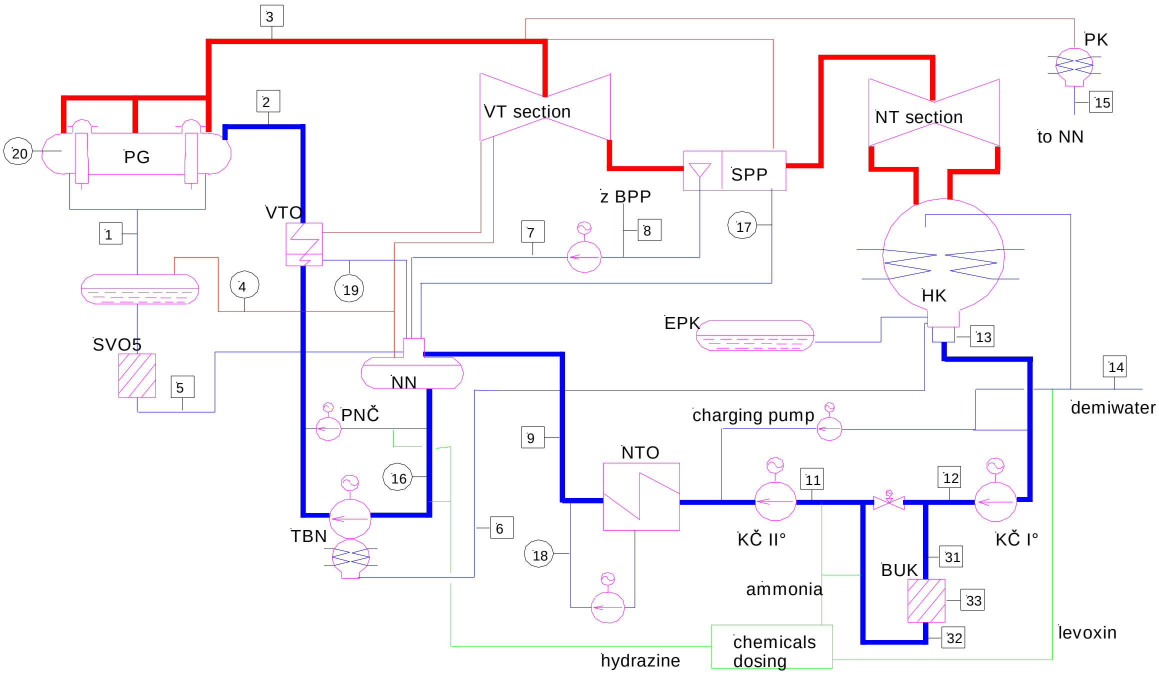


Figure A1-11 Simplified Schematic Circuit Diagram of the Secondary side of Temelin WWER-1000

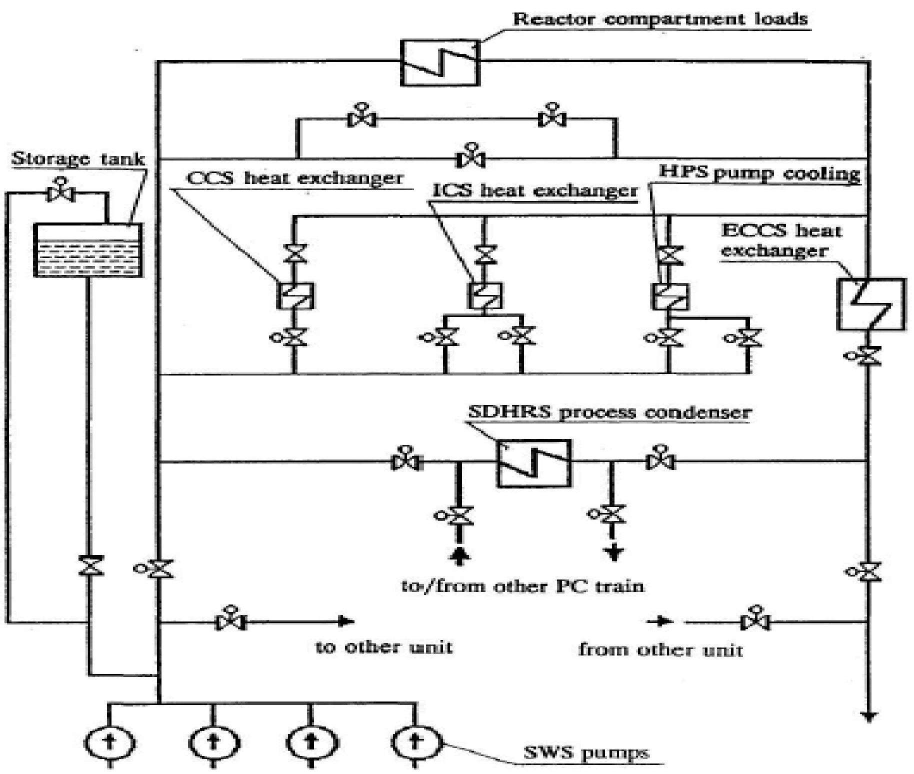


Figure A1-12 Principal Schematic Circuit Diagram of the Service Water System in a WWER-440 V-213 Unit

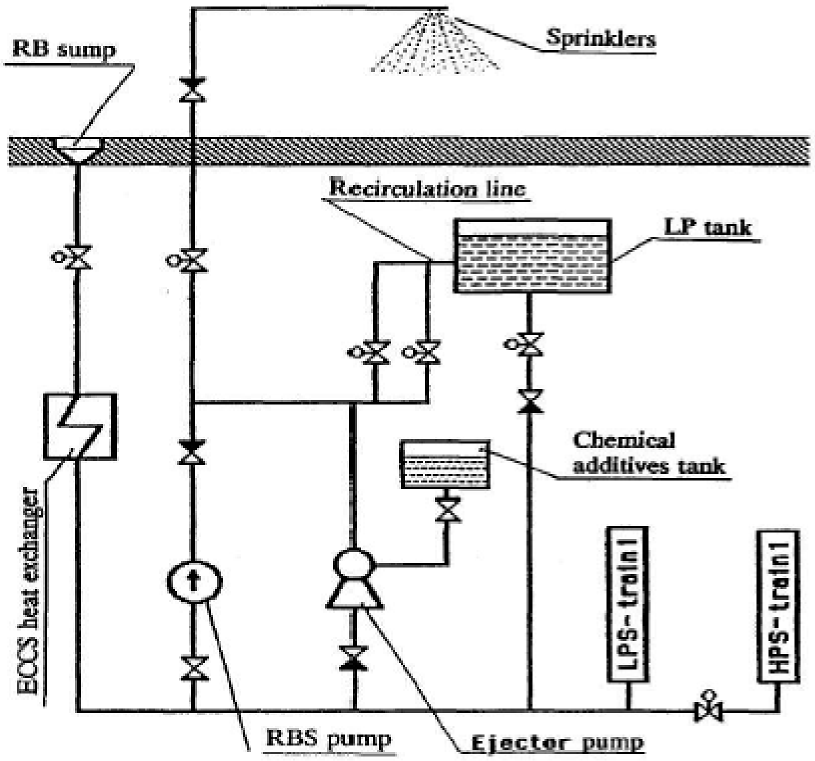


Figure A1-13 Principal Schematic Circuit Diagram of the Containment Spray System at a WWER-440 V-213 Unit Cooled by the Service Water System

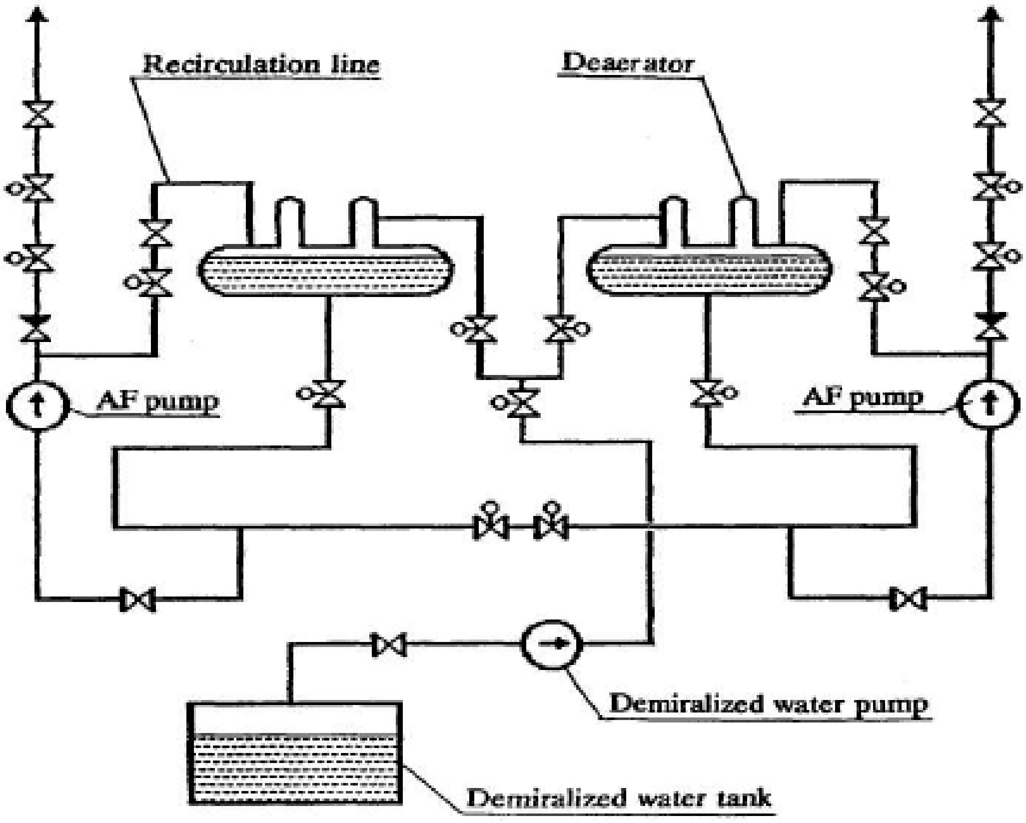


Figure A1-14 Principal Schematic Circuit Diagram of the Auxiliary Feedwater System at a WWER-440 V-213 Unit

References to Appendix 1.

A1 R Roofthooft et al."Primary Circuit Chemistry of Western PWR and WWER Power Plants", Unipede Report, 02004Ren9653, 1996.

A2 K Garbett. EPRI Technical Report 1003382 Review of WWER Primary Water Chemistry and the Potential for its Use in PWRs, September 2002.

