

# OSART Good Practices

## CHEMISTRY

### Chemistry Control in Plant Systems

#### Bugey 2/5, France

Mission Date; 8-25 March, 1999

The primary systems resin management programme has made a significant contribution to the reduction of solid waste and reducing chemistry operating costs.

The design resin bed configuration for the chemical and volume control circuit (RCV) is two mixed beds for circuit purification followed by a side-stream cation bed, for lithium removal. Common industry practice is to use mixed beds that operate in the lithium/borate form, and specially prepared mixed resin (cation resin > 99 percent  $7\text{Li}^+$ ) is purchased. This resin is very expensive when compared with  $\text{H}^+$  form cation resin. The station's primary circuit resin management programme dispenses with the purchase of the expensive lithium form resin and takes advantage of the production of lithium-7 within the primary circuit by the neutron absorption reaction of boron-10.

One of the two mixed beds is loaded with  $7\text{Li}^+$ /borate form resin. This is in use for normal primary coolant purification during operation. A new cation resin charge, hydrogen form ( $\text{H}^+$ ), is then loaded into the other mixed bed vessel. The volume of cation resin loaded is equivalent to only the cation portion of a mixed bed charge, so the vessel is only part loaded. This bed is used for periodic lithium removal and is slowly saturated with lithium over several cycles. When the cation is saturated with lithium, an anion charge is loaded on top of the cation and is then saturated with boron. When the purification bed is exhausted, it is discharged to solid waste treatment. The other vessel then enters service as the purification charge and the emptied vessel is re-loaded with  $\text{H}^+$  form cation and placed in service as the lithium removal bed. The sidestream cation resin vessel is kept empty in case of need during an incident when it can be loaded with resin as required. To avoid saturation of either mixed bed during the shutdown oxygenation phase, the RCV demineralizers are bypassed completely, and the letdown diverted towards the deborating demineralizers of the primary effluent treatment and boron recovery system (TEP) system. The demineralizer bed common to both units, TEP 006 DE, is not used for deboration, being instead loaded with a stratified cation/anion bed which is then used for primary coolant clean-up during the shutdown oxygenation phase. This resin bed is also retained for use over several cycles.

This management programme has had a significant positive impact in reducing solid waste production and by reducing the number of resin change out operations, has contributed to dose reduction efforts while also contributing to a reduction in chemistry operating cost.

## Bugey 2/5, France

Mission Date: 8-25 March, 1999

The Chemistry Department has developed a technique for monitoring primary to secondary leak rates, using lithium as a chemical tracer, which is especially beneficial in instances where the primary means of detection, Nitrogen-16 monitoring, may be ineffective.

The principal leak detection system for primary to secondary leaks is monitoring of the Nitrogen-16 activity in the live steam at the exit of the steam generators (SG). This is supplemented by tritium measurement in the condensate or feedwater, Xenon measurement in the incondensable gases exhausted from the condenser and radioelement detection in the steam generator blowdowns. Tritium is especially useful in determining the presence of a leak because of the low detection threshold ( $< 0.5$  L/h) and the precision of the method. However, it cannot be used to determine which SG is leaking. Similarly, Xenon detection is normally performed on the incondensable gases from the condenser and cannot be used for individual SG leak detection (it is possible to measure Xe in the live steam but it is difficult to sample). The principle means of monitoring an individual SG has been the detection of radioelements in the SG blowdown. The detection threshold with this method is variable, as is the precision (30 to 300 percent). The plant has developed the lithium detection method as an alternative means of determining the leak rate in a specific SG. Lithium is, of course added to the primary circuit as the pH adjusting agent and the method has the advantage that it does not require counting equipment or any additional chemistry instrumentation and the analysis time is short. It is thus a very rapid assessment method. The detection threshold, as reported by the station, is good ( $< 1$  L/h) as is the precision (20 percent). A relatively short equilibration period of about 8 hours is required.

This technique is a very good method for confirming the information provided by the Nitrogen-16 measurement system, but the real value may be in that it is still possible to determine leak rates in instances where the Nitrogen-16 method fails because of long delay times across the leak, such as in the case of a leak across a tube that was previously plugged (i.e. the plug is leaking). Development of this method has augmented the capacity to ensure the integrity of the steam generator tubes.

## Gösgen, Switzerland

Mission Date; 8-25 November, 1999

In co-operation with nearby industries , KKG have developed a recycling process for chemicals, which leads to a significant benefit in terms of reduction of waste and environment pollution, as well as large savings for the plant and associated industries.

In order to produce the right quality of water for the cooling tower, the plant needs to operate a decarbonisation plant. The decarbonisation process requires a yearly amount of 3000-3500 tons of  $\text{Ca(OH)}_2$  and at the same time produces about 10 000 tons of chalky sludge that would normally be treated as waste and sent for disposal. The main component of the chalky sludge is lime, which is recycled to a nearby cement factory.

A nearby acetylene factory that produces acetylene from calcium carbide produces 1700 tons per year of  $\text{Ca(OH)}_2$  which instead of going to waste is recycled to KKG for the decarbonisation process.

This co-operation has given rise to several benefits such as:- Considerable benefits in terms of reduction of environment pollution.

