- Adjust the concentration of hydrogen and lithium in the primary coolant, based on the type of outage targeted;
- Reduce as soon as possible the activity concentration of the primary coolant by purification;
- Minimize the risk of surfaces recontamination out of the primary circuit neutron flux;
- Minimize the risk of material degradation of the primary circuit (corrosion);
- Facilitate planned interventions during outage, near the primary circuit and its adjacent auxiliaries (fuel handling, maintenance);
- Minimize the risk of personnel contamination by fission gas release in case of breach of the integrity of the primary circuit;
- Control environmental impacts;
- Manage the outage planning.

Depending on initial and final state, it would be possible to change from basic and reducing conditions to acid and oxidizing conditions. These modifications can lead to a number of risks that need to be taken care of, in particular:

- H2/O2 mixtures: ignition, detonation,
- Integrity of materials: corrosion,
- Radiation protection,
- Environment: radioactive and chemical effluents generation,
- Availability: outage duration extension.

To achieve the goals stated above, some parameters can be adjusted to optimize the chemical treatment of the primary coolant. It is essentially the pH (Li concentration) and redox potential (H_2 or O_2 concentration). Shutdown and restart transients lead to important changes of the physical and chemical parameters of the reactor primary coolant.

^{110m}Ag

^{110m}Ag can contribute to ≥ 90% of the total dose rates in these auxiliary systems, though it only contributes 5 – 15% of the total dosimetry. The indication of ^{110m}Ag contamination can impact the outage schedule, and may require additional control rod inspections and/or replacements.

Unlike other corrosion products for which dissolution is at the maximum concentrations during the oxygenation peak, silver dissolution shows a trend to go on after the effective oxygenation (dissolved oxygen concentration close to 1 mg/kg). The volumetric activity of ^{110m}Ag in the primary coolant stays at a low level (1-10_MBq/m3) due to the low silver solubility in a reducing medium. Activity increases to > 10 MBq/t indicate ^{110m}Ag contamination post-oxidation. During shutdown, in case of silver pollution, the observed levels of activity increase by several decades during and following oxygenation. These changes are most likely due to changes in solubility and transitioning from reducing to oxidizing conditions.

Generally, the silver peak activity appears 1 to 12 hours after the ^{58}Co peak. Table 8 gives further data about silver peaks for EDF fleet in the year 2000 during shutdown.

Comment [E17]: D Perkins – do you have more recent numbers or have they been about the same?

Table 8. ^{110m}Ag peak activity, 900 and 1300 MWe French Standardized plant series in 2000

Standardized plant series	^{110m}Ag average	^{110m}Ag maximum	^{110m}Ag minimum

900 MWe	1.47 GBq/ m^3	6.17 GBq/ m^3	0.07 GBq/ m^3
1300 MWe	0.16 GBq/ m^3	0.48 GBq/ m^3	0.04 GBq/ m^3

There is no clear correlation between the ^{110m}Ag activity peak and the other corrosion products. A first level of assessment can lead to consider that RCS is polluted when ^{110m}Ag peak during shutdown is higher than 0, 5 GBq/m^3 on primary coolant sample.

The observation of different and unpredictable behavior of silver, mostly measured by gamma-spectroscopy and particularly during different cold shutdowns, even in a same plant, seems surprising when the operation schedule seems stable. Measurements demonstrated that it is possible to decrease the steam generator channel head silver contamination and to increase CVCS exchanger contamination.

Depending on the chemical environment and physical properties (pH, redox potential, etc.) silver would be:

- In ionic form in solution, Ag (I) cation,
- In colloidal form.

Studies conducted by EDF outlined the essential simultaneous impact of redox potential, pH, and temperature on silver behaviour. Over a large range of pH (corresponding to the nominal operating conditions or to the shutdown ones at 300 °C, 80 °C and 30 °C), and in different locations of the RCS, CVCS and RHR, Ag(0) and Ag+ can be simultaneously found on thermodynamic stability diagram and are very sensitive to the redox variation and the concentration.

Comment [p.18]: **"Impact of Main Radiological Pollutants on Contamination Risks (ALARA) Optimisation of Physico Chemical Environment and Retention Technics during Operation and Shutdown", A. Rocher and al, ISOE Symposium, Portoroz, 2002**

On the opposite, pH is determinant on colloids behaviour. Electrostatic repulsion between them is the lowest at the iso-electric point, i.e., at the pH for which the zeta potential is zero. However, the kinetic behaviour of silver under primary coolant conditions is not well understood.

Thus, optimization of its removal is difficult, with preferential deposition of ^{110m}Ag taking place in "cold points" of the auxiliary systems exchangers, where the thermal gradient is important. This also may elucidate the apparent degrading conditions of the purification. The goal will become to manage the silver so as to transport it in a form removable by the purification system.

Shutdown purification

During oxygenation, antimony is not retained on a 0.45 μm filter and therefore is considered to be dissolved. When antimony pollution occurs, the reactor coolant lithium content has to be lower than 1 ppm in order to improve purification by the ion exchange resins. In order to obtain acidic conditions, purification is completed using the non-saturated lithium cation bed demineralizers of the Boron Recycle System. Nevertheless, it should be noted that an acid-oxidizing reactor coolant seems to increase antimony deposition on the primary circuit surfaces. This is likely related to presence of antiminates and their interaction with positively charged oxide surfaces.

As for silver behaviour, to deal with antimony pollution, operators face some difficulties related to the different physical and chemical conditions of the RCS and the auxiliary systems. Except for removing the root cause, the objective consists in the optimization of the chemical form of the antimony to enable the purification line to remove it.

^{110m}Ag purification is performed on a dedicated ion exchanger operating at the maximum possible flow rate. During shutdown, when the filters are replaced, purification must not be suspended. Filters consistent with colloid removal are required (lower mesh with zeta-polarised filtration medium). Thus, silver removal is improved and downstream resin pollution may be avoided (poisoning by colloids). If the upstream filter is not redundant, the filter replacement must lead to reduce by half the CVCS flow rate purification to minimize resins pollutions. The background and the resin features show that macro porous mixed-bed would be the most adapted for soluble silver and silver colloids. The pressure drop must be specially monitored.

Comment [HBO19]: Reference??
The reference will be provided by Alain.

To be followed up with Alain. 7/12/2013

Until now, the feedback demonstrated that withdrawing lithium from the primary coolant with a non-lithiated mixed bed ion exchanger during shutdown, resulting in a lower pH, improves the silver removal efficiency. Without fuel cladding failure, lithium can be eliminated starting from the rods drop.

Antimony

Comment [E20]: To be reviewed based on current EDF values and practices.

Committee – 7/12/2013

In some French PWRs, ^{122}Sb and ^{124}Sb volumetric activity peaks have been observed, at various times with peaks higher than ^{58}Co peaks (Table 9). These two radionuclides compound dosimetry measurements and produce difficulties with waste processing management. ^{122}Sb and ^{124}Sb are two multi gamma emitters with radioactive half-lives of 2.7 days and 60.2 days, respectively. Though released in higher concentrations, ^{122}Sb with a short radioactive half-life has minimal impact on radiation fields to workers, but provides staff with the ability to use in source determination.

Table 9: Mean and maximum volumetric activities encountered at the oxygenation peak on the EDF fleet (1995-2007)

Standardized plant series	Values	^{122}Sb (MBq/m^3)	^{124}Sb (MBq/ m^3)	^{58}Co (GBq/ m^3)
900 MWe first series	Mean	6	5	224
	Maximum	8	8	460
900 MWe	Mean	7	6	113
	Maximum	24	19	550
1300 MWe	Mean	14	13	146
	Maximum	136	137	240

Two major sources have been identified in the PWR fleet:

- Pumps bearing wear in the Boron Recycle System, where the bearings are graphite impregnated with ~10 % antimony;
- Secondary Start-up Sources: In some cases, PWRs utilize a secondary start-up source to produce neutrons for reactor start-up. These sources are composed of an antimony-beryllium source encased in stainless steel and used over several cycles and then replaced, as required, for subsequent cycles. These start-up sources are composed of ~50-50% beryllium-antimony, respectively.

A few grams of activated antimony can explain such peaks of ^{122}Sb and ^{124}Sb. Calculations demonstrate that about 7 grams can lead to a ^{124}Sb peak of 100 GBq/ m^3. The important antimony released activity has an impact both on dosimetry and waste management. ^{124}Sb deposited activities on out-of-core surfaces increase significantly as shown in Table 10.

Table 10: RCS recontamination after a ^{124}Sb peak of 70 GBq/ m^3

^{124}Sb (GBq/m²)	Before H_2O_2	After H_2O_2 injection
Hot leg	0.29	1.02
SG tubing	0.32	0.95

As a result, ^{124}Sb contribution to the total dose rates can reach 10 % in some parts of circuits. And the dosimetry for maintenance during a plant shutdown can increase to about 5 % because of ^{124}Sb contamination.

EDF studies, elaborating pH-Potential diagrams at normal operating conditions (300 °C) and at forced oxygenation conditions at 80 °C confirmed the behaviour observed on plants. It seems that, under nominal conditions at 300 °C, metallic antimony is likely more stable in aqueous reducing medium. For shutdown conditions at forced oxygenation, it seems that the more stable species is at the limit of the SbO_3^- area in aqueous solution. Eliminating antimony as well as possible becomes easier in this zone.

Preventive strategy

To avoid antimony pollution, the incriminated pump bearings have been replaced by antimony free pump bearings. As indicated in the table below (Table 11), this allows making the ^{124}Sb peaks decrease.

Table 11: Bearing replacement consequence during the 14th cycle

Cycles	13	14*	15
^{124}Sb (GBq/m^3)	100	60	20

3.3.3 Water-Water Energetic Reactors (VVERs)

The Russian designed VVER is similar yet, very different compared to other PWR designs. The distinguishing or key design differences compared to other OWR designs include the usage of horizontal steam generator tubes (stainless steel), application of hexahedral fuel assemblies, and a high capacity pressurizer for safety.

The horizontal steam generator tubing applies stainless steel compared to the application of Inconel™ 600, 690, and 800 in the steam generators, thereby minimizing the corrosion product source term for activation. Figure 14 captures an overview of the VVER primary circuit layout. The VVER materials result in excellent corrosion product behaviour, which in turn produces lower circulating nickel and cobalt concentrations and low ^{58}Co and ^{60}Co surface activities. These lower activities provide the basis for the lower dose rates or source term.