A3 IAEA-TECDOC –742 Design basis and design features of WWER-440 model 213 NPPs, May 1994.

A4 IAEA-TECDOC –1044 Generic Safety issues for NPPs with LWRs and measures taken for their resolution, September 1998.

A5 IAEA-TECDOC –992 Performance analysis of WWER-440/230 NPPs, January 1997

A6 Nuclear Energy Agency, Committee on the Safety of Nuclear Installations, Validation Matrix for the Assessment of Thermal-Hydraulic Cades for WWER LOCA and Transients, Appendix A and B. NEA/CSNI/R(2001)4, July 2000.

A7 V P Denisov et al. Modernising the WWER: A Soviet Perspective, Nuclear Engineering International, 18, July 1991.

A8 V.I.Baranenko et al. Usage of titanium for manufacturing of the equipment at Russian nuclear power plants. 5th Int. Sci.-Tech. Conf. "Safety of WWER plants". 29.05-01.06.2007. Podolsk, Russia.

A9 K. Mäkelä et al. The effect of the new feedwater distributor design on the impurity concentrations in one of the Loviisa 2 unit steam generators. Conference on Water chemistry of nuclear reactor systems 7, vol. 1. BNES, London 1996, p 393-398. Published by Thomas Telford Publishing, 1 Heron Quay, London E14 4JD – GB.

Appendix A2. pH and conductivity Calculations

The pH calculation and crosschecking this value with measured value is important for several reasons.

pH_T is governing many corrosion phenomena or solubility and type of species in presence in the water.

The main reason for pH control is concerning the primary and secondary systems and also some of the auxiliary system when these contain carbon steel requiring a sufficiently alkaline environment

Primary Coolant pH

Solubility and transport of corrosion products in the primary coolant strongly depends on the pH_T (at operating temperature) and has a direct impact on dose rates.

However, the pH_T is not directly measured and there is not constant correspondence between pH_T and the potentially measured $pH_{25°C}$.The reason is that boron and alkali (potassium, lithium, sodium) concentrations are varying along the fuel cycle. Boric acid is a weak acid while alkali are strong bases. Thus, alkalinity is almost proportional to the total concentration of alkali (with a small ionic strength correction) while boric acid is a weak acid and boron acidity is decreasing when boron concentration increases.

In other words, a much lower molar concentration of alkali than boric acid content is necessary to maintain a slightly alkaline pH at the beginning of the fuel cycle with a high boron concentration. Later on, alkali molar concentration does not decrease in the same way as boron one along the fuel cycle.

But at low temperature, the dissociation constants respectively of boric acid and alkali are not the same than at high temperature.

Consequently, for the same high pH temperature, the room temperature $pH_{25°C}$ will be different at various moments of the fuel cycle.

Finally, it is more reliable and simple to measure the alkali and boron concentration and calculate the pH_T than measuring or calculating the room temperature pH.

Practically, the reverse logic is applied and a pH_T is defined as an objective and the corresponding total alkali concentration is inferred from this pH_T and the boron content for a specific solution.

The conductivity value which is also varying with the composition of the primary coolant does not provide any additional information to the calculated pH. Then cation or anion conductivity cannot be used to monitor potential impurities in the primary coolant due to the presence of reagents with a conductivity much higher than the one that would be looked for impurities limits.

The optimum line (------) in the two curves 2.x and 2.y given in section 2.4 for WWER-440 and WWER-1000, according to standard international calculation (EPRI code and Czech – NRI calculation) respectively correspond to $pH_{300°C}$ of about 7.2 and 7.1, although a straight line may not exactly correspond to a constant pH due to the various constants involved with a different ionisation for boric acid (weekly dissociated) and alkali (highly dissociated).

Secondary System pH and conductivity

It has been seen in Chapter 3 that the pH and reagent selection is of high importance for mitigation of various types of corrosion for the materials in presence.

The treatment with reagents and pH is selected according to various parameters and design or operating data. This pH is monitored at 25°C in the feedwater (or in some cases in the condensate water).

Thus, it is interesting to crosscheck the measured $pH_{25°C}$ value with the expected one according to the concentration of the reagents in presence, mainly ammonia and any amine added in the system. Hydrazine, in the typical concentration range added in the system has a marginal impact on the pH due to its low dissociation constant. On the other hand, hydrazine impact on the pH is mainly observed through ammonia produced by thermal decomposition of hydrazine.

Some discrepancy may be noticed between the measured pH and the calculated pH based on the measured concentrations of the various reagents (ammonia and amines if any). In such a case, the difference may come:

- either from the presence of impurities in the system, including boric acid from a primary to secondary leak,

- or from decomposition products of the injected amine reagent, with likely another alkaline amine such as methylamine, which increases the measured $pH_{25°C}$,

- or finally to any uncertainty in any of the measured concentration of compounds or of the measured $pH_{25°C}$.

If the origin of the discrepancy between the measured and calculated pH cannot be explained easily, the measurement of total conductivity, directly depending on the presence of alkaline dissociated reagents, and thus of the pH, will help to clarify the situation.

- If both total conductivity and measured pH are higher than expected, the difference is likely due to the presence of other amines as decomposition products;
- If only the measured pH is higher, the pH measurement is likely uncertain;
- If the measured pH is lower than the calculated one and if there is a cation conductivity higher than that of almost pure water, this means a presence of anions with acidic behaviour, that could be boric acid from primary to secondary leak (particularly at the beginning of the fuel cycle), organic acids, carbon dioxide (from air ingress) or other anions from strong acids (chloride, sulphate, …) due to a pollution that should be looked for;
- If only the measured pH is lower than the calculated one and if the conductivity is unaffected, likely, the pH measurement is uncertain.

These examples show the benefit of checking for the pH and if necessary also for the conductivity (total or cation conductivity as appropriate).

This is why the comparison of the measured and calculated pH and conductivity according to the curves below is useful.

These have been calculated with:

- ➢ the EPRI method using EPRI pH Calculator, Version 3.0 (with permission from EPRI) for Figures 1 to 4.
- ➢ CALIN Code provided to Energoatom in Ukraine by Electricité de France, except for Figures 5 to 16
- ➢ Czech Republic code provided by V. Hanus for Figures 17 and 18.
- ➢ F. Nordmann data for Figures 19 and 20.

The twenty graphs included are the following.

- A.1. Calculated $pH_{300°C}$ Values Corresponding to the Specifications for WWER-440 Units
- A.2. Calculated $pH_{300°C}$ Values Corresponding to the Specifications for WWER-1000 Units
- A.3. Specifications for WWER-440 Units Shown with Calculated $pH_{300°C}$ Values
- A.4. Specifications for WWER-1000 Units Shown with Calculated $pH_{300°C}$ Values
- A.5. pH 25° versus Ammonia (0.1 – 10 mg/kg)
- A.6. Total Conductivity versus Ammonia (0.1 – 10 mg/kg)
- A.7 . pH 25°C versus Morpholine (1 – 20 mg/kg)
- A.8. Total Conductivity versus Morpholine (1 – 20 mg/kg)
- A.9. pH 25°C versus Ethanolamine (0.2 – 10 mg/kg)
- A.10. Total Conductivity versus Ethanolamine (0.2 – 10 mg/kg)
- A.11. pH 25°C versus Morpholine (1 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)
- **A**.12. pH 25°C versus Ethanolamine (1 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)
- A.13. Total Conductivity (log scale) versus Morpholine (0.5 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)
- A.14. Total Conductivity (linear scale) versus Morpholine (0.5 – 10 mg/kg) for various ammonia content (0 to 5 mg/kg NH_3)
- A.15. Total Conductivity (log scale) versus Ethanolamine (0.2 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)
- A.16. Total Conductivity (linear scale) versus Ethanolamine (0.2 – 10 mg/kg) for various ammonia content (0 to 5 mg/kg NH_3)
- A.17. Conductivity (log scale) at 25 °C versus CO_2 (log scale) concentration (from 0.001 to 100 mg/kg)

- A.18. pH at 25 °C versus ammonia (log scale 0.01 to 100 mg/kg as NH_4) for various CO2 concentration (0 to 100 mg/kg)
- A.19. Cation Conductivity at 25 °C for low concentrations of “strong” anions (Cl, SO_4 and F from 0 to 25 µg/kg)
- A.20. Cation Conductivity at 25 °C for high concentrations of “strong” anions (Cl, SO_4 and F from 0 to 500 µg/kg)

Figure A.1 Calculated $pH_{300°C}$ Values Corresponding to the Specifications for WWER-440 Units.