- Savings for KKG due to reduced cost of  $\text{Ca(OH)}_2$ , and chalky sludge disposal., as well as savings for the acetylene and cement factories concerning deposition and chemicals costs.

## North Anna 1/2, USA

Mission Date; 24 Jan-11 Feb, 2000

High pH operation with ETA (EthanolAmine) treatment in the secondary system is very effective in reducing the feedwater iron concentration.

North Anna has replaced the copper materials in the secondary system, which makes it possible to adopt high pH control. However, they control feedwater with high pH operation and also inject ETA.

As a result, iron concentration in the feed water is below 1.0 ppb due to the effectiveness of ETA in preventing the erosion corrosion on drain lines.

The plant periodically carries out sludge lancing in each steam generator and removes only a few Kg of iron-oxide. This demonstrates the effective use of the secondary side chemistry control.

The station checks the erosion/corrosion rate in the drain line pipes during every outage and confirms the good results.

## Mühleberg, Switzerland

Mission Date; 6-23 November, 2000

Noble metal chemical addition, a chemical treatment used in conjunction with hydrogen injection to provide protection against intergranular stress corrosion cracking (IGSCC) while minimizing the impact of hydrogen injection upon dose, has been implemented. The use of noble metal chemical addition will enable the plant to protect single phase wetted surfaces of the vessel components against IGSCC while remaining within the radiation protection limit of 100 \*Sv/week at the site fence. The site developed a plan to ensure that the dose limit at the fence would not be exceeded with implementation of hydrogen injection following the application of noble metal chemical addition. As part of this project the plant also installed electrochemical potential (ECP) electrodes and a durability monitor. The data from the ECP electrodes are used to monitor and trend the effectiveness of the selected hydrogen injection rate in lowering the ECP. The data from the durability monitor will be used to determine when another noble metal application will be required. The plant is the first BWR in Europe to implement this technology.

The team determined that the initiative to protect reactor vessel components using noble metal chemical addition in conjunction with hydrogen injection is a good practice.

## Mühleberg, Switzerland

Mission Date; 6-23 November, 2000

The plant has implemented an innovative technology to generate the hydrogen and oxygen required to implement hydrogen injection in conjunction with noble metal chemical addition. This system eliminates the need for an external manufacturing and or supply system and the safety concerns associated with keeping supplies of oxygen and hydrogen on site and transporting them to the injection point.

The generation of hydrogen and oxygen is performed using a polymer electrolyte membrane technology which takes condensate and generates the hydrogen and oxygen required to meet the plant goal for ppm hydrogen in the feedwater, provide oxygen to the offgas and maintain a stoichiometric ratio of oxygen to hydrogen

## Temelin 1/2, Czech Republic

Mission Date; 12 Feb.-1 Mar., 2001

Secondary side erosion/corrosion monitoring is well structured and implemented. The plant has installed a comprehensive corrosion monitoring program for continuous evaluation of the corrosion state of secondary side equipment and systems especially in steam lines and feedwater piping. Parts of this program are the following:

- Continuous and periodic corrosion potential measurements are carried out using the Corratel electrodes built into different parts of the water system to determine corrosion tendencies.
- To quantify the corrosion processes, corrosion loops are also established to determine the exact corrosion and deposit formation rates in those systems.
- Using mobile and fixed corrosion monitors the same parameters can be determined for any new material type as well.
- The corrosion processes are followed by detailed wall thickness measurements and visual inspections;
- The selected locations are systematically measured and by means of the CHECKMATE program the equipment residual life time is regularly predicted based on measured values. By this means the appropriate preventive actions can be implemented when necessary.

## Dukovany 1/4, Czech Republic

Mission Date; 5-22 November, 2001

A regular small-scale primary feed and bleed process is implemented with the following positive impacts to primary water chemistry and the environment:

- Fluctuations of hydrogen and ammonia concentrations and consecutively pH(300) are reduced with corresponding corrosion product transport minimization.
- Oxygen ingress into primary coolant associated with large scale feed and bleed process is minimized.
- Releases of  $^{41}\text{Ar}$  into atmosphere are reduced by 40%.

## Tricastin, France

Mission Date; 14-31 January, 2002

The automatic injection system of lithium to the primary circuit was established in Unit 2 as a prototype. The system uses a special software for continuous calculation of lithium needed for the circuit. The on-line measurement of conductivity with the feedback loop makes it possible to comply with lithium/boron specifications during operation and during hot standby. An alarm is provided to the control room operators when a problem occurs with the injection system.

This system is especially useful for power plants operating in load following mode with very frequent variation of power (up to the hot standby), which are always accompanied by boration and dilution operations. This phenomenon is compensated by an automatic lithium injection system, which is used to compensate in real time whenever the limit of the lithium-boron diagram is exceeded, and to prevent excursion at low pH. 25 load reduction transients were carried out, which qualified the prototype and the lithium concentration was constantly maintained with a deviation below 0.05 mg/kg relative to the reference value.

To optimize hydrogen water chemistry (HWC) the plant has carried out some experiments at different hydrogen injection levels based on sophisticated and extensive measurements of the electrical corrosion potential in the bottom plenum of the reactor pressure vessel.