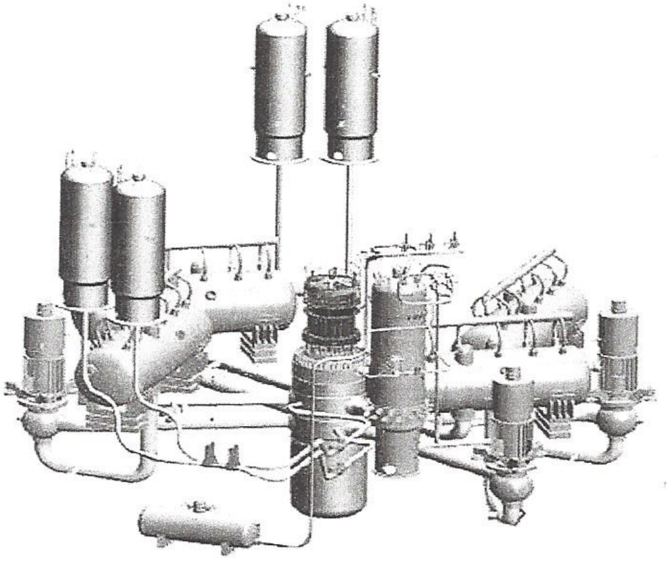

Figure 14: Genric VVER Priamry Circuit Layout

Comment [E21]: Added this figure – if you like we will keep, if not we can delete.

Reference: Development of the NPP Designs Based on the VVER Technology, Asmolov, VG, Russian Federation, September 2009, Paris, France

Primary chemistry controls are slightly different compared to the other PWR fleet units. PWRs, previously described utilize lithium-7 hydroxide to maintain a slightly alkaline environment with hydrogen applied through makeup tanks or the volume control tank. The VVER fleet applies potassium hydroxide to support the primary circuit pH goals with ammonia and hydrazine decomposition to support hydrogen production. Section 3.3.3 provides an overview of the VVER considerations.

3.3.3.1 pH Control

Primary chemistry specifications represents a standard part of fresh fuel delivery documentation and was elaborated by Kurchatov`s Institute in Moscow. The specifications for most of the parameters are very similar to those for PWRs. Some key primary chemistry differences are listed below:

- Potassium is used for pH control instead of lithium - this results in a less restrictive startup chemistry and allows to a more favorable $pH_{(T)}$ to be reached. Therefore, CIPS risks are much lower, and when occurred they were rather consequences of primary equipment decontamination as discussed later

- Ammonium hydroxide is used to generate hydrogen in the primary coolant instead of injecting gaseous hydrogen. This gives rise to some difficulties in maintaining a stable $pH_{(T)}$ as ammonia competes with potassium on the primary clean-up cation resin. The role of ammonia in the reduction of dose rates is still not well understood.
- Full primary pressure ion-exchange clean-up system (VVER-440) is used with additional primary clean-up system capacity on the feed and bleed system
- High temperature, high flow filters loaded with porous (sponge) titanium (VVER-1000) - these filters definitely remove significant activity from the primary coolant but the need for their regeneration in the case of exhaustion/saturation was not foreseen by the design. Some wash-out processes have already been tested in Russian reactors.

Within the primary chemistry standard, the specification of the potassium - boron relationship was originally specified as shown in the Figure 15 and 16 - blue boundaries. The latest version of the boron - potassium chemistry specification - see violet boundaries in both figures, is very similar to current PWR specifications and allows higher $pH_{(300^\circ C)}$ values at the cycle beginning, but also reflects the different primary system construction materials [8].

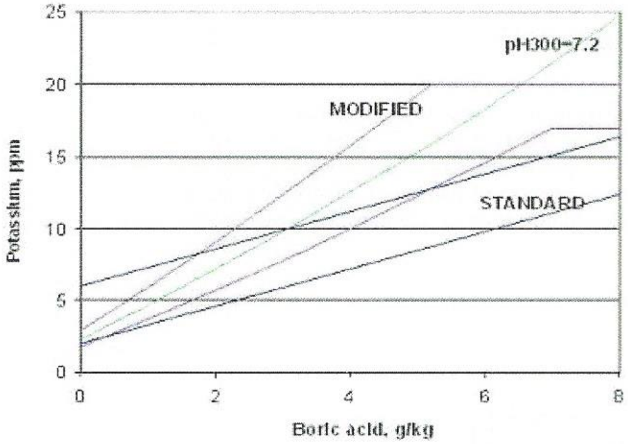

Figure 15. Boron/potassium co-ordination for the standard and modified/updated water chemistry of VVER-440 units

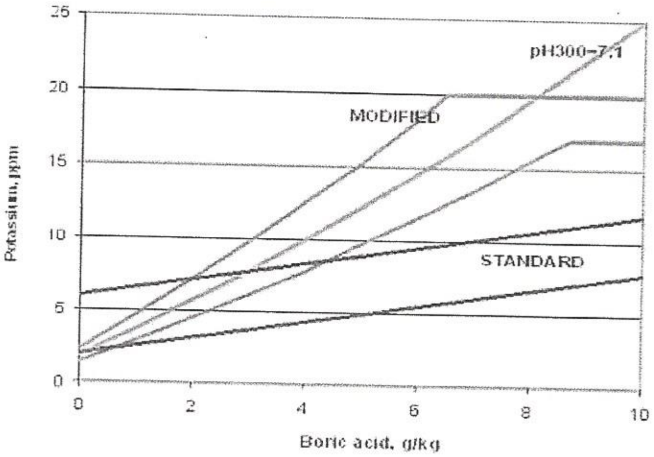

Figure 16. Boron/potassium co-ordination for the standard and modified/updated water chemistry of VVER-1000 units

From the very beginning of this type reactors operation, the standard specifications lead to low pH$_{(300°\,C)}$ values at the beginning of cycle and allowed relatively high pH$_{(300°\,C)}$ values at the end of cycle. There were also several temporary standards developed in the 1990's and some non-Russian plants have introduced their own specifications approved by the nuclear regulatory authority. Modified or updated chemistry in this regard brought boron-alkali coordination to a comparable status as for PWRs.

An example of the actual pH$_{(300°\,C)}$ during a cycle with standard and modified boron-potassium coordination is shown in figure 17.

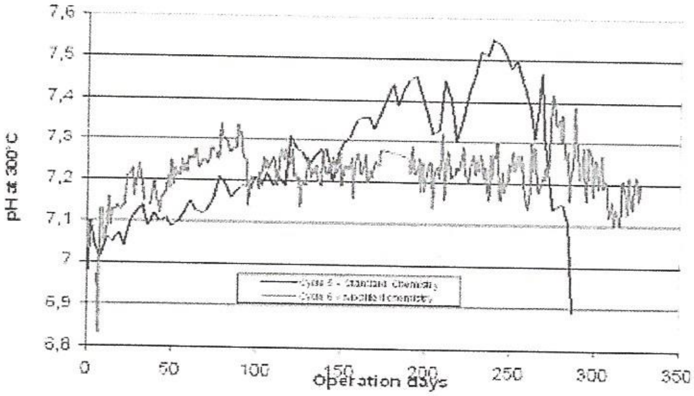

Figure 17. Example of typical pH$_{(300°\,C)}$ for the standard and modified water chemistries during the reactor cycle (VVER-440 unit) [8]

Despite several analytical studies and also experimental work performed in the recent past, the role of some primary chemistry factors in the build-up of radiation fields has not yet been clarified. Usually several factors contribute concurrently to corrosion and corrosion product transport processes, such as boron -potassium control mode, ammonia concentration, hydrogen concentration, makeup and clean-up system operation modes, various shutdown practices, HFT passivation process and, in recent years, power uprating. There is no systematic database of the VVER fleet that allows a comprehensive evaluation of chemistry and operating practices, and therefore no clear identification of positive factors can be easily made. The role of the following chemistry factors has been investigated:

Ammonia/hydrogen

The ammonia concentration has to be maintained to assure a specified concentration of hydrogen. Depending on the primary makeup operation mode (rate of makeup flow/primary coolant degassification), the desired concentration of hydrogen can be achieved with an ammonia concentration in the range 5-50 ppm as shown in the Figure 18.

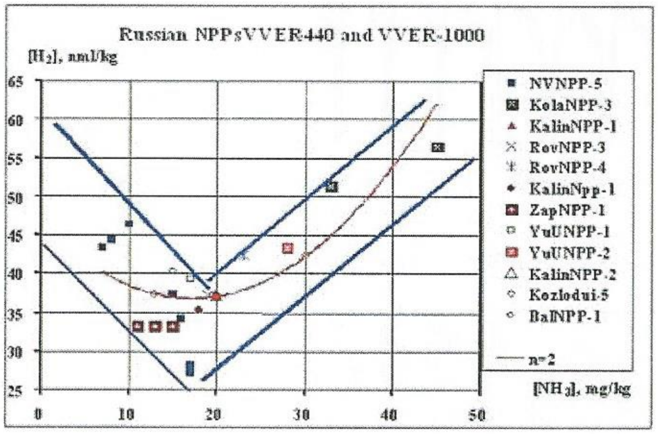

Figure 18. Hydrogen/ammonia ratio at Russian NPPs with reactors VVER-440 and 1000 [8]

As use of ammonia brings some problems in liquid radioactive waste processing at VVER units, there is an on-going effort to minimize its concentration either by minimization of primary coolant degassing or by replacement of ammonia by gaseous hydrogen injection as is done at PWRs.

VVER operators are using various ammonia/hydrogen approaches: low constant ammonia, high constant ammonia or variable ammonia with high concentration at the cycle beginning to moderate/low ammonia at the end of cycle (this mode is used to control the potassium concentration). The hydrogen concentration can vary without clear link to ammonia based on primary coolant degassification rates.

As an example, the history of NPP Bohunice unit EBO-3 primary chemistry and primary loop surface activities is shown in Figure 19. Here it can be seen that the transition from low ammonia / hydrogen in years 2000-2006 to variable ammonia since 2007 did not influence primary loop surface activities (or this effect cannot be clearly identified because of the complex factors and environment).