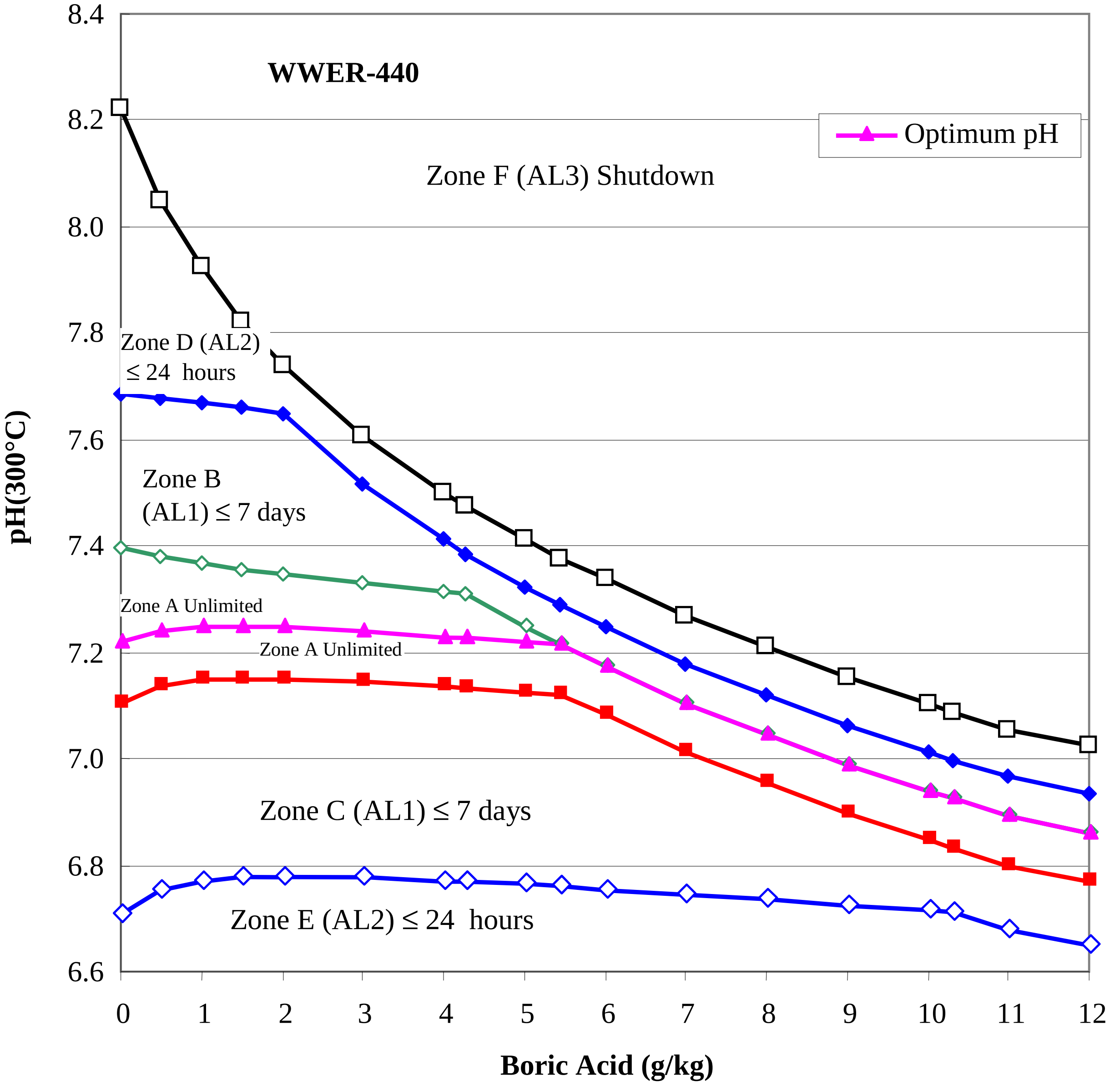
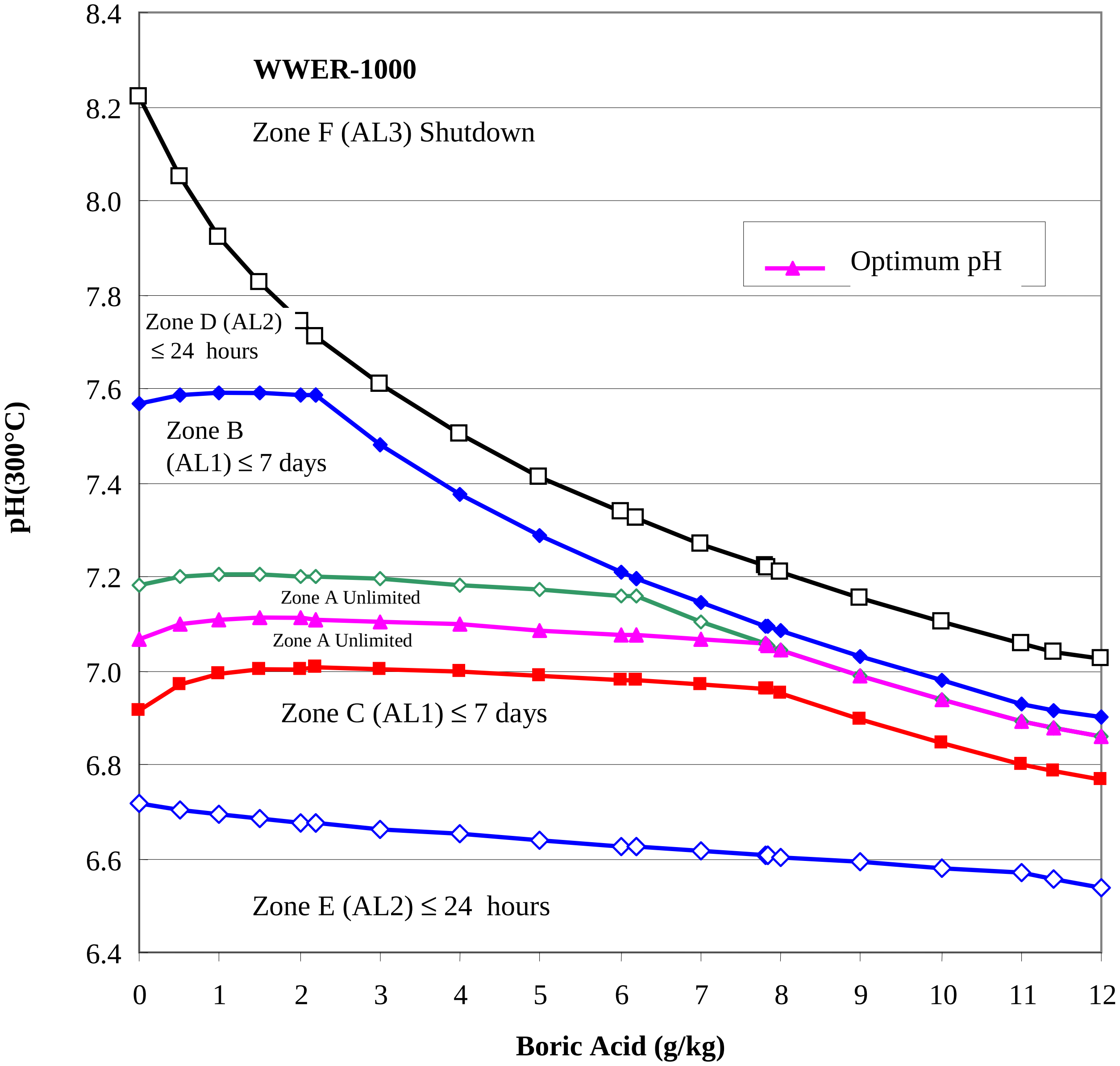


Figure A.2 Calculated pH$_{300°C}$ Values Corresponding to the Specifications for WWER-1000 Units.



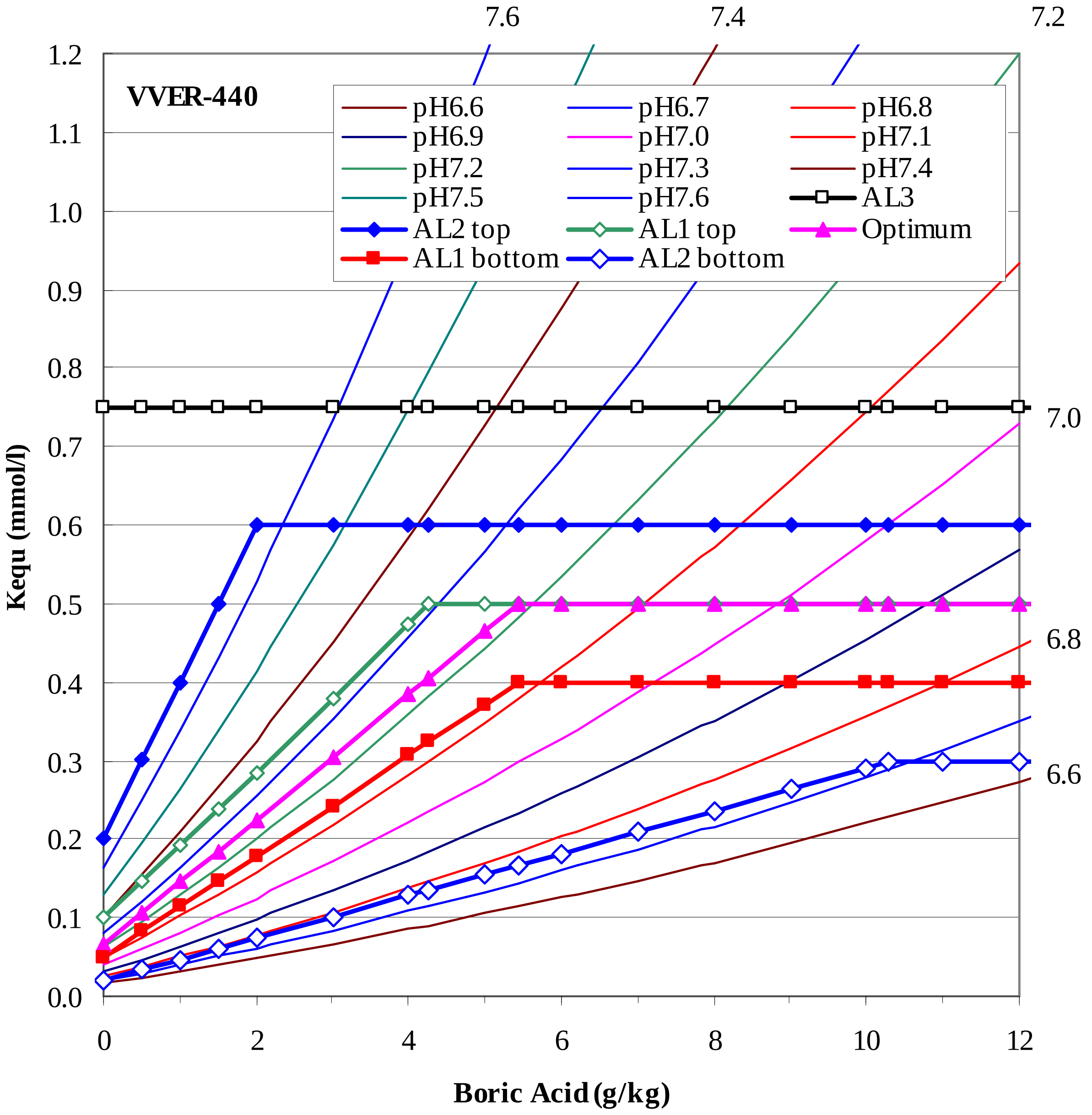


Figure A.3 Specifications for WWER-440 Units Shown with Calculated $pH_{300°C}$ Values.