The plant has taken the decision to protect the bottom plenum of the reactor vessel and its internals against Intergranular Stress Corrosion Cracking (IGSCC) phenomena. It was necessary to carry out a special minitest, maybe unique in the world. Hydrogen water chemistry was implemented for the first time at the plant in 1986. The first goal was to protect the recirculation loops against IGSCC. With the results coming from the minitest, it was determined that the feed water hydrogen concentration necessary was 0,3 ppm to reach -230 mV, which is considered good enough. Afterwards, in 1996 the plant took the decision to protect the bottom plenum of the reactor vessel and its internals. It was necessary to install a total of 13 electrodes in four different positions of the bottom plenum, nine of them were mounted in three modified LPRMs, which were installed in their normal positions, and the fourth one was mounted in the bottom head drain line flange. The reference electrodes used were Pt and Fe/Fe<sub>3</sub>O<sub>4</sub> and the measurement electrodes were stainless steel. During this minitest many other parameters different from ECP (Electrochemical Corrosion Potential) were measured, such as hydrogen concentration, oxygen concentration, conductivity, ionic analysis, metallic analysis, activity etc, in waters coming from reactor and from the feed water system and dose rates were also measured in different plant areas. In most other NPPs it is usual to calculate the feed water hydrogen concentration necessary to protect any zone of the vessel using radiolytic models which are much less reliable. The experimental method used at the plant has also been used to adjust the radiolytic models mentioned before. But, as it is known, the response to hydrogen injection is different in each plant.

The magnitude of the work related to the experiment performed at the plant, technically and economically speaking, has been very big but the effort made has been extensively compensated by the success obtained. This experience has allowed the plant people to know exactly that 0.9 ppm is the feed water hydrogen concentration necessary to reduce the ECP below -230 mV in the bottom plenum, mitigating by this way the IGSCC phenomena with no more hydrogen than necessary and optimizing, at the same time, the dose rate at the plant.

The plant saves money, radioactive waste and minimizes sulphates ions input in the reactor vessel by optimizing treatment of condensate demineralizer filters.

In all plants, which have deep bed resins in their condensate demineralizer systems, it is usual, when the resins are exhausted, to remove them and to install new ones. Many years ago there was the practice to regenerate all the condensate demineralizer system resins but later, in many plants, it was decided not to regenerate any more because the sulphates limits in the reactor water were reduced very much. The first regeneration step is to carefully separate the anionic and cationic resins but some small amount of resins of each class always remains with the other resin. In such a case when the cationic resin is regenerated with sulphuric acid some small amount of anionic resins are regenerated too, but in the form of  $SO_4=$  instead of being in the form of  $OH^-$  which is normal. This contamination of the anionic resins produce some leaching of  $SO_4=$  when the bed is put into service. This is very undesirable because they contribute to increasing the sulphate concentration in the reactor water. As is well known, sulphates are one of the most detrimental substances for reactor because they enhance the intergranular stress corrosion attack in sensitized materials.

In the plant a special procedure has been developed which allows the separation of the resins. For this reason, it was decided to regenerate only the anionic resin, which is the most expensive of the two resins. Its volume represents half of the total volume. After assuming this improvement, the chemical results in the reactor water are the same as when anionic resins were also removed. This practice represents a resin cost reduction to one third of the total price, it also reduces the volume of wastes produced and, as a consequence, a reduction is also obtained in manipulations of the wastes in the Radwaste System, which represents important dose savings.

## Sta. M. Garona, Spain

Mission Date; 18 Feb.-2 Mar., 2002

To minimize personnel dose during the outage the plant has decontaminated the recirculation loops by a new method and water chemistry for minimizing recontamination has been optimized.

To reduce the dose a chemical decontamination has been performed on the recirculation loops. The system design was unique in the world. It allowed the chemical to be circulated through the loops for better decontamination. A decontamination factor (DF) of 40 was obtained. After decontamination iron and zinc injection were implemented to avoid recontamination and a dose saving estimated to be 1,6 Sv. (160 man Rem) in the last two outages was achieved.

The decontamination process applied was CORD and it was performed using a closed circuit, which was thought to be important to obtain a good DF. To close the circuit was necessary to connect special devices inside the reactor vessel. The many tools necessary to close the circuit were designed by NUCLENOR and they allowed performing the decontamination process without dismantling the 20 jet pumps, which belong to the recirculation system. This work, performed in such a way, allowed to reduce the length of the outage by about 6 days. The decontamination process was complemented by zinc and iron dosages to avoid recontamination. The concentrations which were maintained were 5 ppb Zn in reactor water and 1 ppb iron in feed water. The recontamination found after one operation cycle was only 20 %.

It is very important to perform the decontamination process using a closed circuit and at plants, which have jet pumps, it is very important to design tools avoiding jet pump dismantling. To minimize recontamination it is necessary to establish zinc injection and a control in feed water iron concentration.

## Chemistry Control of the $^7\text{Li}$ in Plant Systems by membrane electrolysis

The Chemistry Department has developed an electrochemical membrane technique to control the lithium concentration in the primary coolant.

During a fuel cycle about 1,5 kg  $^7\text{Li}$  are added and about 9 kg of  $^7\text{Li}$  are extracted. This means, that 7.5 kg  $^7\text{Li}$  are generated in total from boron burn out.