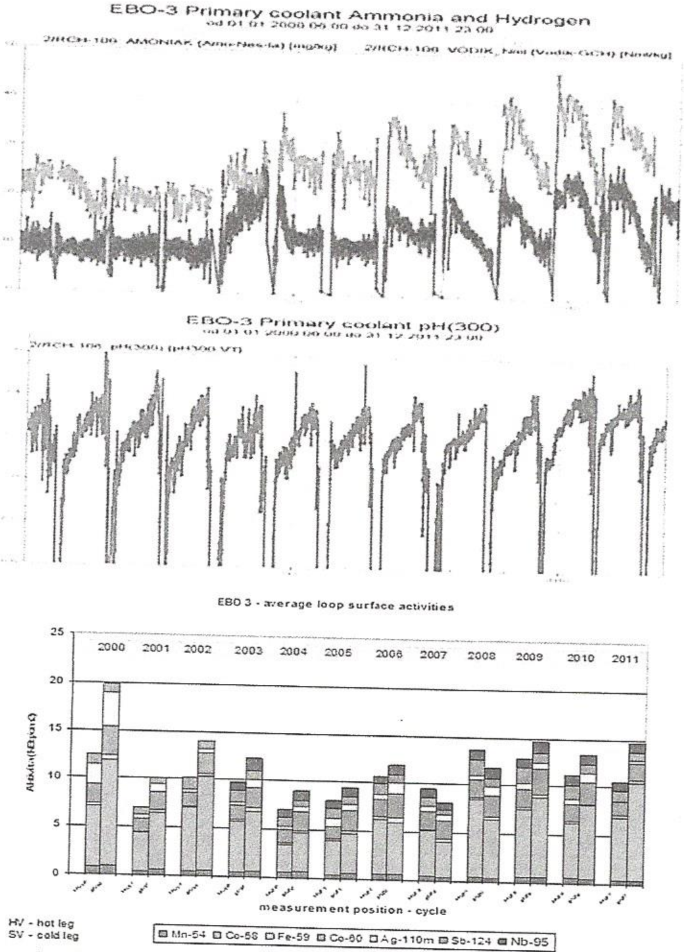

Figure 19. Primary chemistry and primary loop surface activities history of VVER-440 unit EBO-3

In order to test the influence of ammonia in the primary coolant, low and high ammonia comparative tests have been performed at the experimental loop facility in NRI Rez in Czech Republic in the years 2003-2006 [9].

Based on results of these tests showing positive effect of high ammonia, a plant trial was performed at the unit Dukovany-4 (VVER-440) during three cycles and later on at Dukovany-3 during two cycles [10]. As shown at following picture primary loop surface activities increased during after two cycles at both units and then slightly decreased after the third cycle at Dukovany-4, but significantly decreased after the following cycle with return to normal ammonia values, so the influence of ammonia concentration when evaluated individually seems inconsistent.

A specific type of high hydrogen, high ammonia chemistry involves injection of hydrazine, which had been first tested at the Russian Kola NPP [Pashevich V.I. Thermal Engineering 31 (11), 595, 1984, Pashevich V.I. Thermal Engineering 32 (11), 29, 1985] and later tested or implemented at tother plants including NPP Paks in the 1990s. This chemistry was based on continuous injection of hydrazine into the primary coolant and it was aimed at removal of rough outer oxide layers and the creation of a compact smooth protective oxide layer with reduced corrosion product deposition. One of the observed side effects was a significant increase in radiation fields during the first outage as the primary clean-up system was unable to remove all the mobilized corrosion products. As a result they were redistributed throughout the entire primary circuit, also causing problems with reactor protection cluster absorbers mobility. As hydrazine chemistry is also accompanied by high ammonia and hydrogen concentrations, the effect of hydrazine cannot be easily and clearly distinguished from those of ammonia and hydrogen. Moreover, at some plants like NPP Paks, its effect has been combined with other operational influences (variation of $pH_{(300° C)}$ which made evaluation even more difficult. As hydrazine chemistry results were not convincing there is a declining tendency for use at plants where it is still being used.

Potassium - Boron ratio or $pH_{(300° C)}$

As mentioned above two basic specifications exist, so comparison of results with the old and updated relation can be made to assess the influence of this parameter on dose rate build-up processes. Such an analysis was made for the Slovak NPP Bohunice units EBO-3 and EBO-4. In this analysis, the influence of $pH_{(300° C)}$ on start-up, mid cycle and pre-shutdown periods was studied [11] . In this work, the results did not identify consistent positive feedback of keeping minimal deviation of $pH_{(300° C)}$ from value 7.2, but as mentioned above, due to several overlapping factors identification of simple parameter role is very difficult as can be seen in Fig 20 and Fig. 21. On the other hand, a recent comparison of $pH_{(300° C)}$ data for "best" and "worst" cycle (by surface activities) within the period 2006-2012 shows that there is a potentially negative impact of high $pH_{(300° C)}$ in the last period of the cycle to the dose rate build up due to increased ^{58}Co surface activity, as demonstrated in Fig 21 and 22.

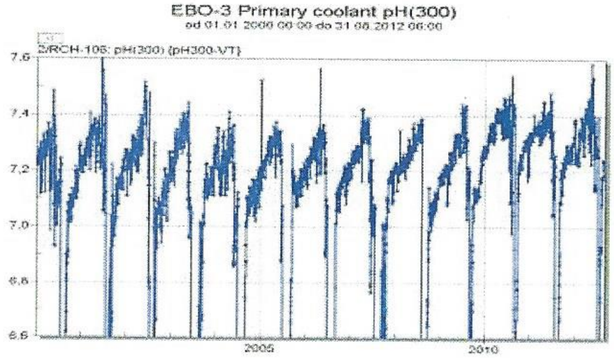

Figure 19. NPP Bohunice Unit EBO-3 Primary coolant pH (300)

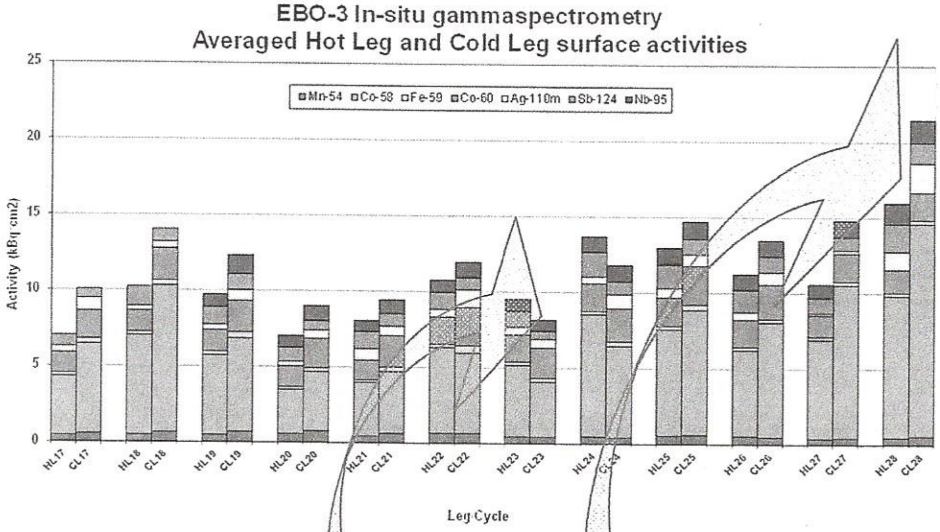

Figure 20. NPP Bohunice Unit EBO-3 Primary surface activities

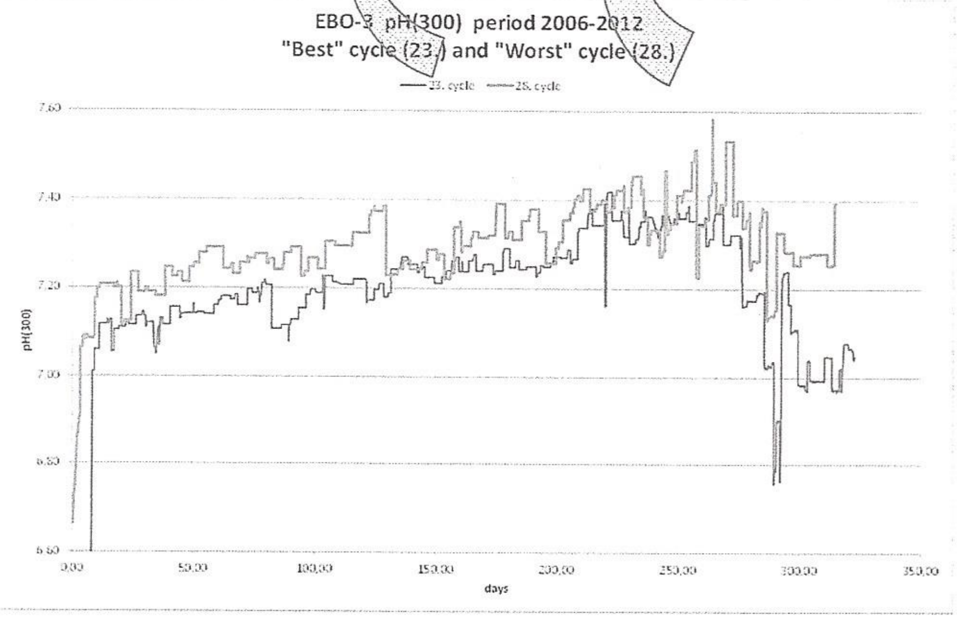

Figure 21. NPP Bohunice Unit EBO-3 Comparison of primary coolant pH (300)

3.3.3.2 Zinc injection

Mainly due to differences in material concept discussed in Chapter 3.3.2.1 which leads to much lower cobalt isotope activities, the need for zinc injection technology is less pronounced at VVERs. That is reason why there is no real experience with zinc injection at VVER units at present. Some theoretical studies are on-going and loop tests performed by NRI Rez have demonstrated the potential for dose rate improvement for VVER -units [9]. Zinc injection is not recommended for operating VVER-1000 units due to the risk of cobalt washout from the titanium sponge high temperature filters.

Comment [IS22]: There is very limited work done and published on this topic for VVERs. Another possible reference is

Svarc. V et al Minimisation of corrosion product deposition risks by primary water chemistry optimisation, NRI Rez Report No. Z1698, 20061

but this is a source for reference 9.

Comment [WD23]: This is a very interesting comment and likely limits the ability of VVER's to use zinc.

Isn't there NRI work on this subject. Could we provide a summary of that work here if it is available?

4th meeting
Will be checked by Ivan for further references
I am afraid - probably no reference with compiled experience

Yes, the committee agrees with the note. Comment resolved – 7/12/2013

3.3.3.3 Shut down and start-up operations

Similarly to PWRs, the major pollutants responsible for over-contamination are:

- $^{110\,m}$Ag, the origin of which is still not satisfactorily resolved - it may come from materials like welds, solders, various seals; or even as an impurity in chemicals such as ammonia, potassium hydroxide
- ^{122}Sb / ^{124}Sb coming from seals of various pumps - at Loviisa NPP, one of the most important sources is the graphite seals of the Main Coolant Pumps, where the content of antimony is > 25%.

