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The Efficiency of Nuclear Ion Exchange Resins Applied in the Primary Circuit Demineralizers of NPP Krško

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ABSTRACT

Chemistry can influence dose rates by two aspects: chemistry conditions applied in the primary circuit and removal of (in)soluble particles. Since the primary coolant activity can have a significant impact on area dose rates and personnel doses, the main objective of purifying the primary coolant is to act on the radioactive source and keep it as low as reasonably achievable. Reduction of occupational exposure maintains confidence among workers and the public. Other factors, such as fuel duty, cycle operation, length and history, materials, steam generator (SG) surface area and particulate redeposition, also have significant contribution to the doses.

Ion exchange (IEX) is one of the most common and effective liquid effluents treatment methods in nuclear fuel cycle operations. IEX technology encompasses the sciences of thermodynamics, kinetics, ion chemistry, fluid mechanics, and economics. In the industrial water treatment, cation exchangers are used in combination with downstream anion exchangers or as a mixed bed demineralizer (combination of both cation and anion) for full demineralization. IEX is also an effective treatment method for liquid radioactive waste. In spite of its advanced stage of development, various aspects of ion exchange technology are being studied to improve its efficiency and economy in its application to radioactive waste management and coolant cleaning processes.

Over the years desire to improve the efficiency of fine colloidal particles removal and corrosion particulate removal in the primary systems has increased. There is a need for more and more efficient purification in order to decrease worker's dose during maintenance but also to decrease volumes of radioactive resin waste. Homogenization of products and usage on primary coolant treatment take into account the compromise between source term reductions, liquid and solid waste, and buying and disposal cost. As the disposal costs are much greater than the buying costs, optimization of the lifetime of the purification media, along with an increasing efficiency of pollutant removal is a major goal.

One of the effective purification methods for particulate removal is layering of macroporous (MP) resin in clean-up beds, spent fuel pit (SFP) and radwaste beds.

Lately, MP resins were also implemented in the primary circuit demineralizers of NPP Krško. The paper evaluates resin purification efficiency of different primary media, and assesses performance of gel and macroporous resin types.

Keywords: *ion exchange, resin, macroporous, gel, primary water purification, demineralizer, dose rate*

1 INTRODUCTION

The most important parameter in controlling and reducing source term in the reactor coolant system (RC) and associated systems is the control of pH. A principal contributor to source term is large inventory of components containing nickel and cobalt in the reactor primary systems wear during plant operation, resulting in activation when transported to the reactor core. This process contributes to elevated concentrations of the major contributors to radiation fields ^{58}Co and ^{60}Co nuclides in the reactor coolant and the subsequent incorporation into the oxide layers of primary system piping and components. Shutdown plan (chemistry, operations and radiological protection), proper water chemistry and media clean-up must be correct for maximum reduction in source term and critical path reduction opportunities.

Generally, purification of the various circuits in nuclear facilities is ensured by a chain of filters and demineralizers. A combination of cation, anion and/or mixed bed resins is used to remove the undesired ionic species dissolved in the fluid such as those which can induce corrosion or radioactive elements that affect local dose rate. A fine filter upstream of the demineralizers traps solid particulate matter and a filter downstream protects the circuit from resin fines.

For decades, limited number of different resins has been applied in the nuclear industry since there are very few producers of the nuclear grade resins. NPP Krško ion exchange resin practice is very similar as worldwide. Resin efficiency is constantly controlled and very good resin operability is attained.

There is a desire for more improvements of the fine colloidal particles and corrosion particulate removal in the primary systems. CVCS configuration does not provide efficient removal of colloids and extremely fine corrosive particulates which are present in RC, especially in phase of shutdown and cooldown of the plant. One of possibilities for improved efficiency of a particulate removal in the primary system is usage of a MP ionic exchange resins.

MP resins are currently used in more than 50% of the US PWR units (many comprehensive studies were performed, e.g. Duke Energy NPPs) and EPRI strongly supports such a practice. EDF also has a long-time experience with application of MP resins and uses them to a certain extent.

MP resins are one option to mitigate the effect of radiation source term; greater dose is being retained on clean up beds during outage activity and lower activity is remaining in systems and being released to radwaste treatment. The larger surface pore geometry of MP resin is more conductive to physically absorbing colloidal materials as they pass through the demineralizer bed. Matrix composition (polystyrene crosslinked with divinylbenzene, DVB) and chemical functionality (anion with quaternary ammonium as functional group and cation resin with sulfonic acid as functional group) are identical in gel and macroporous resins; they are different in internal physical structure and that gives MP resins advantage in colloidal removal. MP IE resins have pores of a considerably larger size than those of the gel type resins (resin beads are about 300 to 500 μm in diameter). The theory behind MP resins is that they can remove particles more effectively than gel resin. Gel resin is a smooth gel bead that allows water to diffuse into the bead for ion exchange. MP resin beads are a conglomeration of much smaller beads that allows water to diffuse into the "macropores" allowing ion exchange on the surface. The pores allow for more surface area and "nooks and crannies" to capture the particles. Their surface area may reach 500 m^2/g or higher. Cation MP resins have higher cross-linkage in the matrix and are more resistant to the oxidation decomposition from the hydrogen peroxide than the gel resins. This property is extremely useful for usage in SFP demineralizer. Industrial experience also showed that a let-down filter change outs during the shutdown decreased with MP resin usage.