In PWR of former lines, ion exchange resins are used to reduce the  $^7\text{Li}$ -concentration and  $^7\text{LiOH}$  is injected to increase its concentration respectively. The  $^7\text{Li}$  that has been extracted gets lost with the resins and has to be dumped as radioactive waste, which is very expensive. One calculates about 2 m<sup>3</sup> of waste resins per cycle.

Membrane techniques like membrane electrolysis are not yet implemented in power plant construction. The method uses the property of electrically charged particles, the ions, to migrate in an electric field.

Efficiency of the developed technique was demonstrated with a pilot. The work is documented and recorded.

This procedure makes it possible to remove  $^7\text{LiOH}$  selectively out of the primary coolant and to concentrate it up to 10 g/kg. In this form it can be stored until it is needed in the next cycle. Radioactive cesium, that is also concentrated together with the lithium, can be removed with a new Cs-selective, inorganic ion exchanger. The dosage of  $^7\text{Li}$  can simply be realised by reversing the polarity of the two electrodes. The  $^7\text{Li}$  then migrates back into the primary coolant. Since  $^7\text{Li}$ -removal and  $^7\text{Li}$ -dosage are now continuous processes, no sudden changes in pH value occur.

With pole inversion this procedure is predestined to load following operations.

By implementation of the described procedure it would be possible to extend the service time of the coolant polishing system by several years. Every year it may be possible to save about 2 m<sup>3</sup> of wasted resins from the mixed bed filter that is installed in front of the boron recycle evaporator and the  $^7\text{Li}$ -removal filter. Furthermore less additional  $^7\text{Li}$  would need to be bought. Thus, it may be possible to economise on this operation.

By replacing the cation selective membrane by an anion selective membrane electrolysis could be used to control the concentration of boric acid in the primary coolant. Some preliminary experiments have already been performed successfully.

Radioactive activation- and fission products can also be removed, so this technique will replace the coolant polishing system.

## Kashiwazaki 3/6, Japan

Mission Date; 1-18 Nov, 2004

In the water quality control manual there is a short description of the ground for setting the values. It also describes the reason why the parameter is analyzed. This is a good idea, newcomers will get a good understanding in why the parameter is analyzed, and what impact the parameter can have on the process systems. Also, on the daily sampling schedules there are pictures of the sampling places. This helps the technicians to identify that he/she is at the right sampling place.

## Cernavoda, Romania

Mission Date; 22 Jan.-10 Feb, 2005

### Biofouling Control for Cooling water and fire water

The plant cooperates with a specialized Research Institute to assess micro and macro biological fouling of cooling circuits and fire water resulted in better maintenance planning and fouling combat. Care for surface waters biosystem is also surveyed through comprehensive long-term studies.

Raw service water (safety support system): The plant was actioned to identify suitable strategies for Zebra mussels mitigation since commissioning phase and starting of first year of commercial operation a treatment using a quaternary amine based biocide is applied to eliminate the remaining adult zebra mussels in raw service Water. The biocide quantity added at each treatment depends of biological water quality, analysis being performed by a specialized research institute and existing macro fouling into the system. The initial shock application has been switched to maintenance one with the intention to accommodate fouling control, cost reduction as well as environmental aspects. The biocide treatment applied at U1 since May 1997 shows good results so far. Since 1998, no unit shutdown occurs due to emergency core cooling heat exchanger reduced service water flow occur.

Fire Water System (safety support system): Monitoring of the Fire Water System to evaluate the biofouling has been started in 2002, periodic analysis being performed by a specialized research institute. Occasionally few larvae have been identified but no living mussels.

Before fire water tanks cleaning, the chemistry technical group personnel evaluate the biofouling status and compares it with the previous inspection reports.

The recommendations of the specialized research institute, to continue biofouling monitoring and to clean/fill the tanks during cold period, to avoid biofouling development are implemented by plant personnel.

Circulated Cooling Water: Three categories of monitoring are weekly performed during one-year period (action started on June 2004):

- monitoring of the main components of macrobiotic retained and recovered on filtration sieves of the raw water from distribution basin (aquatic phanerogames, macro algae, invertebrates and fish);
- monitoring of ichthyoplankton passed through the filtration sieves and reached in the water subsequently circulated into the cooling systems of the NPP (eggs, larvae, juveniles, and eventually fingerlings/fry);
- monitoring of micro biota (microalgae + tiny invertebrates) from the water filtered through the sieves and subsequently circulated into the cooling systems of the NPP.

## Volgodonsk, Russia

Mission Date; 1-19 October, 2005

Early detection of leaking SG tubes during start-up operations

The working program "Early detection of SG leaky tubes during start-up operations" defines the scope, time schedule, sequence and technique used for early detection of SG leaky tubes at the stage of the unit start-up after the outage.

A value of the leak from the primary to the secondary side is assessed based on measurement of the boric acid concentration in the samples of the boiler water taken from bottoms of SG-1-4 and gamma-spectrometry data of the primary coolant and boiler water from the SG bottom.