Depending on the plant their overall input to dose rates varies from fraction of a per cent to tens of per cent as shown later, and correspondingly, various targeted mitigation strategies are implemented.

When the shutdown process is considered it can be mentioned again that, mainly due to the much lower cobalt radioisotope activity, there is no need for forced oxygenation during shutdown and shutdown practices are much less developed and unified at VVER units when compared to PWRs.

Many plants developed their own procedures including early hydrogen removal and conversion to acidic primary coolant conditions by removal of potassium from the coolant, but some plants are also using coordinated pH chemistry, injecting potassium during primary coolant boration in order to minimize mobilization of highly active in-core deposits. None of implemented procedures has been found to result in an undisputable positive effect in radiation fields reduction so far and there are still studies underway focused on this subject.

Startup chemistry play also important role in deposit formation as discussed previously. There is general consensus on the need to reach $pH_{(T)}$ close to 7,0 as soon as possible after startup. At VVER plants this is often influenced by primary cleanup resin replacement. ~~When fresh resins are loaded,~~ ~~c~~Cation resins are converted ~~have to be converted~~ into ammonia-potassium ~~cycle~~ form during startup. This ~~and this~~ conversion is ~~.~~ made by multiple injections of potassium-ammonia into the primary circuit that may ~~, may~~ ~~bring~~ delay ~~in~~ reaching the desired pH for up to 2 weeks. ~~Nevertheless, a~~A study performed at NPP Bohunice did not identify a clear influence of the startup chemistry on the primary loop surface activities [11].

Comment [WD24]: The following questions come to mind and we may want to explain them in the section.

did they operate the fuel with a pH(T) of < 6.9 for extended times? If yes, did they see any differences during these cycles?

Not really extended time (one to two weeks)- time to reach pH(300) >7 is still being shortened
4th meeting
Ivan will be in touch with Dan for clarification

HFT passivation

Hot functional test (HFT) passivation was understood to have significant role in future dose rate buildup, so this process was more closely monitored and controlled in recently commissioned reactor units. There is a very clear demonstration of the influence of the quality of HFT passivation on primary loop surface activities from Slovak NPP Mochovce experience as shown in Fig. 23, where a systematic difference between the two units remains remarkable over long operational period [12].

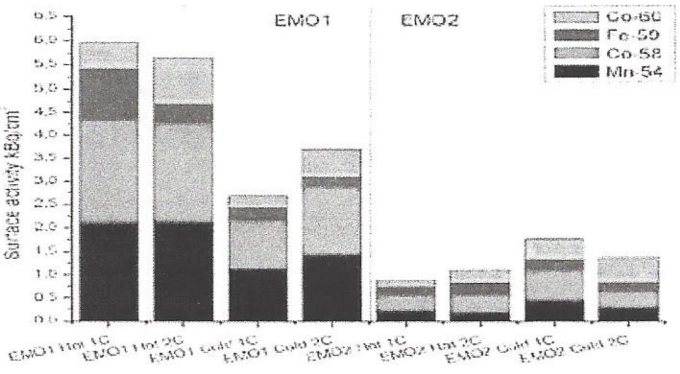

Figure 23. Surface activities measured after first and second cycle of Mochovce-1 (partial HFT passivation) and Mochovce-2 (good HFT passivation)

3.3.3.4 Purification

Last vintages of VVER-440 reactors are by design equipped with full pressure primary coolant purification in two parallel cleanup systems, one with mixed bed filter and second with separate cation and anion filters with a design flow of 20 m^3/h. These two systems are used in different ways by various VVER operators, some of them switching between them in subsequent cycles, some of them operating both all the time. The cation resins in these systems are working in an ammonia/potassium cycle and therefore they are buffering any changes of potassium and ammonia concentration in the primary coolant

In addition, the primary feed and bleed purification system is available with separate cation and anion filters and a design flow of 40 m^3/h. This system is mostly used for potassium and boric acid removal and during the reactor shutdown process for corrosion/fission product removal. So far there has not been any reported consistent correlation of this clean-up system operation and radiation fields.

Advanced designs of VVER-1000 reactors are equipped with full pressure, full temperature filters filled with porous Ti particles - depending on design there are two to four such a filters powered by pressure drop of the MCP and working with a flow 100 m^3/h. These filters are removing corrosion products from primary coolant.

Similarly to VVER-440, the primary feed and bleed purification system is available with separate cation and anion filters and a design flow of 40 m^3/h. This system works permanently and specific filters are used for potassium and boric acid removal and during reactor shutdown process for corrosion/fission product removal.

3.3.4 Pressurized Heavy Water Reactors (PHWRs)

3.3.4.1 Chemistry

PHWRs have a separate moderator system for reactivity control so that the primary coolant does nt contain boric acid, leading to a much simpler primary coolant chemistry regime compared to PWRs and VVERs. The dissolved lithium concentration (pH_a) of the HTS is kept constant during normal operation and shutdown; pH_a is the pH measured in heavy water by a glass-membrane pH electrode that has been calibrated using light-water buffer solutions [Turner and Guzonas]. The control parameter for alkalinity during at-power operation is the Li^+ concentration to ensure that measurements of alkalinity are reliable. At high temperature the OD^- (OH^-) concentration is directly related to the concentration of dissolved Li^+ because LiOD (LiOH) is a strong base over the entire temperature range of interest and there is no boric acid. The concentration of OD^- (OH^-) controls the solubility behaviour of the HTS oxides.

The lower end of the Li^+ concentration specification is chosen to ensure a positive magnetite solubility dependence on temperature at all locations in the core, which keeps the core essentially free of deposits. There is a small amount of deposition on the inlet fuel bundles, but on-line refueling eventually shifts these inlet bundles further into the core, where the deposits dissolve at the higher temperatures. The data show that operation in H_2O with a pH (25°C) above 9.75, corresponding to a pH_a of about 10.2 (Li^+ concentration of 0.35 mg/kg) prevents deposition of corrosion products on fuel sheaths. The upper limit for pH_a was originally set to minimize carbon steel and Zircaloy corrosion, and to minimize activity transport. The discovery of flow-accelerated corrosion (FAC) of the carbon steel feeders at the outlet of the reactor core resulted in a decision to reduce the upper limit on pH_a [2] to 10.4. The majority of the dissolved iron in the CANDU HTS results from the FAC of the carbon steel feeders.

Based on extensive characterization of reactor artefacts [Husain and Krasnai; Miller and Burrill; Semmler et al.] the fundamental principles underlying activity transport in PHWRs is now well understood and can be modelled []. FAC of the carbon steel outlet feeders' releases dissolved iron into the primary coolant; the dissolved iron precipitates in the steam generators and inlet piping once the coolant temperature drops in the steam generators to a value at which the solubility of magnetite is less than the coolant dissolved iron concentration. Inactive parent isotopes released by corrosion of the piping or by wear (e.g., antimony in Sb-impregnated graphite pump seals and bearings) deposit in-core by precipitation, particle deposition and/or adsorption (e.g., antimony), are neutron activated, and then released by corrosion or wear and transported from the core. Circulating radionuclides are incorporated, essentially irreversibly, into this constantly growing magnetite film, giving rise to out-of-core radiation fields. The overall process is illustrated in Figure 24.

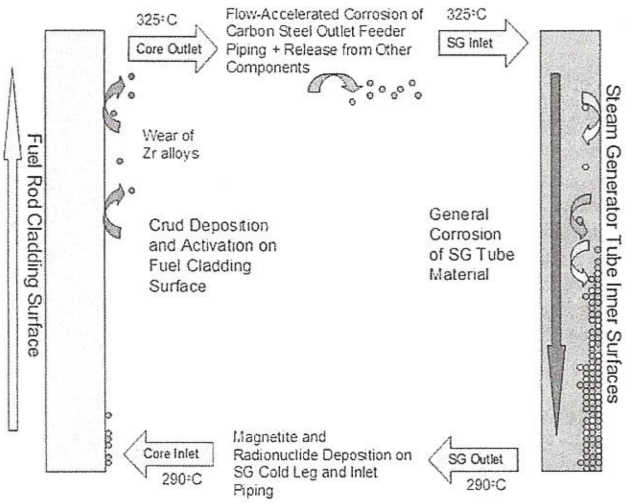

Figure 24. Processes involved in PHWR activity transport [Guzonas, 2010].

Radioantimony

Radioantimony contributes to radiation fields in CANDU stations mainly by acute releases due to Sb transients during shutdown. At the Canadian PHWR at Gentilly-2, acute release of ^{122}Sb and ^{124}Sb from in-core surfaces in the 1990s as a result of oxygen ingress during maintenance during shutdown adversely affected maintenance. At Gentilly-2, the antimony source was the site-specific use of Sb-impregnated carbon primary HTS pump seals and bearings.

Chronic build up of radioantimony fields on out-of-core surfaces is limited due the short half-lives of ^{122}Sb and ^{124}Sb, and the limited production rate of ^{125}Sb in the absence of fuel defects. However, while ^{122}Sb has only a 3 d half-life, it had been present in significant quantities at Gentilly-2 prior to the removal of the Sb-impregnated carbon bearings and the routine use of an antimony removal process, and could take a week or more to decay to low levels, significantly affecting outage maintenance work. For example, in 1993, the out-of-core radiation fields rose from 0.5 mSv/hr (50 mR/h) to 2.50 mSv/hr (250 mR/h) due to an Sb excursion.

An oxidizing antimony removal process developed by Siemens for PWRs was optimized for the CANDU HTS by Siemens, AECL and Gentilly-2 for the removal of in-core radioantimony [Dundar et al]. The process was routinely used at Gentilly-2 at the start of each maintenance outage until the station was shut down. In this process, H_2O_2 is added to the HTS coolant during shutdown to create oxidizing conditions in the coolant and force the mobilization of in-core Sb. The Sb released is easily removed by anion exchange resin.

3.3.4.2 Purification

Main Heat Transfer Systems

The main HTS purification system designs used in different CANDU plants are similar in basic concept but differ in implementation; in particular, whether the system is pressurized or not, and the number of ion exchange columns. A small fraction of the HTS coolant flow is diverted through the purification system, cooled, and then passed through mechanical filters followed by ion-exchange columns. The purified coolant is then returned to the main HTS. The design evolved from the early Nuclear Power Demonstration (NPD) design through the Douglas Point Nuclear Generating Station (DPNGS) system, which incorporated some of the improvements suggested by the NPD experience, in particular the requirement that the purification half-life be as short as possible. Ultimately, a purification system with a 2 hour half-life was installed at DPNGS to control radiation field growth due to ^{60}Co. Recommendations were made to further reduce the purification half-life, and current CANDU 6 designs typically operate with a purification half-life of about 1 hour. CANDU plants with low pressure purification systems operate with longer purification half-lives.