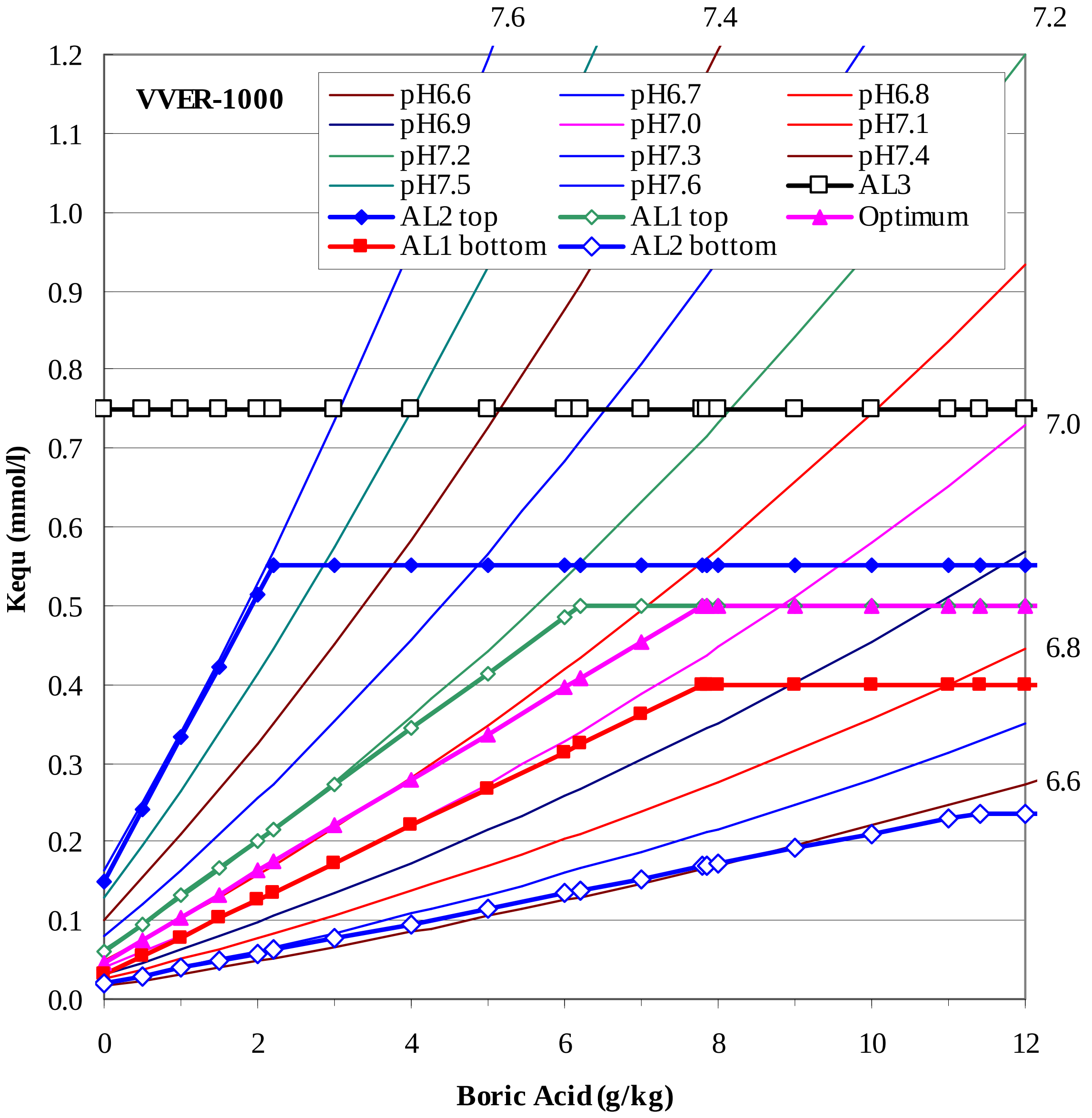


Figure A.4 Specifications for WWER-1000 Units Shown with Calculated $pH_{300°C}$ Values.

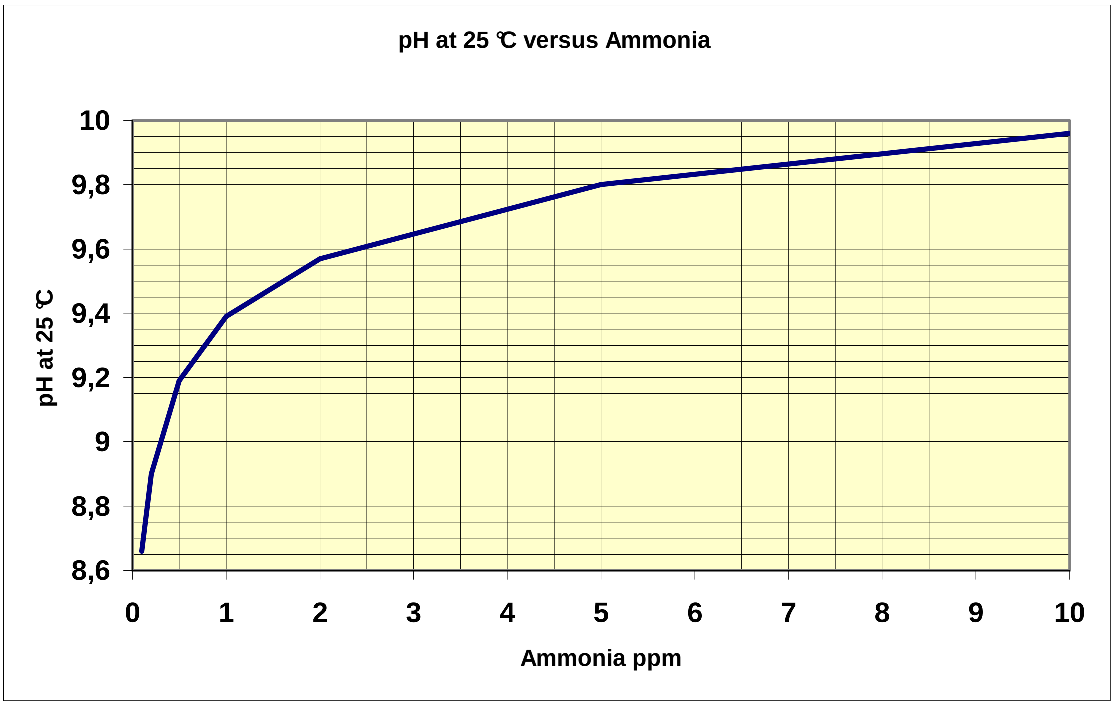


Figure A.5. pH 25° versus Ammonia (0.1 – 10 mg/kg)

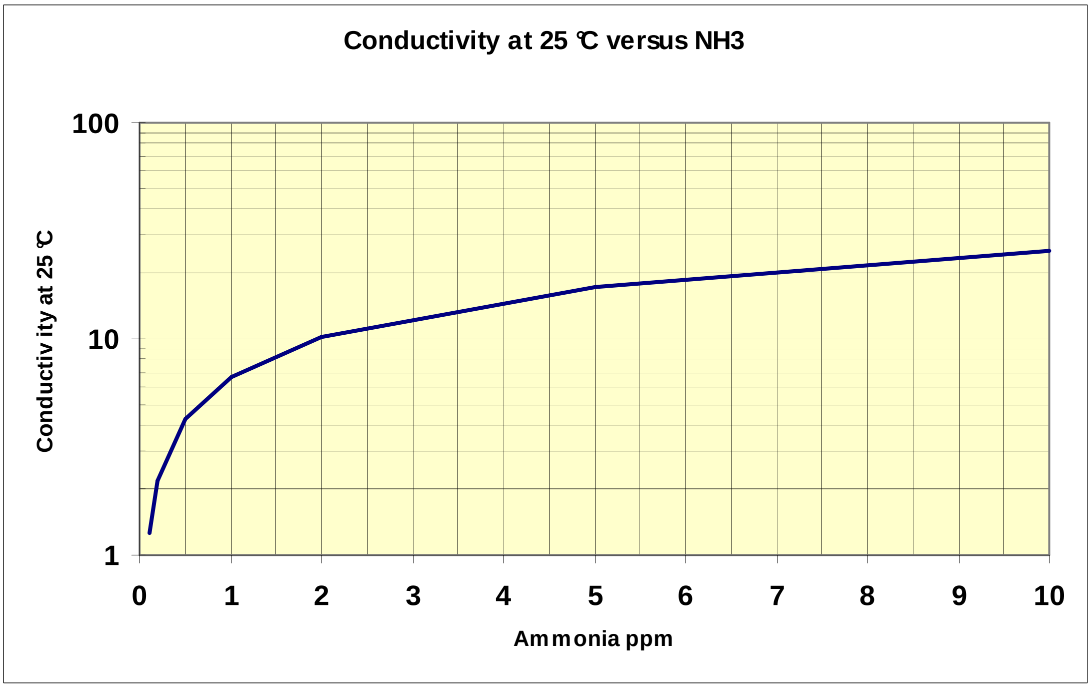


Figure A.6. Total Conductivity at 25 °C versus Ammonia (0.1 – 10 mg/kg)

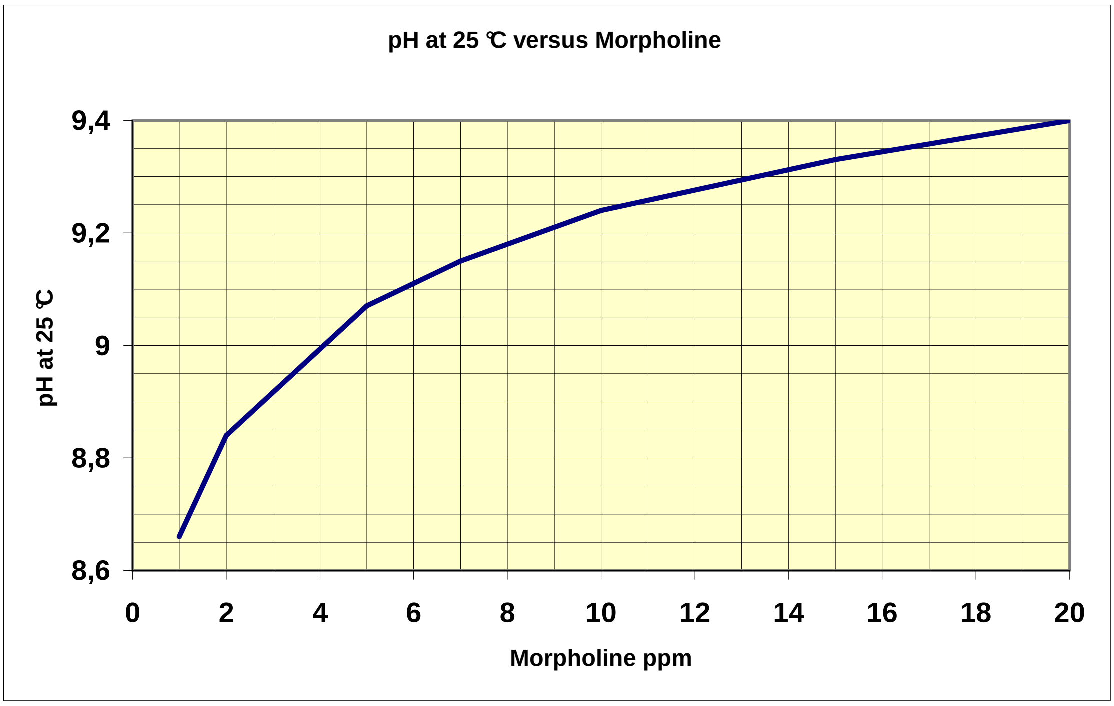


Figure A.7 . pH 25°C versus Morpholine (1 – 20 mg/kg)