The working program is implemented at stages of the reactor start-up from the end of the primary and secondary circuit fill up to the time of the reactor heat up to nominal parameters:

Stage 1 -primary and secondary circuit hydraulic tests at 35/20 kg/cm<sup>2</sup> accordingly.

Stage 2 -from the end of the primary and secondary circuit hydraulic tests at 35/20 kg/cm<sup>2</sup> up to the beginning of reactor installation heat up for hydraulic leak tightness tests (integrity tests) P 1 circuit(0-15 kg/cm<sup>2</sup>).

Stage 3 -reactor installation heat up for hydraulic leak tightness tests (integrity tests) P 1 circuit (15-20 kg/cm<sup>2</sup>), P 1 circuit(100-120 C).

Stage 4 - primary and secondary circuit hydraulic tests at 180/88 kg/cm<sup>2</sup> accordingly.

Stage 5 -reactor installation heat up to nominal parameters.

The program defines acceptance criteria and personnel actions in case of leak detection from the primary to the secondary circuit.

## Borssele, Netherland

Mission Date; 8 Nov.-7 Dec., 2005

A proper annunciation to the main control room in case of unavailability of boron on-line measurement equipment allows for alternative boron monitoring and timely corrective actions.

The on-line boron analyzer has to measure, at every hour, the primary system boron concentration and to show automatically the results in the main control room for proper trending and control. Based on two internal experiences, when the analyzer was accidentally switched off and the technical specification was not met, the plant developed a control system of correctly actualization of measured data. This system gives an automatic alarm in the main control room in case a new boron concentration value is not registered in the main control room for 90 minutes. This prevents exceeding the required interval between boron measurements and permits timely use of an alternative method for boron measurement and for necessary corrective actions.

As results of this modification, no deviation was recorded by the plant in the last 10 years for on-line boron monitoring.

#### Deaerated start-up of unit

Usually when choosing water chemistry method for specific reactor, special attention is paid to the normal operation parameters - basic operation mode. In such a case the facilities are designed for the achievement and the maintenance of the necessary parameters. The norms and means of achievement of the specific parameters are not always provided for transients due to their short duration. One of such parameters affecting the Inter Granular Stress Corrosion Cracking (IGSCC) is the oxygen concentration in the primary circuit water during hot hydraulic tests and during start-up phase after a continuous shutdown. After the welded joint defects of IGSCC type had been detected in the downcomers between separator drums and main circulation pump (MCP) the plant developed the programme of primary circuit water desaeration prior to start-up. Desaeration procedure includes the following stages:

1. At temperature 70 °C the non-nuclear heating of the reactor coolant is started by running the main primary pumps. Initial contents of dissolved oxygen is around 6 ppm.
2. When temperature in the primary circuit reaches 100°C the circulation is started in through the desaerator. The steam generated in the separator drums is conveyed together with the oxygen to the desaerator where the feed water for primary circuit is warmed up.
3. At temperature 110°C the reactor heating is maintained till oxygen concentration decreases lower 200ppb.
4. Simultaneously with the removal of dissolved oxygen from the primary circuit water the feed water of the primary circuit is desaerated. Therefore the primary circuit make-up from the desaerators results only in minor increase of oxygen concentration in primary circuit water (which is less than 100 ppb)
5. During further heating till the nominal parameters the oxygen concentration decrease until 20-30ppb.

Actually no additional equipment is required for this procedure. Its performance causes extension of start-up activities by 5 to 6 hours, however it ensures to avoid the cracking effect in sensitive zone.

Powdex process on the cartridge filter for primary coolant purification system. Primary Coolant Purification System (PCPS) is used for maintaining the water chemistry parameters. It operates under the same pressure as the reactor, however the temperature shall not exceed 50°C. The system comprises 5 cartridge filters, 2 mix bed filters and a filter-trap.

In 10 years of operation the defects were identified on the valves caused by the abrasive qualities of the applied inorganic absorbent PERLITE. Only 20% of radioactivity of corrosion products were present in the primary circuit as particles with the size more than 45µm. Other radioactive pollutions were present in ion or colloid forms for which the efficiency of the cartridge filters with PERLITE was very low.

In 1993 the usage of the powdered ion-resin was tested and held at PCPS. Since 1994 the ion exchange powdered resin has been in use at INPP. Taking into consideration the composition of impurities in the primary circuit water, as well as economical factor, the mixture of cationite and anionite of Microlite type was chosen with the ratio 2:1 and size of particles 20-80µm.

The following advantages were achieved using powdered resins:

- Powdered resins ensure an efficient purification not only for particulate impurities but also for the ion impurities and charged particles of minor size.
- Total exchange capacity of the powdered resins is used in a more complete way. The ion exchange kinetics has been improved which causes the increase of purification coefficient. As a result, after system installation the specific conductivity has decreased from 0.09 to 0.07 µSm/cm.
- In accordance with the practical experience during purification of water with specific activity equal to 2.5E-5Ci/l performed in real conditions the cartridge filter with powdered resin makes the activity 5 times lower while the cartridge filter with PERLITE reduces it only for one third.
- It reduces the dose rate of the resin in the mix bed filters, decreases its destruction and the aforementioned resin can be used much longer (the life time of the resin in the mix bed filters is twice longer at about 2 years)
- When using the ion-exchange powder resin the lifetime extension of the cartridge filters with the powdered resin and reduction of pressure drops were identified.
- Due to the lifetime extension of the cartridge filter with the powdered resin and mix bed filter the capacity of the spent resin from the by-pass purification facility of the primary circuit has been decreased 2-3 times.
- Due to the exclusion of the abrasive absorbent PERLITE from the process the operation of equipment of the absorbent preparation unit and filter material retrieval has improved.