Gentilly-2 was the first CANDU plant to implement the use of submicron filters based on successful operating experience in the US and Europe. Following this successful implementation, Darlington NGS began a program to implement sub-micron filters, replacing the 1 μm filters in Unit 1 with 0.45 μm absolute filters in 2002 [Walker et al., 2003]. Measurements during the Unit 1 outage 6 months after installation of the 0.45 μm filter revealed a 20% decrease in fields inside the vault, and the station realized a 6-rem dose saving during the outage. None of the concerns expressed by the station at the start of the program (e.g., effectiveness, filter plugging, limitations for filter change-outs, and high differential pressure across the filters, purification system pressure increases, and future limitations for increasing purification flow) materialized. Since 2003/2004, DNGS moved to the use of a 0.1 μm filter as the in-service filter, with a 0.45 μm filter in the spare filter housing as a back-up. Wolsong Unit 1 changed the HTS purification filter cartridge from 6.0 μm absolute rating to 0.45 μm absolute rating in 2006 [Park, 2008]. The ^{58}Co concentration in the system decreased by 75% in the 19th plant outage as compared with the 14th outage and the ^{54}Mn and ^{95}Nb concentrations decreased by 9.8% and 6.2% respectively in the19th outage compared with the 18th.

3.3.4.3 Fuelling Machine

As discussed in Chapter 3.2.3, one of the main sources of ^{59}Co in a PHWR is the Stellite load balls in the fueling machines. Not all PHWRs have sufficient ion exchange capacity (some have none) in their fuelling machine purification circuits. Model calculations [Strikwerda et al.] suggest that, without ion exchange provisions, about 17 g/year of ^{59}Co enters the reactor system from each fuelling machine at the Darlington NGS. The majority of this cobalt is in particulate form with the balance being dissolved (in this case dissolved is defined operationally as any Co that passes through a filter of a particular mesh size). Most of the dissolved Co is generated from the surfaces of the ram balls, the remainder being from the surfaces of particles trapped on the filter. The potential reduction in cobalt ingress from ion exchange operation was estimated to be 21% or 3.5 g/year per fuelling machine. It was estimated that the net plant dose savings that would result from ion exchange operation over the period 2010 - 2022 would exceed 4.80 Sv, an installation of ion exchange purification capability in the heavy water auxiliary system was strongly recommended.

3.3.4.4 Hot Conditioning

Hot conditioning during reactor commisioning or after refurbishments is routinely used in PHWRs; [Venkateswarlu and Mathur, 1992], [Bose et al., 2006]. One of the objectives of this preconditioning is to produce an adherent, uniform and protective coating of magnetite on the carbon steel surfaces to minimize corrosion during operation. Bose et al. [2006] noted that preconditioning also reduces activity transport during reactor start-up, minimizing dose and minimizes carbon steel corrosion in the interim period between light water commissioning and final commissioning in Indian PHWRs. While such preconditioning provides a number of short term benefits and is recommended, preconditioning is not beneficial for reducing long-term activity transport because FAC of the outlet feeders supplies the majority of the Fe deposited in the SGs and at the reactor face.

3.3.4.5 Zinc

The addition of zinc to the CANDU HTS was to reduce activity build-up and corrosion of system materials was extensively studied in the 1990s. Initial testing performed using carbon steel and 410 stainless steel showed that the reduction in ^{60}Co uptake was much greater for 410 SS (~25x) compared to carbon steel (~2x), consistent with observations from BWRs that the effect of Zn is greater for a chromite phase (e.g., inner oxide layer in BWRs) than a ferrite phase.

Since almost all of the iron deposited on HTS surfaces originates from FAC of the outlet feeders, the effect of zinc addition on carbon steel corrosion was assessed. Testing of 106B CS in the presence of 15 ppb Zn [Walker et al., 1996] showed no effect of Zn on the corrosion rate within the experimental uncertainty.

Both Raman and Mössbauer spectroscopies indicated the incorporation of Zn into the corrosion layer on carbon steel results in the formation of zinc ferrite. It was not clear if oxide was composed of both stoichiometric zinc ferrite and magnetite or if the Zn was uniformly distributed throughout. It was found that the zinc ferrite layer formed in zinc-containing solutions dissolved in zinc-free solutions.

A significant negative effect was the measured decrease in the thermal conductivity of zinc ferrite (0.86 W/m°C) compared to that of magnetite (2.3 W/m°C) [Walker et al., 1996]. Therefore, if all of the magnetite deposited in the SGs was converted to zinc ferrite, the thermal efficiency of the steam generators would be adversely affected.

Zinc addition to the CANDU HTS is currently not practised and is not recommended.

3.3.5 Boiling Water Reactors (BWRs)

The original state of chemistry that was sought in BWRs was pure water chemistry, now known as NWC (Normal Water Chemistry). The injection of various chemicals was introduced in order to improve performance within the areas of construction materials in the primary circuit and radiation environment. The major strategy choices are briefly described below, and the aim is to affect one or more of the transport and activation steps of the source term build-up:

- Corrosion of materials,
- transport of corrosion products to the core,
- activation of corrosion products,
- transport of activation products to out-of core surfaces,
- deposition of activation products on out-of core surfaces.

3.3.5.1 Purification

The removal of corrosion products is a basic step in the control of source term build-up, and it is in line with the original aim of BWR chemistry control – to achieve pure water chemistry. In a case where high concentrations of corrosion products are allowed to enter the reactor, the amount of activated corrosion products will increase due to deposition and activation on the fuel as crud, and the crud build-up process may also be affected adversely. Since the activated corrosion products are mainly incorporated in the fuel crud, a stable crud is preferable once it has been formed.

The in-flux of corrosion products to the reactor mainly arises from the feed water, especially in cases where forward pumping purification is applied, *i e* where a part of the feed water flow has not been passed through the condensate polishing plant. Corrosion of the turbine system may contribute several hundred kilograms of iron per year to the condensate[4]. This makes a properly functioning condensate polishing plant essential to achieve clean water chemistry.

To a lesser extent, corrosion products enter to the reactor coolant due to the corrosion of internal parts, fuel and other systems within the RCPB (Reactor Coolant Pressure Boundary). Once the corrosion products have reached the reactor, they will accumulate in the fuel crud, in the reactor water, on system surfaces and in the filters of the reactor water clean-up circuit. The corrosion products in the fuel crud become activated with time and contribute to the radioactive source term. With effective clean-up the concentration of corrosion products in the water and available for deposition will be reduced.

To enhance water purification the main tool is the optimization of the condensate polishing plant and the reactor water clean-up circuit. Filter efficiency and the amount of water that passes the filters are key parameters even though increasing the flow rate or volume of flow would constitute major plant modification.

3.3.5.2 Iron

Purification for the removal of corrosion products can, in some cases, results in very low feed water concentrations of iron. EPRI recommends a feed water iron concentration of 0.1–1 ppb in order to meet fuel performance requirements, but a part of the international BWR fleet is at levels well below 0.01 ppb [13]. At such low concentrations it can be expected that an activated corrosion product such as ^{58}Co (activated from ^{58}Ni) and ^{60}Co will not be retained as well in the fuel crud as otherwise.

Iron injection has been utilized in for example Japan and Sweden. The purpose has been to raise the reactor water iron concentration to allow it to affect crud formation and thus also the reactor water concentration of cobalt isotopes. The means to inject iron require some consideration. Methods that have been used include the injection of a solution into the feed water, purposely degrading the function of the condensate polishing plant, or passive addition of iron through controlled corrosion [14].

3.3.5.3 Zinc

Zinc can be added to the feed water to limit the source term build-up. Ideally, the zinc will prevent incorporation of cobalt into the oxide films on system surfaces as well as on the surface of the fuel bundles. The zinc will thus reduce both the activation of cobalt and the subsequent migration into systems of any ^{60}Co still produced. The concentration of ^{60}Co in the reactor coolant is also expected to become lower over time since the amount of activation is reduced.

Zinc injection needs to be supervised with care. The amount of zinc that is injected needs to be balanced and determined for each plant that intends to use it. The target concentration of zinc in the reactor coolant is often in the range of 3–10 ppb [15]. The proper amount is estimated from a combination of experience, ^{60}Co concentration and iron concentration. Also, the zinc injection must be continuous in order to have the intended effect as the effect on the cobalt uptake on system surfaces has been shown to respond quickly to changes in reactor water chemistry [16].

The zinc injection can be done using either natural or depleted zinc oxide (NZO or DZO). The drawback of NZO is the activation of ^{64}Zn to ^{65}Zn, affecting the radiation source term.

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[4] This can be shown by multiplying the iron concentration of the condensate (typically 10–20 ppb) with the condensate flow (typically 1000–1500 kg/s) and a time period of one year.

3.3.5.4 ECP Control

The most important connection between reactor chemistry and construction materials is corrosion that can be seen as the result of the chemical or electrochemical reactions of the material. The corrosion of metallic construction materials can be divided into common and local corrosion. The common corrosion takes place evenly over large surfaces and increases the amount of corrosion products in the water and on core and system surfaces. Local corrosion, mainly in the form of stress corrosion cracking, instead threatens the integrity of the RCPB.

Stress corrosion cracking can appear in transgranular or intergranular form. Intergranular stress corrosion cracking (IGSCC) is considered the most important form of corrosion with regard to RCPB integrity. IGSCC requires the presence of oxygen or hydrogen peroxide. With hydrogen injection to the feedwater, HWC (Hydrogen Water Chemistry) can be achieved. The purpose of the addition of hydrogen is to recombine with the oxygen and hydrogen peroxide formed by water radiolysis to reform water, thus removing the harmful species and reducing the ECP (electrochemical corrosion potential).

The purpose of HWC is to counteract IGSCC but the radioactive source term will likely be affected as HWC in introduced. It has been shown that as the chemistry is adjusted from NWC to HWC (or the opposite) the fuel crud will rearrange its structure in such a way that a considerable amount of ^{60}Co may be released into the reactor water and also likely deposit onto system surfaces [17]. In order to minimize the negative impact on the radioactive source term, any unnecessary cycling between oxidizing and reducing conditions should be avoided. Also, the system surface uptake of cobalt isotopes can be mitigated with zinc injection in such situations [16,17].