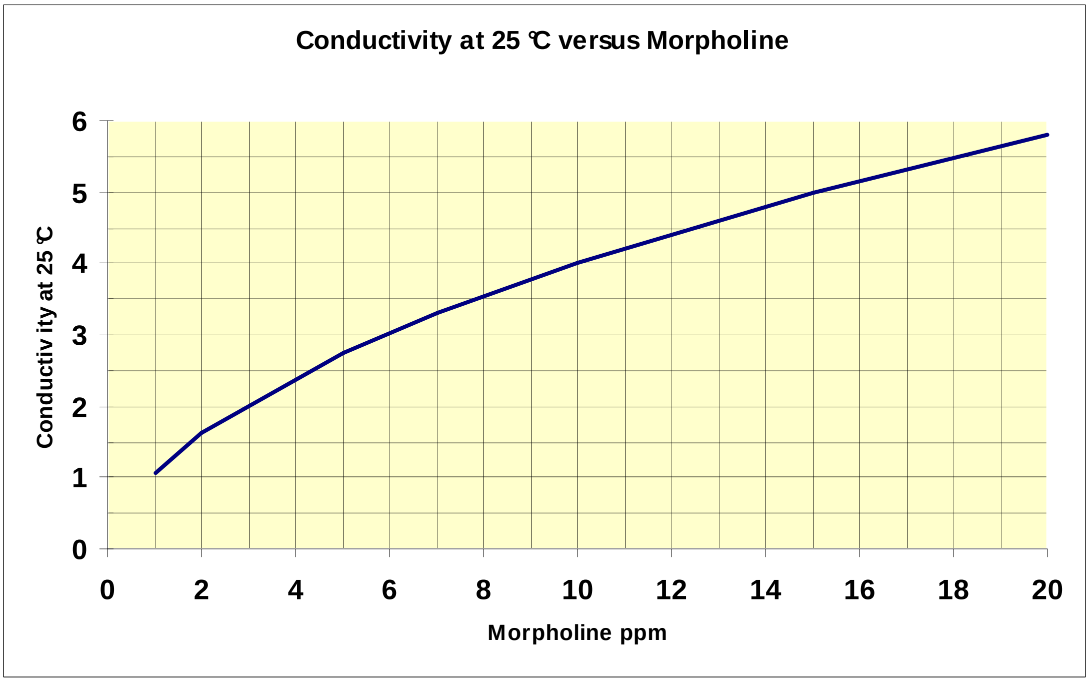


Figure A.8. Total Conductivity at 25 °C versus Morpholine (1 – 20 mg/kg)

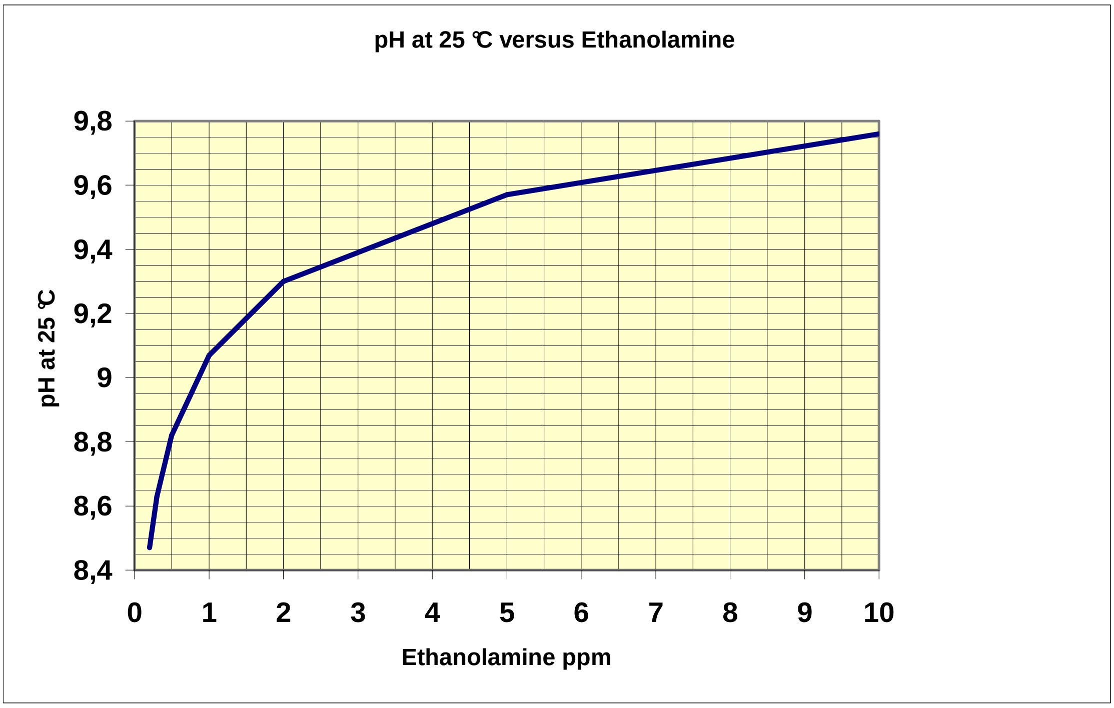


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Figure A.9. pH 25°C versus Ethanolamine (0.2 – 10 mg/kg)

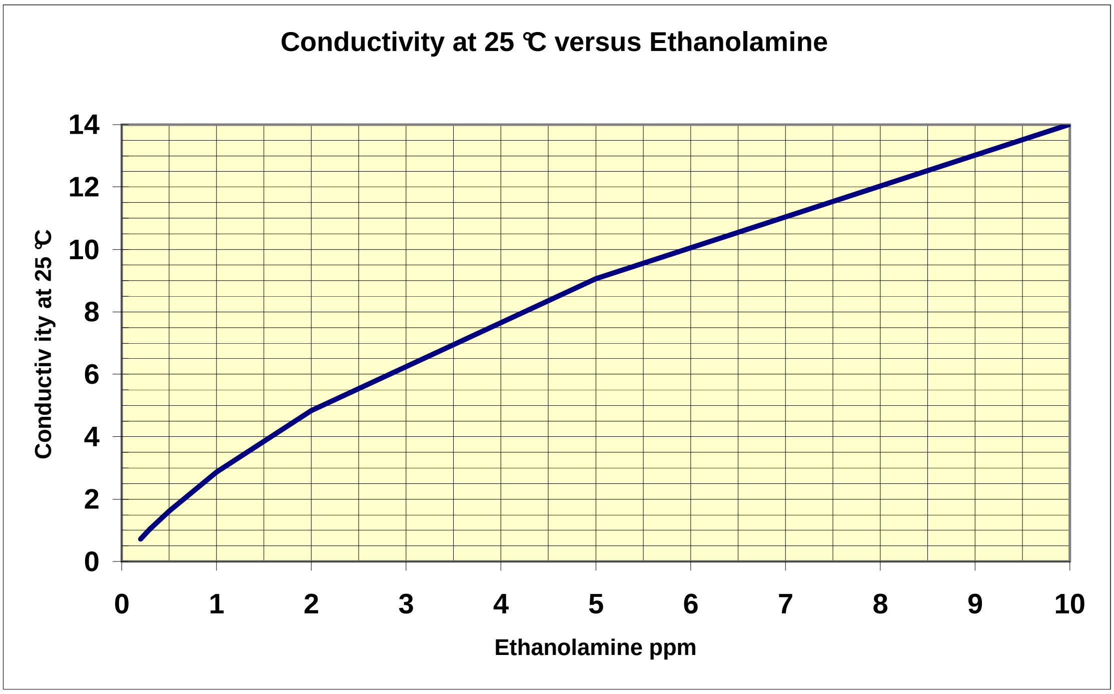

Figure A.10. Total Conductivity at 25 °C versus Ethanolamine (0.2 – 10 mg/kg)

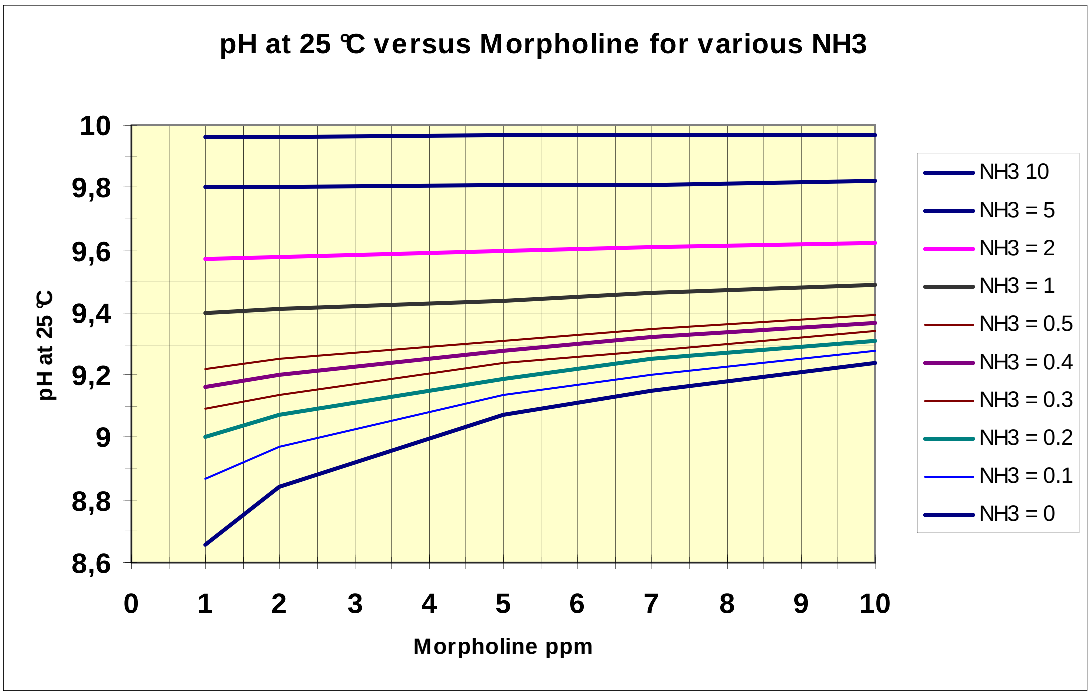

Figure A.11. pH 25°C versus Morpholine (1 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)