Modification of purification facility of low salt water (LSW).

Special purification facility of low salt water was installed at INPP to purify water from impurities coming from the following equipment and systems:

- Blowdown of cooling circuit of control and protection system,
- Condensate with lubricant of turbine equipment,
- Spent fuel pool,

It consisted of three cartridge filters, H+filter(strong acid cation)and OH-filter(strong base anion).

The facility had a lot of operation deficiencies:

- Often cationite resin got oily due to the high concentration of oil (lubricant) in the water of turbine equipment
- Non-conformance between the exchange capacity of H+filter and OH-filter, which caused overrun of regeneration solutions
- Unsatisfactory quality of regeneration due to the tunnel effect.

As a result the filter lifetime stopped at ~50 000m<sup>3</sup> and conductivity at the outlet was equal to 0.6-0.8μSm/cm.

After implementation of the Fast Acting Scram system where 24 channels were cooled in a film mode and the channel cavity was blown by the gaseous nitrogen the load to the LSW purification facility increased due to the necessity to retrieve nitric acid obtained as a result of irradiation. In order to improve the operation of facility and to prevent occurrence of tunnel effect, the plant developed the organisational and technical measures on reduction of oil capacity getting from the turbine equipment. The plant started modification of LSW purification facility for counter-current regeneration. As a result filter lifetime extended till ~ 80 000 - 100 000m<sup>3</sup> with conductivity at the outlet at about 0.3-0.5μSm/cm.

Although the significant improvement was evident the non-conformance between exchange capacity of H+filters and OH-filters still remained. In order to correct this last deficiency the plant decided to implement a modification on the OH-filter.

- Specialists performed calculation of the top and bottom distributor system. The special filter nozzles with the gap 0.25mm were installed on the bottom distributor system and with the gap 0.5mm - on the top distributor system.
- Protective device was developed and installed on the ventilated pipe.
- Floating inert material IN42 was loaded.
- Type of loaded anionite was changed.
- The capacity of loaded anionite was changed from 6 m<sup>3</sup> to 7.8 m<sup>3</sup>.

Thus, the "compacted bed" concept was implemented on the OH- filter which resulted in the following changes:

- Filter lifetime extended till 160 000-220 000 m<sup>3</sup>
- Water quality improved from 0.3-0.5μSm/cm to 0.12-0.18μSm/cm
- Capacity of drain water decreased of one third
- Regeneration time reduced for 30% and therefore specific amount of reagents for chemical regeneration and, respectively, the amount of radioactive wastes reduced
- Resin removal from the filter during backwashing was eliminated
- Stream is distributed along the filter cross-section in a more equal manner

All costs on this modification will be paid off within 1.5 -2 years.

In conclusions the modifications implemented at INPP are not expensive, however their performance resulted in great advantage as described in the following:

- 1.Improvement of coolant quality
- 2.Cost reduction for reagents and ion-exchange resin
- 3.Significant decrease of the amount of liquid radioactive wastes (more than twice)

4.Improvement of equipment reliability and reduction of water chemistry impact to the IGSCC in downcomers.

## Mochovce, Slovak Rep.

Mission Date; 4-20 Sept., 2006

Monitoring and evaluation of active corrosion products in the primary coolant system in order to reduce dose rate.

When in the previous years an adverse trend was noticed in dose rate at the main circulation loops of the reactors, the Mochovce NPP management created a working group in order to analyze the situation and decrease dose rates.

NPP has implemented a system for the monitoring of creation, migration and deposition of active corrosive products in the coolant in the primary circuit. By mutual comparison of activity and the radiation situation among the units of NPP Mochovce and the other units of VVER 440 type, the power plant creates good database of information for understanding the causes of current radiation situations in the primary circuit.

Power plant personnel monitor the concentration and activity of soluble and insoluble forms of corrosive products in the primary coolant, and on the inner surfaces of selected locations on primary circuit equipment. In addition, NPP monitors efficiency of purifying stations for the capture of corrosive products in the individual modes of the unit, especially during plant shutdowns.

Further indicator is dose rate at 54 defined positions in the six loops of the primary circuit. Median of the data is a good indicator of radiation field and serves for comparison with previous cycles or with other NPPs.

There is also cooperation with several experts from external organizations. The team regularly evaluates the state of the radiation situation and submits proposals of measures for further improvement to management of NPP. Operation procedures are revised in order to minimize deposit creation and release.

In the 2006, a new specific way of „soft“ decontamination of the reactor coolant during reactor shut-down stage was introduced for the first unit outage. Chemical parameters of coolant are characterized by higher oxygen concentration and this oxidizing environment supports re-suspension of corrosion products from inner surfaces of the primary circuit. As result of the procedure, the primary circuit dose rate median decreased by 25 percent in comparison to the previous year and the collective dose for the outage was the smallest one in the history of operation of the Mochovce NPP Unit 1.