It has become increasingly more common to combine hydrogen injection with the injection of noble metals. This can be done either by a single addition (which may later be repeated) or on-line. The purpose of the noble metals is to catalyse the recombination reactions between hydrogen, oxygen and hydrogen peroxide. The resulting ECP becomes very low and causes the outer part of the oxide layer to dissolve. The remaining thin oxide layer has the ability to incorporate cobalt to a large extent /ISH05, EPR08/. This, again, can be mitigated well with a balanced zinc injection program [13].

A novel approach to ECP control is the use of surface deposition of TiO_2. As TiO_2 is subjected to UV radiation (supplied as Cerenkov radiation from the reactor core) water near the surface will be oxidised. In this manner an anode current through the material is supplied, instead of the same thing happening due to the oxidation of the metal of the construction material [18, 19].

3.4. Remediation of Contamination during Outages

Remediation includes full system decontamination, system / component decontamination, flushing, and hydrolasing of components. Section 3.4 basically reviews these processes.

3.4.1 Full system decontamination

Decontamination

An evaluation of BWR full system decontaminations (FSD) was performed by EPRI in 1992[5]. At that time, eleven different reactors had experience with full system decontamination. One reactor had had the equivalent of 15 FSDs, five with a Citrox type process and ten with LOMI[6]. Additional techniques (OPP, OPG, phosphoric acid, oxalic acid, ammonium citrate, CAN-DECON, AP, and NP) have been employed at other reactors. None of these decontaminations at that time had produced any serious problem during the decontamination or during subsequent service.

Comment [E25]: Move footnote 5 to references

Full-System Decontamination of a BWR Using the LOMI Process. EPRI, Palo Alto, CA: 1992. TR-100049

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[5] *Full-System Decontamination of a BWR Using the LOMI Process*. EPRI, Palo Alto, CA: 1992. TR-100049.

[6] U.S. Patent 4,705,573.

Base on this positive experience and the rigorous corrosion testing performed with the LOMI process on BWR structural materials, it is concluded that the LOMI process could be safely applied to the full system of the BWR. The sole PWR FSD in the USA was performed at Indian Point 2 in 1995 with the AP/CAN-DEREM process. Recently, the BWR Owner's Group has undertaken an evaluation to implement full system decontamination with fuel in the core.

Comment [HBO26]: Reference:

EPRI, TR-107039, Full System Decontamination of Indian Point 2 PWR.

AREVA has developed FSD process called HP/CORD® UV (Chemical Oxidation Reduction Decontamination). HP/CORD UV represents a regenerative multicycle decontamination process. As first step the oxide layer containing radionuclides are oxidative treated with Permanganic acid ($HMnO4$; "HP"). After the reduction step, the corrosion products and the radionuclides are chemical dissolved. During the regenerative process the corrosion products and radionuclides are transferred on ion exchange resins. At the end of the decontamination cycle Oxalic acid as decontamination chemical, is decomposed photo catalytically to $CO2$ and $H2O$. This process was successfully applied at several operating PWRs and BWRs in Europe and Japan with DF in the range 10-1000.

Comment [E27]: Add references and format

Ref : Christoph Stiepani **Full System Decontamination – Sustainable Dose Reduction for Operating Nuclear Power Plants,** ISOE International Symposium, Cambridge, UK, 17-19 November 2010

Above mentioned process has been further improved in order to minimise recontamination and it was successfully applied at German NPP Grafenrheinfeld in year 2010. This concept consists of passivation in hot subcritical conditions with pH(T) as high as possible for the given limits and constraints , injection of Zinc as soon as possible use of fresh resins and maximal clean-up flow and steady power operation for three months after start-up. Following such a treatment dose rates remain at the level of 30% after two years of operation.

Comment [E28]: Add reference and format
Ref: Stellwag B. et all **FSD for operating NPPs as Part of Sustainable Dose Reduction – Recontamination Evaluation for German PWR Grafenrheinfeld,** International Nuclear Plant Chemistry Conference, Paris, September 23-27 2012, p.O05-162.

Full system decontamination was applied at NPP Loviisa-2 in 1994 in order to minimise dose rates of coming long outage. In this case, a Siemens developed CORD/UV process with mobile AMDA equipment was applied. Reactor was defueled before decontamination and solution was circulated with MCPs. Very good DF values were achieved - 150 inside SGs, 12 for hot leg and 10 for cold leg of primary loop and through this decontamination more than 8 manSv of doses was saved [20]. Effect of decontamination at loop surface activities is demonstrated at figure 24. Nevertheless increased core deposits appeared during next cycle leading to numerous fuel failures [21].

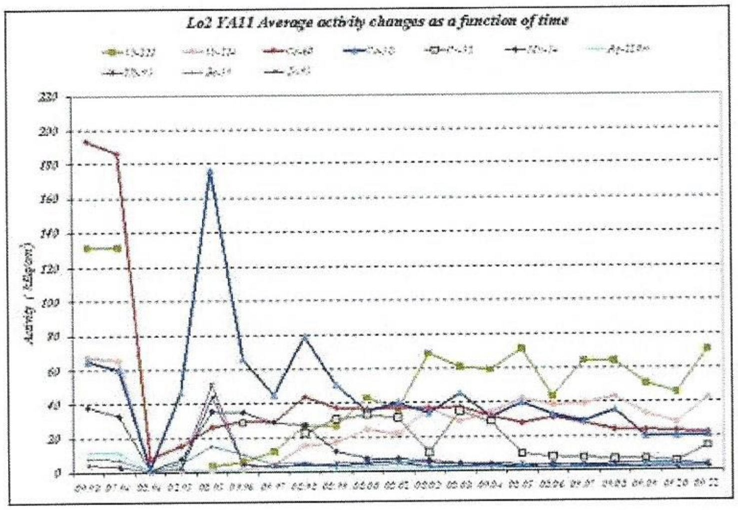

Figure 24: Average contamination levels on the 1st loop of Loviisa 2 (8 points). In 1994 and 1995 the MARC measurements were made twice to follow up the decontamination and recontamination.

3.4.2 System and component decontamination

Comment [HBO29]: Will be extended by EDF

EDF to update by September 1st – committee – 7/12/2013

EPRI to add a discussion on Catawba

For PWRs and BWRs, already mentioned AREVAs process HP/CORD® UV has been also successfully applied worldwide with results similar to those mentioned for FSD. For VVER type reactors decontamination of main primary components is performed to assure favorable radiation conditions and surface status for repair and inspection works. Typically main coolant pumps, main gate valves and control rod drives are components decontaminated during outage. Specific component represents steam generator due to his horizontal configuration and large surface. Several manipulators have been developed for this purpose and typically AP Citrox process was applied. This approach has several drawbacks. At first, there is a high surface-to-volume ratio so iron solution becomes saturated and iron oxalate precipitate is formed and deposited in the tubes due to low velocity during circulation and post decontamination flushing. Second negative impact is that the surface after decontamination remains in corrosionally active state and during subsequent operation generates increased amount of corrosion products. These corrosion products together with deposited iron oxalate represent high risk for increased fuel deposits formation.

Experience form several plants showed that if more than half of steam generators (e.g. 4 SG of 6 at VVER-440) had been decontaminated, this lead to elevated deposit formation on the fuel with unacceptable core power distribution inhomogeneities (which can be considered as a kind of CIPS effect on the VVERs) and also to high dose rates during next outages after redistribution of in-core deposits within out of core primary system surfaces [22].

Effect of decontamination to the surface activity of SG tubes is demonstrated at figures 25 and 26, where two steam generators of NPP Loviisa-1 are compared.

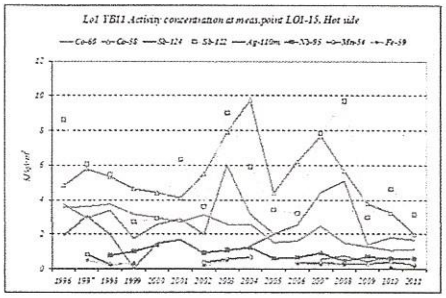

Fig 25: Trending of the activity concentration on the 1st SG hot side on LO1 not ever decontaminated. The concentration is much lower than on the surface of the loops.

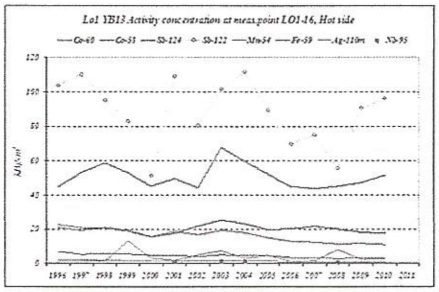

Fig 26: Trending of the activity concentration on the 3rd SG hot side on LO1 decontaminated in 1980. The concentration of Co is slightly lower than on the surface of the loops, but the concentration of Sb slightly higher.

The number of decontamination operations carried out by EDF on medium or large size components has regularly increased for these last 20 years. These operations are carried out on some parts of the primary pipes during replacement of steam generator, on hydraulic parts of primary pumps and CVCS exchangers, filters and pumps. To implement these operations, EDF has been developing over the years three soft chemical decontamination processes used according to the characterization of the contamination :

- EMMAC is used for dissolution of Ni, Cr, Fe oxides without presence of Stellites,
- EMMAC POA is used for dissolution of Ni, Cr, Fe oxides with presence of Stellites,
- EMMAg is used for for dissolution of Ni, Cr, Fe oxides with supplementary Ag pollution with presence of Stellites

The optimization of these chemical decontamination processes are in progress at EDF with a view to decrease the application time ant the volume of generated effluents.

For each PWR concerned, studies begin with a diagnosis of the origins of contamination, the type of pollution, its form (mobile hot spots, oxide layers) and its localization. According to these results, EDF decides to implement the most adapted decontamination process (mechanical or chemical), estimates the Dose Rate Reactor Factor (DRRF) for each possible decontamination scenario and assesses the dosimetric gain (3D local modeling) in order to find out if the operation is profitable or not. The average dose gain is estimated to 0.5 man.mSv per reactor for the five following years.

Comment [GRx30]: Section added par G. Ranchoux (EDF) on 7/18/13

3.4.3 Others

Dilute chemical decontamination

Dilute chemical decontamination (DCD) of subsystems and components of operational nuclear power plants is a mature, well-established technology. Since the first such application in 1979, the industry had grown to the point where about 10 decontaminations are performed each year in the USA in 1999 even though this has dropped to less than three per year over the last five years. EPRI has provided a handbook on the application of this technology that describes in detail the methods and also provides utility application information[7].