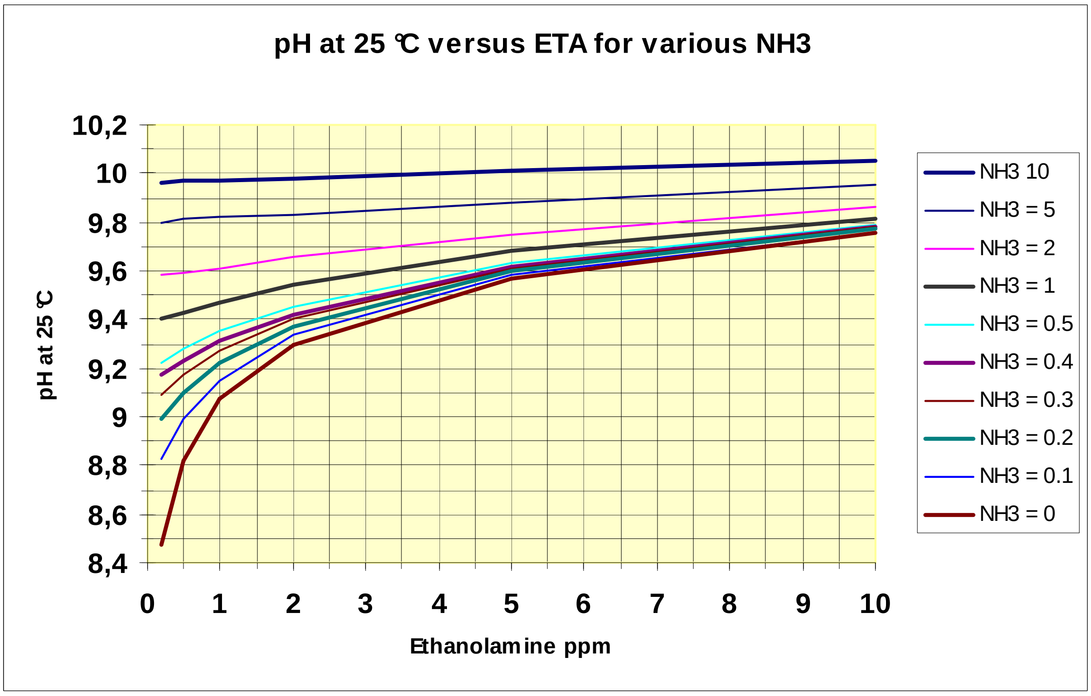

Figure A.12. pH 25°C versus Ethanolamine (1 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)

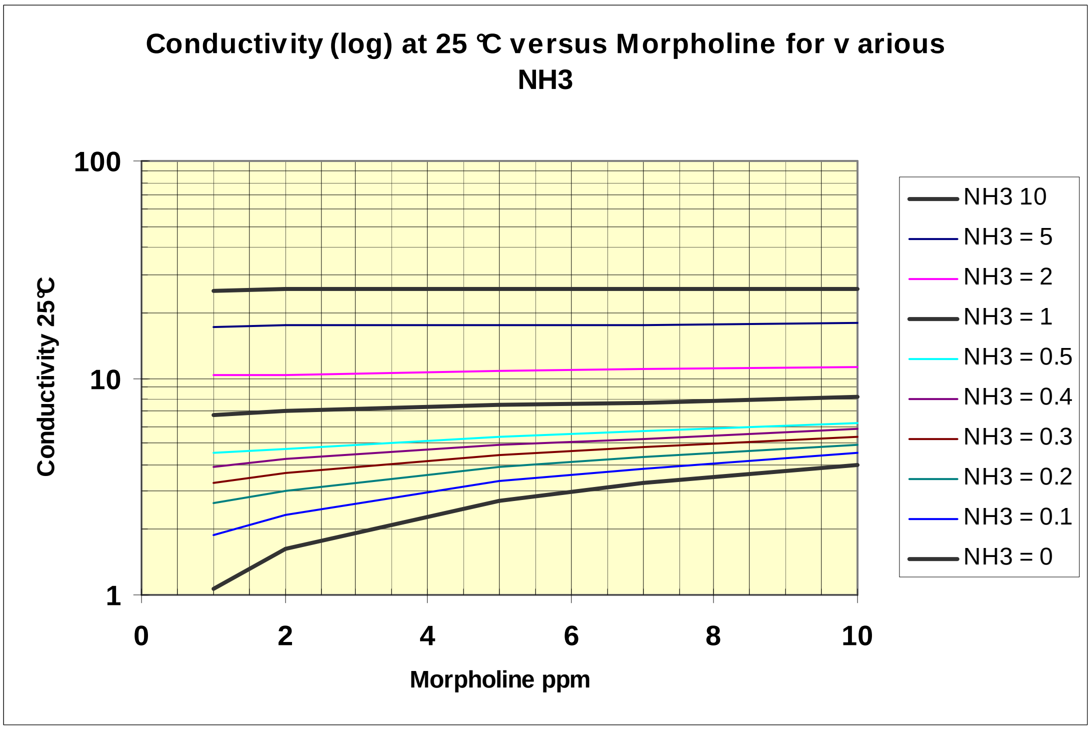

Figure A.13. Total Conductivity (log scale) versus Morpholine (0.5 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)

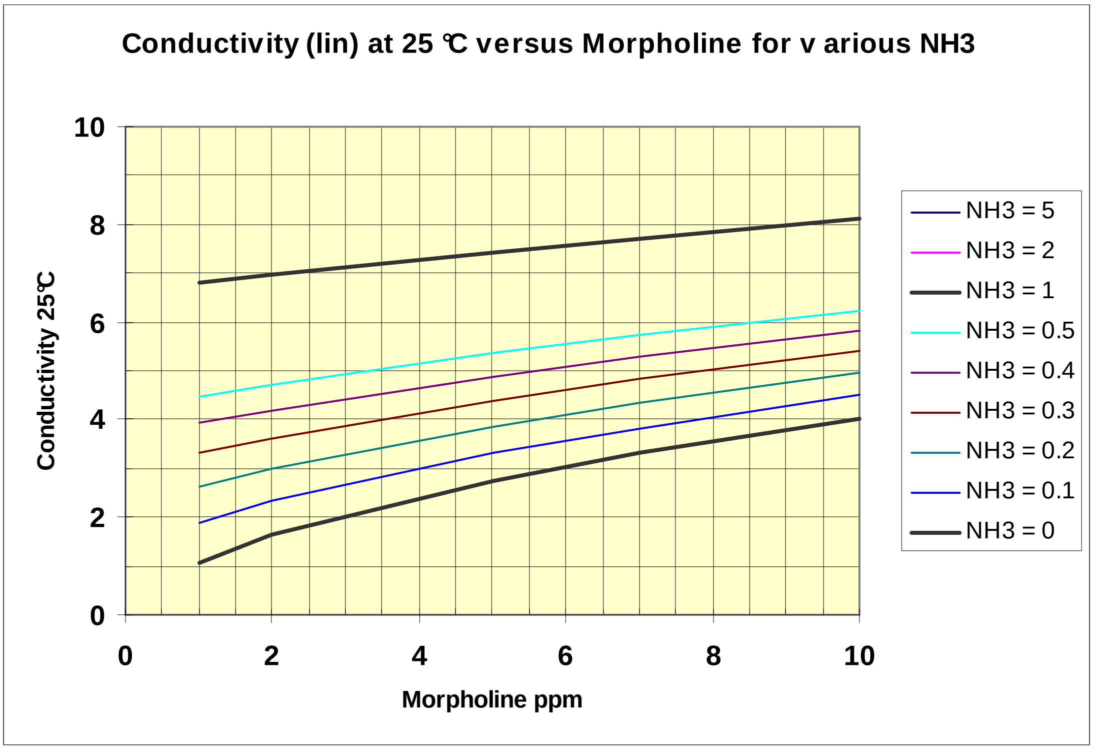

Figure A.14. Total Conductivity (linear scale) at 25 °C versus Morpholine (0.5 – 10 mg/kg) for various ammonia content (0 to 5 mg/kg NH_3)

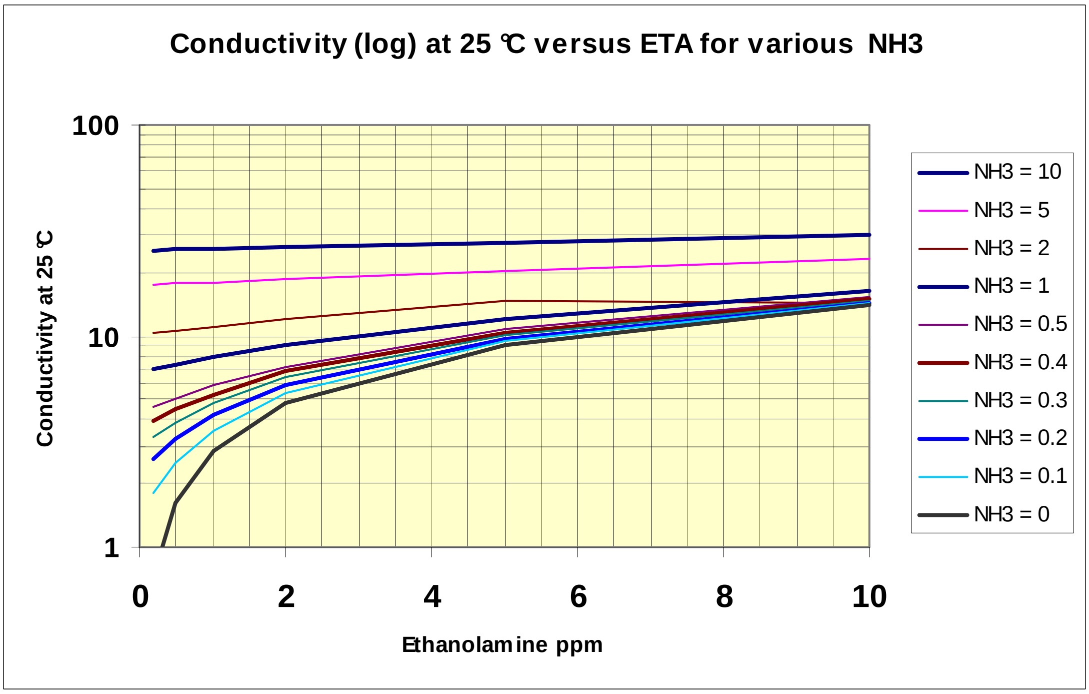

Figure A.15. Total Conductivity (log scale) at 25 °C versus Ethanolamine (0.2 – 10 mg/kg) for various ammonia content (0 to 10 mg/kg NH_3)