The NPP has clear goals. These issues are defined in its main tasks and aims, employees are appropriately motivated for fulfillment of the given tasks. NPP has elaborated the action plan for corrective measures and defined criteria for monitoring of the radiation situation development trends of primary circuit coolant on the units.

## South Ukraine3, Ukraine

Mission Date; 9-25 Oct., 2006

Steam generator hide out return effect programme.

Application of the programme that is coming from the evaluation of hide out return effect of steam generators allows a decrease in corrosion to the secondary circuit and deposits in SG.

According to this programme, with morpholine dosing or LiOH, the plant can ensure the setting of a neutral high temperature pH in the feed water and steam generator crevices to decrease corrosion (Evaluation of optimized chemistry values is based on the relation between cation conductivity and sodium concentration).

Iron and copper concentrations were reduced about three times.

The amount of deposits on SG tube surfaces were reduced five times. Deposits are not fixed very often and are removed easily during the phase of shut down with steam generator blow down.

## Yongwang, Korea

Mission Date; 17 Apr. - 4 May, 2007

There is an online monitoring system of chemistry of the secondary side. The results are displayed on a PC and include a radio alarm system and a detailed flowchart for troubleshooting.

All systems and components of the secondary side of YGN 5&6 are monitored online. The parameters include pH, cation conductivity, sodium, hydrazine etc. These data are visualized in a schematic flow chart of the circuit and displayed on real time in the main control room and several other computers. If an alarm occurs, the shift chemist and the responsible person are informed of the abnormal condition by cell phone (responsible person) and PDA (shift chemist). An integrated flow chart on the diagnosis of water quality problems, by categorizing various sources of water contamination in the secondary water system, supports the chemist to allow location localize and identification of the problem.

The use of formalized, detailed and signed-off check sheets for the preparation and implementation of all chemistry related outage activities is an effective tool for managing increased workloads during outages.

The Chemistry section has a detailed checklist for chemical monitoring of plant shutdown and start-up. The checklist covers both the primary and the secondary loops and is broken down into a series of check sheets which cover the following time periods relating to the outage steps:

- Preparatory actions and measurements taken prior to the outage, for example including: checking the condition of the mixed bed filters, checking the levels in the concentrate tanks, operation of the coolant degasification system, stopping zinc injection.
- The measurement programme running from start-up of the degasification system to the time that the Chemistry section switches into 24 hour cover.
- The measurement programme running from the start of chemistry shift covers in the laboratory until clearance is received in order to open the reactor pressure vessel head. This period includes hideout return measurements.
- The measurement programme runs from clearance to open the reactor pressure vessel head to pond flooding including preparatory work for sipping.
- The measurement programme runs from flooding to start-up including all measurements needed for compliance with the safety specifications.
- The measurement programme runs during the period of the outage when oxygen is removed from the circuit.
- The measurement programme runs after clearance to reheat the primary circuit to operational levels including start-up of the cleaning filter systems.
- The measurement programme and the close-out activities during the first two days of operation after full load conditions have been achieved.

The checklist contains useful additional information, for example measuring parameters, measurement frequency, limits, waiting periods that need to be met, reference to relevant documents, procedures and regulations, and explanatory background information. The chemistry staff on duty sign off each action after completion. After the outage, the check sheets are retained as formal records from the outage within the Chemistry section for reference and in order to ensure lessons learnt are retained in the preparations for future outages.

This approach ensures that all the required actions are taken and that activities carried out are properly communicated among staff.

## Neckarwestheim, Germany

Mission Date: 8-24 Oct., 2007

The use of an ammonia destruction unit on liquid waste provides a significant benefit in reducing the environmental impact of the plant.

The secondary circuits of the two pressurized water reactors (PWR) of Neckarwestheim NPP unit I and II operate on high ammonia chemistry. Ammonia is removed from these circuits by the steam generator blowdown ion exchange resins, which operate in the hydrogen form. The ammonia enters the waste stream each time the steam generator blowdown ion exchange resins are regenerated. The purpose of the ammonia destruction unit, which was not part of the original plant design, is to remove ammonia from the waste water stream prior to discharge into the river.

The ammonia destruction unit comprises a two part stripping column, a chemical reactor, a fan, an air reheater, two heat exchangers and two feed pumps. The strippers remove the ammonia from the waste water, where it is heated in air to about 300°C and the ammonia is converted into nitrogen and water. The process reduces ammonia concentrations from around 1400 ppm to less than 12 ppm.

The system runs for around seven days in feedback mode with one of the collection tanks containing the waste liquid to be treated. The water from the stripping column is fed back to this collection tank to effectively lower the ammonia load of the collection tank. After about seven days, the ammonia concentration in the collection tank is about 10 ppm, and the waste water is then processed for discharge.

This unit provides a significant reduction in the environmental impact of the plant, as ammonia can have an adverse impact on natural waters.

## Chinon, France

Mission Date; 27 Nov. - 14 Dec, 2007

Through three cross-functional committees - As Low As Reasonably Achievable / Effluents and Waste Committee / Waste Reduction Group and through adherence to the radiochemical and chemical specifications, with strong management commitment, the plant is capable of controlling, reducing, and maintaining as low as possible the source term (dose), liquid and gaseous effluent releases (volume, activity, quantity of chemicals) and process-generated waste.