DCD is, in part, responsible for the average radiation dose per reactor being reduced from about 10 Sv for BWRs and about 6 Sv for PWRs in the early 1980s, to about 1 Sv per reactor in 1998. Three DCD processes have been employed for the vast majority of these decontaminations. They are:

1. LOMI (used for 46% of all USA operational decontaminations since 1990, and essentially 100% of the BWR recirculation piping decontaminations)
2. CITROX (36%)
3. CAN-DEREM (18%)

These processes bring about decontamination by dissolving the deposits found on the interior surfaces of pumps, valves, pipes, heat exchangers, etc., and releasing the entrapped radionuclides that are responsible for the external radiation fields. All solubilized material is removed from solution by ion exchange resin. The resin is transferred to high integrity containers (HICs), dewatered, and transported to a licensed radioactive waste disposal site for burial.

These processes will dissolve most iron and nickel-based deposits found in LWRs, but are ineffective on high-chromium deposits such as those found in PWRs and BWRs operating under hydrogen water chemistry (HWC). To dissolve such deposits, the chromium must first be removed. This is done with an oxidizing step based on the use of potassium permanganate. Potassium permanganate oxidizes the chromium in the deposit from the insoluble +3 valence state to the highly soluble +6 valence state. Once the chromium is removed, the decontamination process is applied as described above. Two dilute chemical oxidizing processes have been developed – alkaline permanganate (AP), and nitric permanganate (NP).

Four plants that are permanently shut down were decontaminated in 1998. To reduce radiation exposure ALARA during decommissioning, management personnel at three of the plants elected to perform chemical decontaminations of all major systems prior to the start of major decommissioning activities. Selective subsystems were decontaminated at the fourth. Higher levels of radioactivity removal are required than for operational-type decontaminations. While a decontamination factor (DF) of 10 is generally considered adequate for operating plants, a target DF of 100 or more is not unreasonable for decontamination prior to decommissioning. To achieve such a high DF, removal of a

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[7] *Decontamination Handbook*. EPRI, Palo Alto, CA: 1999. TR-112352.

thin layer of underlying base metal is required in addition to removal of the oxide film. Operational-type process is, by design, too "mild". They have been specifically developed not to remove base metal. Two new processes have recently appeared on the market that are designed to remove a small amount of base metal and give the high DFs required for decontamination prior to decommissioning. They are the DFD process developed by EPRI, and the CORD D UV process developed by Siemens. Both are described in detail in the EPRI Decontamination Handbook[8]. The four applications, three with EPRI DFD and one with CORD, are reviewed.

Comment [E31]: Format referrence consisent with document

TR-112352, EPRI Decontamination Handbook

The effect on decontamination of zinc addition to BWRs is discussed. No effect on the ability of the operational DCD processes to achieve the required DF has been observed with the addition of zinc to the BWR coolant7. The impact of hydrogen water chemistry has also been evaluated, and it has been found that the oxide film in plants on HWC is converted to a high-chromium film similar to that found in PWRs. The film also contains a high proportion of nickel ferrite. The NP/LOMI process is very effective on films of this type. There is also evidence that the HP/CORD process is effective on HWC films.

Comment [HBO32]: Reference

Same as above

Generally, ion exchange resins from decontaminations are dewatered in a high integrity container (HIC) and buried at a licensed radioactive waste disposal facility. The potential exists for creating a mixed waste due to the presence of chromium. However, all wastes to date have passed the toxic characteristic leach procedure (TCLP) and thus are classified as non-hazardous. The potential also exists for creating a waste form that is greater than Class C due to the presence of transuranic (TRU) radionuclides. Such a waste form would be unacceptable for burial at any currently available site. In plants with TRU as the result of fuel failures, the ion exchange resin is taken off line during the decontamination based on TRU loading as opposed to chemical loading. This usually generates more waste, but none of it is greater than Class C7.

Comment [HBO33]: Reference
Categorization of waste???

Same as above

Others /// Mechanical flushing

Comment [HBO34]: Provided by David and Colin

Need to come back and read – D Perkins

Mechanical flushing is practiced at LWRs to remove hot spots on piping runs and tanks. Typically, taps are installed near an elbow or long run of piping prone to CRUD traps. A hydro blaster (or sludge lancer) is employed to provide a 2000- 4000 psi stream of portable water to the pipe to mechanically flush the source term to the radwaste system.

Demineralizer vessels are important to mechanically flush to remove "heels" of old resin that often collect in the bottom of flat bottom vessels. It is recommended to mechanically flush vessels every 5-8 years. Conical bottom vessels may reduce the development of old resin heels but this need to be verified by the insert of a light scope or other visual means.

On BWRs, mechanical flushing is practiced to remove the Co-60 buildup on the outlet piping to the vessel prior to ISI (non-destructive weld testing) on the piping in the drywell. The hydro blaster is lowered from the refueling bridge to each vessel exit piping. An underwater camera is also used to properly position the water flush.

Portable purification

Comment [O35]: Provided by David and Colin

Comment [HBO36]: Too detailed

This section describes the Portable Underwater Demineralized employed at Seabrook Station with lesson learned

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[8] *Decontamination Handbook.* EPRI, Palo Alto, CA: 1999. TR-112352.

- Seabrook is designed with an installed cavity purification system (~100 gpm) through skimmers and CVCS mixed bed demineralizer with return to the cavity via RHR. Many times the installed system has been unavailable in outages because of valve work. This led us to seek an alternate portable system. There were already commercially available submersible systems available from Trinuke but we struggled with the concept of removing either the resin from the demineralizer~~demin~~ or a spent demineralizer~~demin~~ from containment in the outage (Figure 27).
- Seabrook RP staff conceptualized a submersible demineralizer~~demin~~ with tri-nuclear that has multiple small demineralizer~~demin~~ units which fit in our transfer system (Figure 28).
- Filter and demineralizer~~demin~~ housings are permanently stored in the lower cavity.
- The Reactor Cavity Demin System (Model RCDS-120) is a portable underwater demineralizer system designed to clean up the Reactor Cavity water during refueling outages.
- The RCDS-120 system consists of a base unit that can hold eight (8) 8" OD x 7ft long demineralizer columns (Model RCD-7), a submersible pump (Model PP-120/5SC), and a standard Tri Nuclear filter housing.
- When the outage is over, the demineralizer~~demin~~ columns can be transferred to the SFP via the fuel up-ender, the pump and strainer are removed and the base can be left in the cavity during power operations.
- The Reactor Cavity Demineralizer~~Demin~~ System is utilized during refueling outages to purify cavity water, reduce activity and improve water clarity.
    1. Reduces personnel exposure
    2. Limits personnel contamination
    3. Helps prevent errors during fuel movement

Reactor Cavity Demineralizer Components:

- RDCS-120 Base
- Submersible Pump Assembly
- Flow Meter and Sensor
- RCD-7 Demineralizer~~Demin~~ column
- Control Panel
- Strainer Basket
- RCD-7 Floor Storage Rack

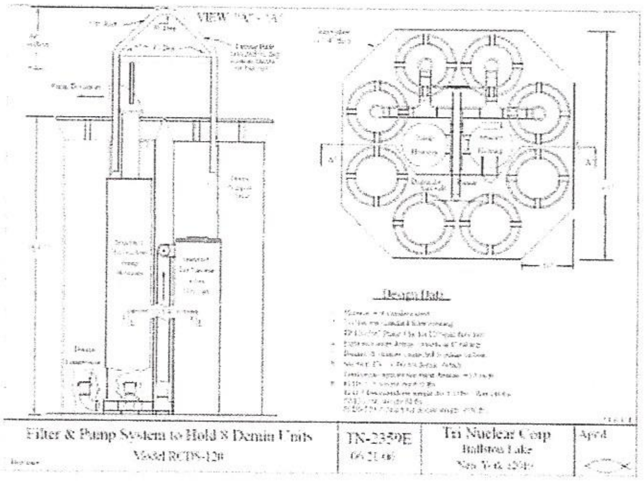

Figure 27: Seabrook Submersable Tri Nuclear Demineralizer

The base plate is 45" square (with 10" cut back on each corner), 86" tall (to the top of the lift bale) and weighs 622# dry.

Figure 28: Tri Nuclear Submersable Demineralizer Configuration

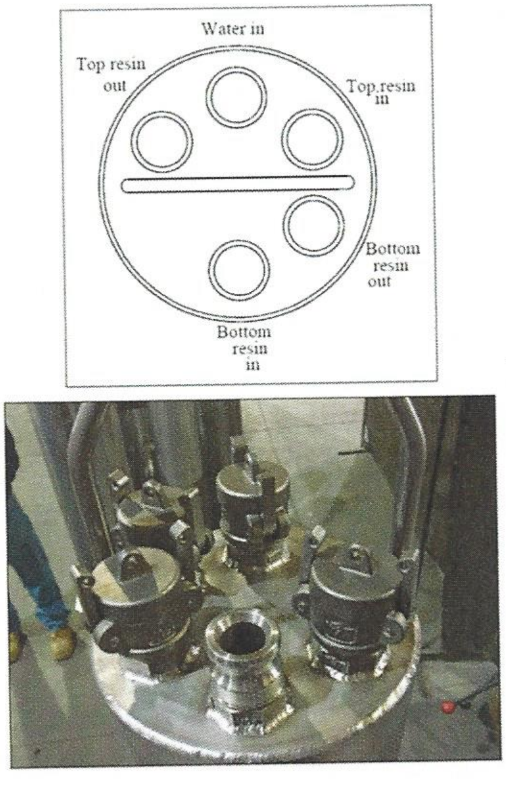

Figure 29: Tri Nuclear Photo and Engineering Plane View of Submersable Demineralizer

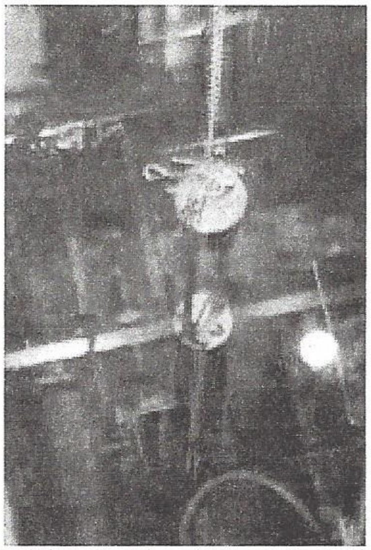

Figure 29: Tri Nuclear View of Submersable Demineralizer

Results:

- The total throughput of Tri-Nuclear Corporation submersible filter units was 7.2 million gallons whereas the submersible demineralizer throughput was about 2 million gallons. Using dose rate to Curie conversion factors (obtained from MicroShield™ models) the estimated activity removal of the filter and demineralizer units is 3.62 Ci and 5.53 Ci respectively. This equates to a total of 9.16 Ci removed using the portable equipment. During OR11, the demineralizer dose rates appeared to peak early and were not as high as would have been expected given the apparent soluble activity in the cavity.
- Then the observed dose rate band near the top of the individual resin columns indicates that the resin was not exhausted. For the resin to be exhausted, the higher dose rate bands would be expected to occur near the bottom of the resin columns.
- This demineralizer unit is credited with the removal of an estimated nine Curies of soluble gamma activity during OR11 when the station observed dose rates over the refueling cavity lower than previously experienced. While the submersible demineralizer is not the only factor contributing to the favorable dose rates over the refueling cavity, the soluble activity removed from the cavity combined with the remote transfer design contributed to our exceptional OR11 ALARA performance. Because of rigging problems, the system was not used in OR12. However the system was used again in OR13 and OR14 with resin loadings modified each outage to better target colloidal cobalt species. Table 1 summarizes the submersible demineralizer system loading.