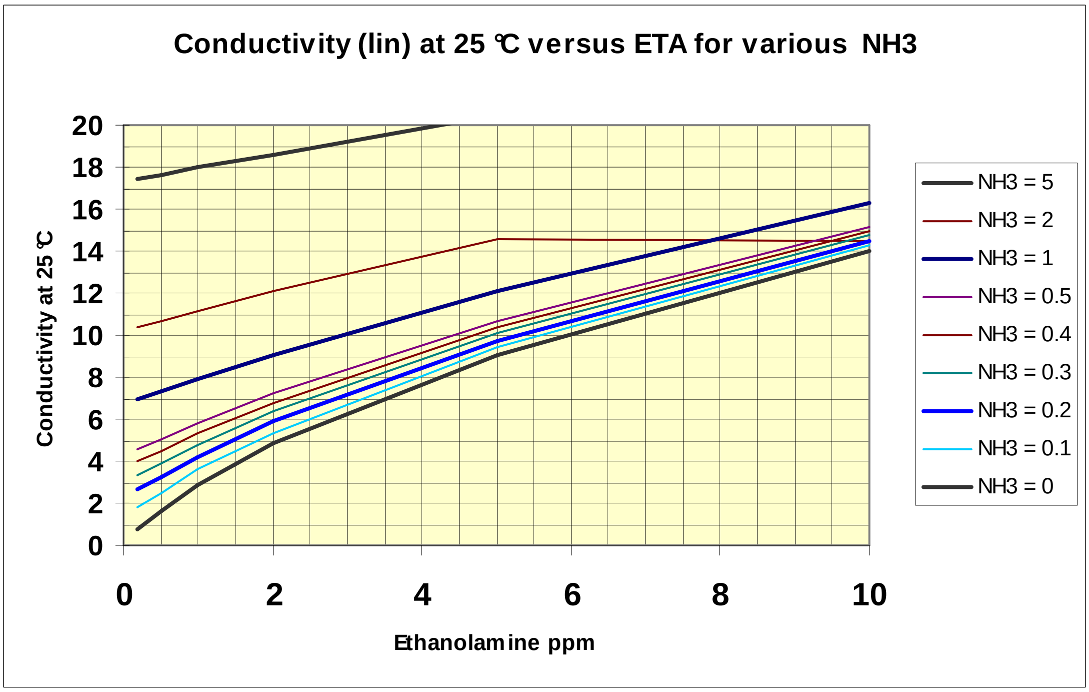

Figure A.16. Total Conductivity (linear scale) at 25 °C versus Ethanolamine (0.2 – 10 mg/kg) for various ammonia content (0 to 5 mg/kg NH_3)

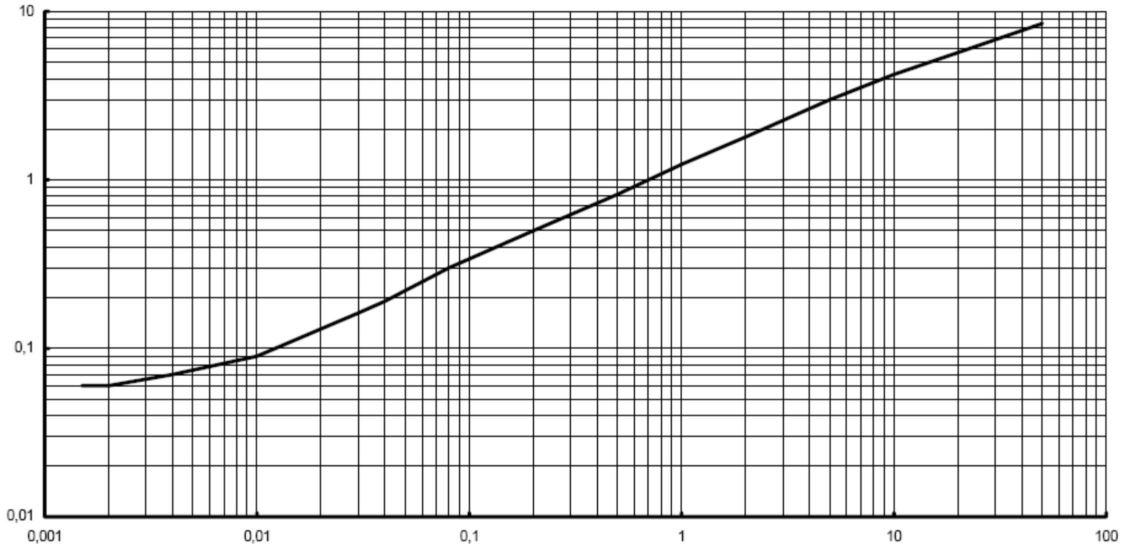

Figure A.17. Conductivity (log scale) at 25 °C versus CO_2 (log scale) concentration (from 0.001 to 100 mg/kg).

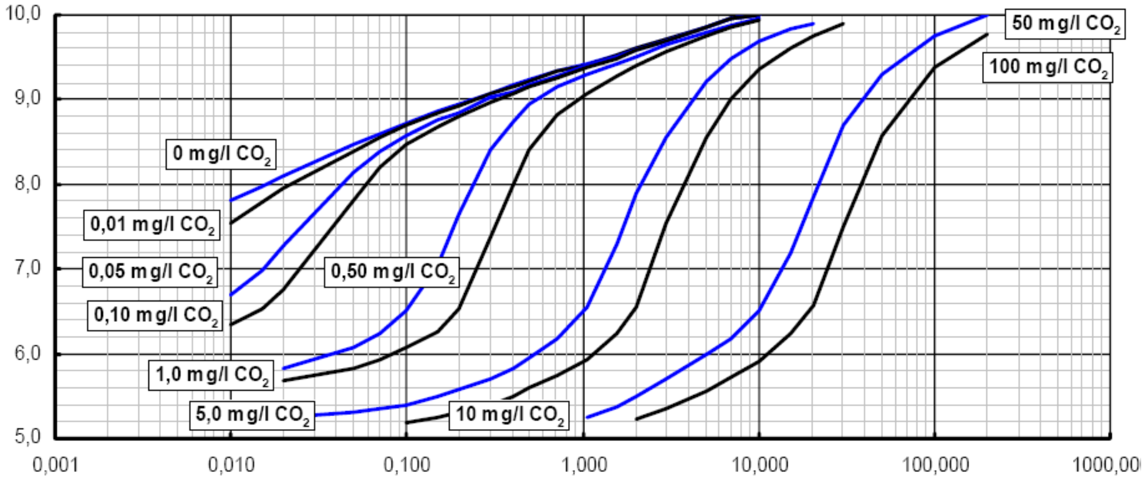

Figure A.18. pH at 25 °C versus ammonia (log scale 0.01 to 100 mg/kg as NH_4) for various CO2 concentration (0 to 100 mg/kg).

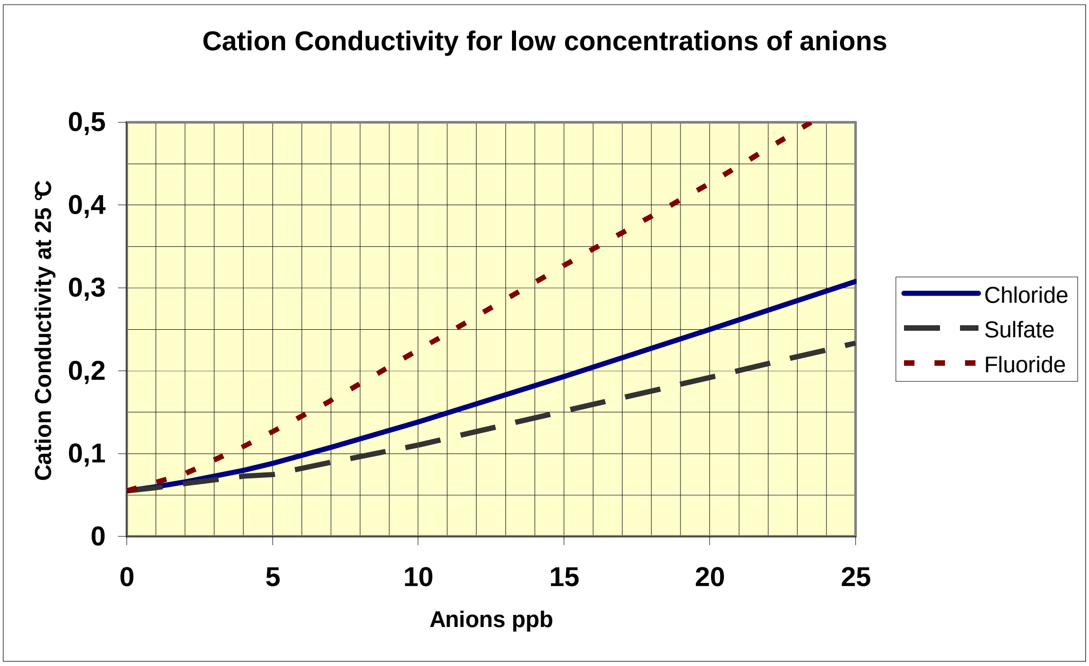

Figure A.19. Cation Conductivity at 25 °C for low concentrations of "strong" anions (Cl, SO_4 and F from 0 to 25 µg/kg).

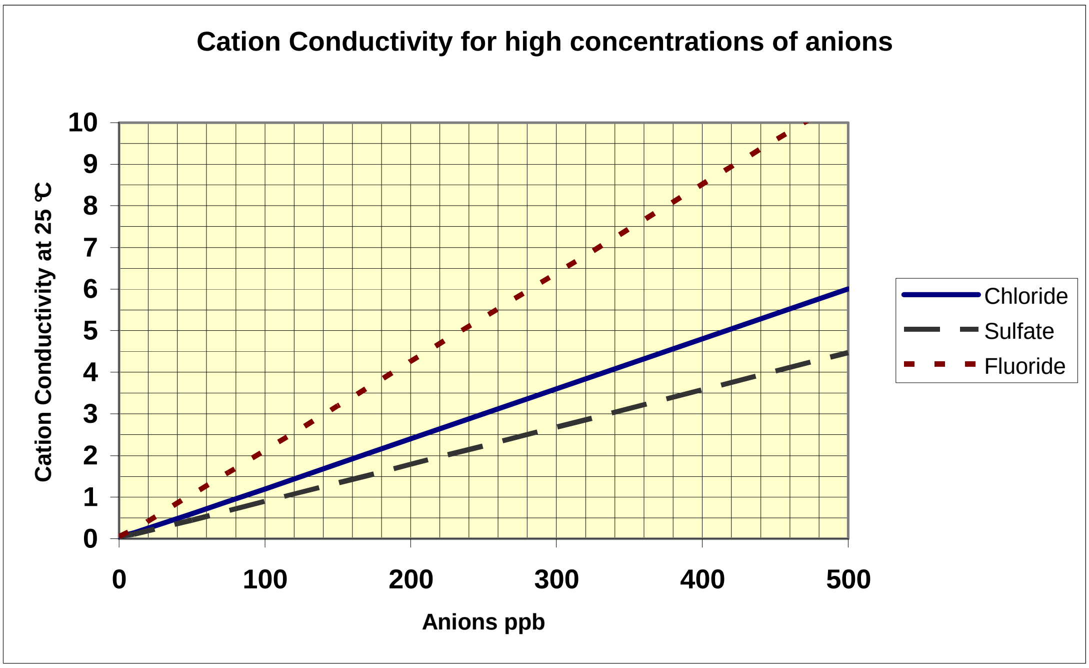

Figure A.20. Cation Conductivity at 25 °C for high concentrations of "strong" anions (Cl, SO_4 and F from 0 to 500 µg/kg).