Over the years since 1990, the plant has progressively implemented a specific organisation structure which, in 2001, gave rise to the creation of three cross-functional committees to which Operations, Chemistry, Waste, Radiation Protection, among others, make their contribution.

These three committees make it possible to control and minimise the source term and its effect on the dose rate and releases into the environment, whilst controlling the production of process solid waste. To do so, within the committees:

- the origin of the dose rate, effluents and waste is closely monitored
- leakages are timely identified and eliminated
- objectives are defined, followed and reprioritised if necessary
- an action plan is implemented and its efficiency is measured
- regular reporting to Plant Management takes place

Plant results demonstrate:

- Extremely low levels of activity in the primary circuit (oxygenation peaks, et.....)
- Actions to improve the source term: replacement of rod clusters, pump bearings
- In terms of liquid waste, released activity has continually diminished over the last 10 years to reach very low asymptotic conditions
- The volume of process waste is controlled

## Forsmark, Sweden

Mission Date; 12-28 Feb., 2008

The Plant has optimized the oxygen content in the drain of the pre-heaters by changing the ventilation from the pre-heaters to the condenser together with installation of a bypass flow through some pre-heaters. Thus the formation of protective Haematite layers was favoured. The mass of transported iron was significantly reduced, as was the power loss due to pressure drop. This modification is even more important as power up rates will change the oxygen content in the systems.

### Implementation of All-Plant Water Treatment Facility (SODV)

Rivne NPP has implemented an All-Plant Water Treatment Facility (SODV) in order to improve the safety and economic efficiency of NPP operation by ensuring scale-free water chemistry of plant water supply systems and essential service water systems.

Implementation milestones:

1983 - Examination of hydraulic engineering structures and safety system components for carbonate deposits and recommendations for ensuring scale-free mode of the service water supply system;

1984 - 1986 - design of make-up water treatment facility (SODV) by Ural Division of ATEP USSR;

1989 - Start of SODV construction;

1993 - Finalization of the design by Designing Institute;

2000 - 2005 - Equipment installation;

2006 - Trial operations;

2007 - Development of process charts and power ascension;

2007 - 2008 - Upgrading of the lime blowdown unit to decrease lime consumption by recirculation of lime milk and amelioration of its quality.

The productivity of the Facility (SODV) is 8350 m<sup>3</sup>/h.

To ensure proper water chemistry with scale-control in service water supply, water treatment is done in two stages:

1st stage: water clarification (decanting) with the help of liming and flocculation process in decanters with a capacity of 1000 m<sup>3</sup>/h (total of 12 tanks);

2nd stage: stabilizing treatment by oxyethylenediphosphonic acid (OEDFK) and acidification by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

Upon the implementation of SODV, Rivne NPP has achieved the following results:

- Scale-free water chemistry mode for essential service water supply system of Reactor Department components (1, 2, 3 safety trains) due to the make-up of spray-ponds (units 3 and 4) after treatment at SODV.

- The consumption of sulfuric acid used for water chemistry correction of circulating water has been reduced by 80% (6267,986 tons per year in 2004 vs. 789,261 tons per year in 2007);

- The admissible limit of sulphate effluents to the environment has been reduced from 425 mg/dm<sup>3</sup> to 380 mg/dm<sup>3</sup> (Permit for special water use by Rivne NPP UKR#1/Rvn);

- The amount of effluents to the River Styr has been reduced by 38% (from 18286 thousand m<sup>3</sup> in 2005 to 11399,6 thousand m<sup>3</sup> in 2007);

- The amount of water intake for service water system of power units 1-4 has been reduced by 8% (from 53149 thousand m<sup>3</sup> in 2005 to 48855 thousand m<sup>3</sup> in 2007);

- The specific coefficient of water consumption per kilowatt-hour has been reduced from 3,3 m<sup>3</sup>/mln kW/h to 2,9 m<sup>3</sup>/mln kW/h;

- Corrosion and scale formation processes have been decelerated; that has lead to the improvement of water chemistry parameters in circulating water of units 1-4.

The inspection of condenser surfaces of Turbine Generator-5 (Unit 3) during the Outage-2007 showed significant reduction of carbonate deposits. This is the evidence of the amelioration of quality of circulating water of Units 1-3.

## Mihama 3, Japan

Mission Date; 15 Jan.- 5 Feb., 2009

Automatic resin separation by use of the colour tone charge coupled device camera (CCD) in demineralizer resins regeneration process.

To regenerate condensate demineralizer resins, it is necessary to separate cation resin and anion resin and immerse them separately in regenerative chemicals. Back washing often varies depending on the water temperature, requiring operators to perform adjustments manually. As a result, impurities could increase at the outlet of the condensate demineralizer in the subsequent operating cycle.

The CCD camera detects the separation boundary and automatically command the adjustment if required for a proper separation of the two resins.

As a result, the concentration of impurities at the outlet of the condensate demineralizer can be prevented from rising in the subsequent cycle and the operators labour for resin separation can be reduced.