Resins Loading on Underwater Demineralizer at Seabrook Station

Outage	Cavity Flood-up Activity (uCi/ml)	Resin Load*	Calculated Activity Removed (Ci)
OR11	3.58E-3	8% Crosslink Gel Cation (GR 2-0)	6
OR13	1.01E-2	Macroporous Anion (NRW501P) over Macroporous Cation (NRW160) over 8% Gel Cation (GR 2-0)	14
OR14	8.25E-3	Macroporous Cation (NRW160) over Macroporous Anion (NRW5070)	27

4. Radiation Field Measurement Techniques

The effect of the radioactive source term on the radiation environment inside a plant is mainly due to radioactivity that has been deposited on system surfaces. The radiation environment can be analyzed in a number of ways, the simplest method would be the follow-up of occupational exposure, such as through ISOE database. With some further effort a more detailed mapping of radiation fields can be done, both with regard to quantity (number of measurement and measurement points) and quality (precision of measurements, proper selection of measurement points, radionuclide specific information versus dose rate etc).

4.1 Dose Rate Measurement Techniques

Radiation Field Sources and Interferences

The primary contributors to out-of-core radiation fields in western PWRs and BWRs have been identified as ^{58}Co and ^{60}Co. The majority of this activity is incorporated into the oxide film of the out-of-core surfaces through soluble oxide growth, with the balance of the activity deposited as particulate activity. Gamma ray spectroscopy measurements of the reactor coolant loop piping have shown that these two radionuclides generally control shutdown dose rates [23].

Because the half-life of ^{58}Co (70.8 days) is relatively short in comparison to that of ^{60}Co (5.3 years), the time elapsed between the plant shutdown and survey dates can have an impact on the measured radiation fields as the ^{58}Co and other short lived isotopes decay. This is especially important in PWRs where ^{58}Co activity is a large fraction of the total activity compared to BWRs where ^{60}Co is predominant. Procedures should be defined to take measurements within 24 hours after completion of the forced oxidation clean-up.

Proper selection of survey instrumentation is important to provide accurate dose rate readings at the intended measurement locations. Localized high radiation areas or hot spots located near a survey location can also influence the radiation field measurements. Examples of such hot spots in PWRs are drain lines, the regenerative heat exchanger, and resistance temperature detector (RTD) manifolds, valves, and associated piping. Dose rate surveys should be taken using a detector with directional bias response in order to accurately measure contact dose rates on each specific component and to reduce the impact on the reading from extraneous background radiation and contributions from nearby components.

Instrumentation

Examination of the radiation field data across large fleets of units shows that significant variations can exist in the data measured at the same location but on different occasions [23]. To effectively present the plant radiation fields trends, the factors that influence the data must be identified, quantified, and considered. These factors can include the source strength, attenuation effects, and instrumentation utilized.

Unfortunately, many historical data do not have adequate descriptions of the attenuation and instrumentation effects; the data were often presented as tables of values without qualification information [23].

There are a variety of radiation measurement devices available to the industry; however, most are either Geiger-Muller tubes or Ion Chambers that are calibrated to known sources.

Data have variously been collected using TLD (Thermo-Luminescent Dosimeter), non-directional surveys meters (e.g., ion chambers), and 'homemade' directional detectors (GM detectors wrapped in lead). Many utilities have also chosen to use Electronic Dosimeters (EDs) because they conveniently interface with plant data collection systems. They are ion chamber detectors, except they often have an electronic bias programmed for conservatism. These data are corrected if the bias is known.

The survey instrumentation used and the procedures applied by the technician are not universally consistent among the plants, which can contribute to difficulty in making comparisons. At a given plant, a non-directional instrument will generally result in dose rate readings higher than the actual contact measurements of interest and will likely contribute to greater variability in the readings taken during different outages.

EDF measurement devices are radiation meters usually fitted with an energy-compensated GM (Geiger-Mueller) type gas detector. Their measuring range is variable and depends on the aims of use. For mapping incorporating the hot spots, the range lies between a few microsieverts per hour and a few sieverts per hour. The energy domain covered ranges from 60keV to several MeV, integrating ^{60}Co gamma rays (1.115MeV and 1.233MeV). Response at high gamma energies, such as those of nitrogen 16 close to 6MeV, is characterised in order to assess the efficiency of the biological protection devices that are going to be installed around the hot spots in the reactor coolant system.

From a purely practical operational point of view, according to the design basis of the detectors, EDF favours the use of radiation meters with a small detector for assessing dose rates at the hot spots. Indeed, the advantage of having devices with small GM detector is that this limits the gamma flux gradients, enabling measurements to be taken using a detector positioned in a homogeneous flux, which will not be the case for large volume detectors, which will tend to underestimate the value of the hot spot. In any event, this type of measurement requires the use of the same type of device in order to ensure that measurement may be reproduced. Given the uncertainty of these measurements, best practice involves taking a measurement on contact combined with a measurement taken at a suitable distance, so as to establish conditions that are consistent and representative of the actual risks faced by operators. EDF has chosen to take measurements at a distance of 1m and 50cm. These measurements enable the room's zoning to be characterised.

Certain site best practices also enable changes in the dose rates of hot spots in the reactor coolant system to be monitored (measurement using gamma radiation monitors positioned close to the hot spot to be monitored and connected to an RP SUPERVISOR located outside the zone) or even to record these changes on a specific radiation meter during operating processes, which allows accurate estimation of the purification of the coolant systems during the unit shut down phases. This means that dosimetric gains can be optimized on line with the duration of filtering of the primary coolant, which contains radioactive impurities that may contribute to a higher dose rate at the hot spots.

The good working order and calibration of these devices are checked regularly, at least once per year. The calibration and all the functions of the radiation meters are fully checked at least once every three years, as recommended by French regulations'.

Remote Electronic Dosimetry

Plants generally have electronic dosimeters installed at various locations in the plant. Those locations can be categorized as being installed either on piping or in general areas. This distinction is made because measurements can reflect distinctly different ways of assessing radiation fields.

Measurements on piping are typically dominated by the activity in the coolant inside the piping. This makes such measurements less directly linked to personnel exposure, since, for example, piping with high activity coolant could be well shielded or personnel could be kept out of the area at times when coolant activity is high. Nonetheless this data is important as these time dependent dose rates on piping are more closely linked with operations and chemistry modifications made to mitigate radiation fields.

General area measurements, on the other hand provide a much more direct indication of potential personnel exposure, if the jobs under consideration require working in the area measured. However, it is possible that such measurements are significantly influenced by local hot spots and are not a good measure of the efficacy of efforts to reduce out-of-core radiation fields.

4.2 Germanium Detectors

The semiconductor detector, or more specifically the high purity germanium detector, offers the highest energy resolution of all the commercially available detector alternatives. This allows for radionuclide specific measurements of gamma radiation where all the sufficiently gamma emitting radionuclides can be separated and identified. Furthermore, the germanium detector is an established tool and it offers good stability and precision. The knowledge of precise and radionuclide specific levels of contamination in the pipes and heat exchangers of the RCPB allows for trending and analysis of the development, as well as analysis of the causes of the contamination.

The drawbacks of the germanium detector as a mobile tool are due to practical issues:

The detector requires constant cooling that is most often supplied by a small liquid nitrogen Dewar vessel that needs to be filled repeatedly during a measurement campaign (typically every 1–3 days). Electrical cooling could be considered provided that cooling is not interrupted as the detector is moved between measurement points and electricity outlets.

The measurement times are longer than for a gross dose rate measurement. A measurement with a collimated germanium detector can require measurements times counted in hours.

The setup is rather cumbersome to move due to the heavy shielding that is required for the detector.

This device allows non-destructive surface activity by gamma spectrometry (HP germanium detector cooled by liquid nitrogen) based on a photon flux measurement converted in activity with the help of a measured or pre-computed transfer function (MCNP, MERCURE or PANTHERE codes for example). A very large range of geometries can be measured as primary circuit (cold and hot side steam generator tube bundle, hot, cold and cross-over legs), CVCS (letdown line, regenerative heat exchangers), RHRS (heat exchanger, piping), …

The measurement can be performed on the primary circuit if full or empty, because the volume activity contribution can be removed. That point can be important in case of a high volume activity in the primary coolant that can notably affect the measurement result and lead consequently to a wrong analysis.

Deposited activities can be measured in a range from 1 MBq/m² to 100 GBq/m² with a counting time depending on the detection accuracy: 30 minutes for current high activity radionuclides (^{60}Co, ^{58}Co) up to 1 hour for the other ones.

4.3 CZT Detectors

This real time acquisition device allows the identification of 10 main radionuclides likely to be found in NPPs (^{58}Co, ^{60}Co, ^{110m}Ag, ^{124}Sb, ^{122}Sb, ^{51}Cr, ^{59}Fe, ^{54}Mn, ^{131}I and ^{137}Cs) and the determination of the radionuclide relative contribution to outside pipe wall dose rates. The dose rates conversion into deposited activity is also possible thanks to a transfer function (code calculation) but very limited due to an incomplete geometry set on one hand and to the necessity to perform the measurement with an extremely low volume activity on the other hand. The CZT gamma spectrometer principle is reminded in figure 27.