Appendix A3. Chemicals and Ion Exchange Resins Quality

Quality of chemicals (reagents used for the treatment) and ion exchange resins (used for system purification) are important for two reasons:

- Achieving the function is it expected for,
- Keep the system purity high enough without bringing unacceptable quantities of impurities.

As far as the chemical reagents are concerned, the first point is generally achieved without difficulty and the second point is also easily achieved in most cases, with the only consequence that the price of the chemical will depend on the specified purity.

This is why it is important to define what is the required purity according to the species potentially present and that may have an impact on the corrosion of components material or, for the primary coolant also on other constraints such as impurity radio-activation.
Then, the chemical selection will be quite easy to do.

For the Ion Exchange Resins (**IER**), the impurity limitation is of several types.

- Manufacturing quality including rinsing should be such that the rinsing time and volume of water when the new IER batch is put in service are compatible with the expectations otherwise, time loss, potential unavailability, corrosion risk and liquid wastes will be unacceptable;
- Impurity content will be low enough to avoid release of undesirable species during operation.

Then, IER manufacturing characteristics should also mitigate pollution risks during operation. This mainly means that:

- the resin diameter should be specified in such a way that any resin fine release is avoided, either directly during operation or in case of regeneration;
- the resin characteristic will be such that the IER stay stable during operation without unacceptable species release, (e.g. highly corrosive sulphur compounds).

Finally, the resin characteristics selection will be a critical decision with various impacts on:

- IER efficiency should match the various purposes, such as, according to the system, impurity elimination for avoiding corrosion (e.g. chloride, sodium) or for radioactivity mitigation (e.g. silver, cobalt, iodine);
- In a few cases, the IER bed is only aimed at eliminating a large quantity of chemical present in the system, such as boric acid or alkali in the primary coolant instead of diluting the water;
- IER duration with the expected performance should be sufficient; the main duration limiting factors are purification efficiency, decontamination factors or of pressure drop. Purification may depends on the total exchange capacity of the IER but not only and a higher capacity does not necessarily mean a higher duration. The duration of IER also depends on specific performance of the resin type and of its initial purity.

Consequently, for the resin selection, the initial purity and total capacity are not the only characteristics to take into account. The resin price versus type (macroporous or gel), potential performances (ability to eliminate during the highest possible time some specific chemical or radiochemical elements), mechanical resistance (keeping the pressure drop low enough) are of great importance. In addition to total capacity, ion bed size and distribution size, the other important characteristic of the resin is the rate of divinylbenzene (DVB) cross-linking.

A high DVB rate allows a better mechanical resistance of the resin and, although it increases the resin cost, it may also increase the resin duration.
Within the specified value, the resin selection will be a compromise of the ratio “resin price / resin duration” for the required efficiency.

For example, if the blowdown resin is expected to operate under saturated form with morpholine or ethanolamine, it will be better to select a macroporous IER which has a higher affinity for sodium as compared to the amine. The resin duration before regeneration or replacement (in absence of regeneration) will be higher and will compensate for the higher cost of the resin. On the contrary, under ammonia treatment, a gelular type IER will be sufficient since the improvement of a macroporous IER may not balance its higher cost.

For the primary coolant, the resin selection will depend on many parameters such as the type of radioactive elements to be eliminated or the duration limitation for other criteria.

Generally speaking, the following criteria should be selected:

- Sufficient exchange capacity
- Polystyrenic skeleton (and not formophenolic) for a better mechanical and thermal resistance
- Regular granulometry of beads to avoid any risk of resin fines into the circuit
- Nuclear grade resins for a better purity, a lower rinsing necessity and a lower risk of manufacturing defect for any system in connection with the primary or secondary system and most of the resins except those for the demineralised station
- Resin already in the H^+ or OH^- form ready to use (except for the purification bed of the primary coolant which may be provided already saturated with the alkali reagent to avoid any risk of excessive concentration and pH variation in the primary coolant).

The tables in A.2.2 only relate the Nuclear Grade Ion Exchange Resins for Primary and Secondary systems.

A 2.1 Chemicals Purity

The proposed tables of chemicals are mainly based on 2 criteria

- The overall content of the chemical itself should be sufficient, in most cases close to 100 %, unless for some reason (eg hydrazine) it is provided with a known proportion of water;
- The impurities content is below what is acceptable. Two kinds of impurities may be specified
  - ➢ Those that may be present due to the manufacturing process and that are specified to guarantee a high quality product;
  - ➢ Those that may be specifically deleterious for the operation of the plant (for corrosion or radio-activation).

- But this does not mean that all the possible impurities are specified and that the total of potential impurities + main compound = 100 %

Boric acid H_3BO_3

Parameter	Unit	Limit
H_3BO_3	%	> 99.5
Sodium Na	mg/kg (weight)	< 10
Chloride Cl	mg/kg (weight)	< 1
Sulphate SO_4	mg/kg (weight)	< 5
Phosphate PO_4	mg/kg (weight)	< 5
Iron Fe	mg/kg (weight)	< 2
Heavy Metals as Pb	mg/kg (weight)	< 5

Potassium Hydroxide KOH

Parameter	Unit	Limit
KOH	%	> 85
Carbonates as K_2CO_3	%	< 1
Heavy Metals as Pb	mg/kg (weight)	< 20
Iron Fe	mg/kg (weight)	< 5
Silica SiO_2	mg/kg (weight)	< 20
Chloride Cl	mg/kg (weight)	< 40
Sulphate SO_4	mg/kg (weight)	< 20

Lithium Hydroxide LiOH

Parameter	Unit	Limit
LiOH	%	48-52
Water H_2O	%	42-52
Li 7 isotope / total Li	%	> 99.9
Lead Pb	mg/kg (weight)	< 10
Mercury Hg	mg/kg (weight)	< 0.5
Chloride Cl	mg/kg (weight)	< 1000
Fluoride F	mg/kg (weight)	< 1000

Ammonia NH_4OH, H_2O in water solution (Impurity level corresponding to a 25 % solution)

Parameter	Unit	Limit
Chloride Cl	mg/kg (weight)	< 2

Sulphur (total) SO_4	mg/kg (weight)	< 10
Iron Fe	mg/kg (weight)	< 10
Heavy Metals as Pb	mg/kg (weight)	< 10
Insoluble in water	mg/kg (weight)	< 150

Morpholine C_4H_9NO

Parameter	Unit	Limit
Morpholine C_4H_9NO	%	> 99
Chloride Cl	mg/kg (weight)	< 50
Sulphur (total) SO_4	mg/kg (weight)	< 10
Iron Fe	mg/kg (weight)	< 50
Heavy Metals as Pb	mg/kg (weight)	< 10
Insoluble in water	mg/kg (weight)	< 500

Ethanolamine C_2H_7NO

Parameter	Unit	Limit
Chloride Cl	mg/kg (weight)	< 10
Sulphur (total) SO_4	mg/kg (weight)	< 10
Iron	mg/kg (weight)	< 50
Heavy Metals	mg/kg (weight)	< 10
Insoluble in water	mg/kg (weight)	< 200

Hydrazine-hydrate $N_2H_4 . H_2O$ in water solution
(Impurity level corresponding to a solution of 64-72 % N_2H_4 , H_2O)

Parameter	Unit	Limit
Chloride	mg/kg (weight)	< 50
Sulphate	mg/kg (weight)	< 50
Sodium	mg/kg (weight)	< 5

Sodium Hydroxide NaOH, H_2O in water solution

Parameter	Unit	Limit
NaOH	%	> 45
Water H_2O	%	balance
Chloride	mg/kg (weight)	< 5
Sulphate	mg/kg (weight)	< 25
Iron	mg/kg (weight)	< 50

Heavy Metals (as Ag)	mg/kg (weight)	< 5

Sulphuric acid H_2SO_4

Parameter	Unit	Limit
H_2SO_4	%	> 92
Iron	mg/kg (weight)	< 200
As	mg/kg (weight)	< 50
Sulphite SO_2	mg/kg (weight)	< 200
Residue	mg/kg (weight)	< 500
Heavy Metals (as Pb)	mg/kg (weight)	< 200

Nitric acid HNO_3 (Impurity level corresponding to a 45 % solution)

Parameter	Unit	Limit
Chloride	mg/kg (weight)	< 5
Sulphate	mg/kg (weight)	< 20
Iron	mg/kg (weight)	< 3
Sodium	mg/kg (weight)	< 100
Heavy Metals (as Pb)	mg/kg (weight)	< 0.2

A 2.2 Ion Exchange Resin Nuclear Grade Quality for Primary and Secondary System

Cation Ion Exchange Resin

Parameter	Limit Value
Size of Resin Bead	0.4 to 1.25 mm > 80 % of beads between 0.4 and 1 mm
Total capacity	> 1.7 eq/L
Percentage active sites (H^+)	> 96 %
Osmotic Stability	> 96 %
Sodium	< 60 mg / kg of dry resin
Chloride	< 1.5 mg / kg of dry resin

Anion Ion Exchange Resin

Parameter	Limit Value
Size of Resin Bead	0.4 to 1.25 mm > 80 % of beads between 0.4 and 1 mm
Total capacity	> 0.9 eq/L
Percentage active sites (OH^-)	> 95 %
Osmotic Stability	> 92 %
Chloride	< 200 mg / kg of dry resin

Sulphates	< 600 mg / kg of dry resin
Silica	< 100 mg / kg of dry resin
Sodium	< 20 mg / kg of dry resin