2 RESIN OPERATION EVALUATION

2.1 NPP Krško primary ion exchange operational practice

More or less since the beginning of operation, gel type IEX resins are used in all primary demineralizers of NPP Krško.

From 2014 MP resins have been introduced in some systems. SFP and WS (refueling water storage tank) demineralizer were loaded completely with MP resins (mixed bed with 300L of strong acidic cation - SAC and 500L of strong base anion - SBA resins).

During refueling outage RFO2015, for the first time, overlayer of MP mixed bed was implemented in CVCS or CS (chemical and volume control system) shutdown demineralizer. Mixed bed contained: 500 L of gel type resin (200 L of anion + 300 L of cation) and 300 L of MP overlay (100 L of anion + 200 L of cation).

Detailed information about the primary resins applied in Krško is presented in Table 1.

Table 1 Current resin practice in primary circuit of NPP Krško

System	**CVCS**			**SFP & (RWST)**	**BR**	**WP**
Resin type	Mixed gel / MP 1. SAC + SBA 2. SAC-^{7}Li + SBA	Cation gel SAC	Anion gel SBA	Mixed gel / MP SAC +SBA	Mixed gel SAC +SBA	Mixed gel SAC +SBA
Number of beds	2	1	3	1 (1)	2	1
Resin design volume* [L]	850	850	2100	850 (1100)	850	850
Mixed bed vol. ratio* [C:A]	3 : 1	-	-	3 : 5	3 : 1	5 :1
Resin capacity [min. eq/L]	2.1 / 1.2	2.1	1.1	2.1 / 1.2	2.1 / 1.2	1.8 / 1.1
Mean bead size [mm]	0.60(0.64) ± 0.05			0.064 ± 0.05	0.60(0.64) ± 0.05	0.57(0.064) ± 0.05

** Resin volumes and volume ratios are variable depending on actual conditions in a treated media*

2.2 Data evaluation

The effectiveness of the resins is evaluated by measuring different parameters in the RC/CS/SFP/WS media (pressure drop, decontamination factor drop, chemical and radiochemical leakages from the resin, resin lifetime, etc.).

Figure 1 shows SFP resin lifetimes in the last cycles. Replacements of mixed bed were made due to high pressure drop over demineralizer and/or reduced flow through the demineralizer.
For now one obvious benefit of MP resins is longer operational time but it should be confirmed in future.

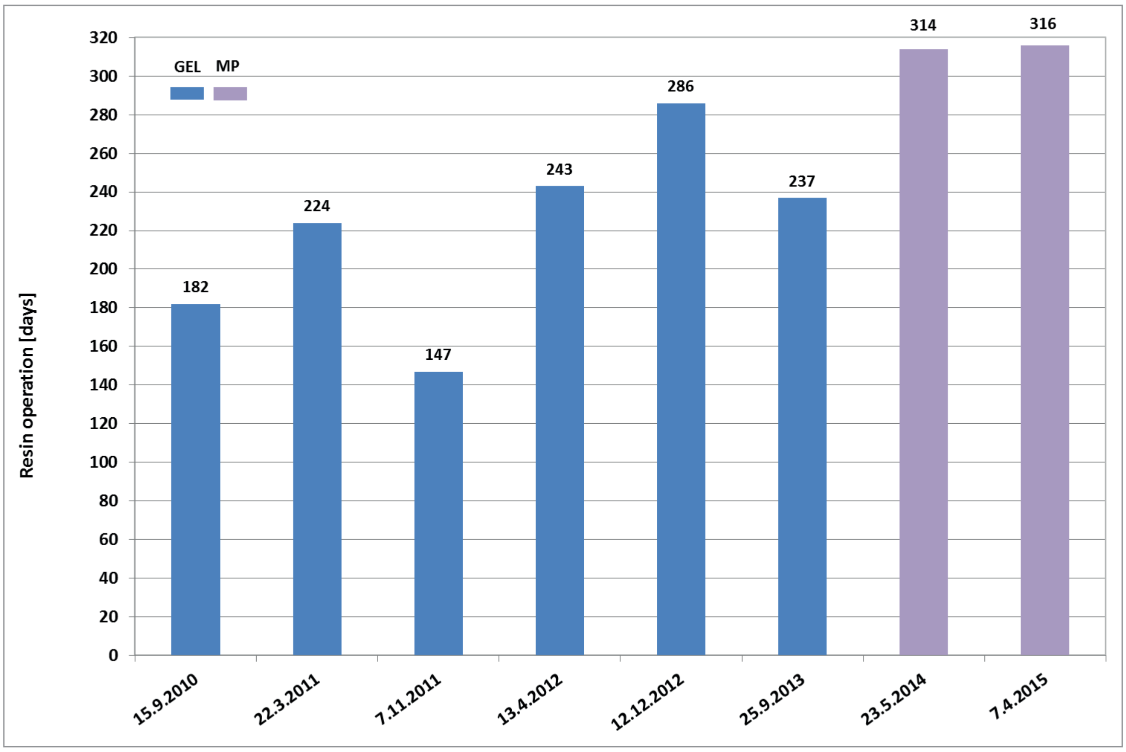

Figure 1. SFP resin operation lifetimes for the last cycles

Concentrations of aggressive ions, fluorides, chlorides and sulfates, in WS and SFP media at power operation are shown on Figures 2 and 3. Macroporous resin is efficiently purifying the media from sulfates and seems like the resin itself is more resistant to oxidizing media than gel type. For clear opinion on this we should wait for at least three complete MP resin operations.

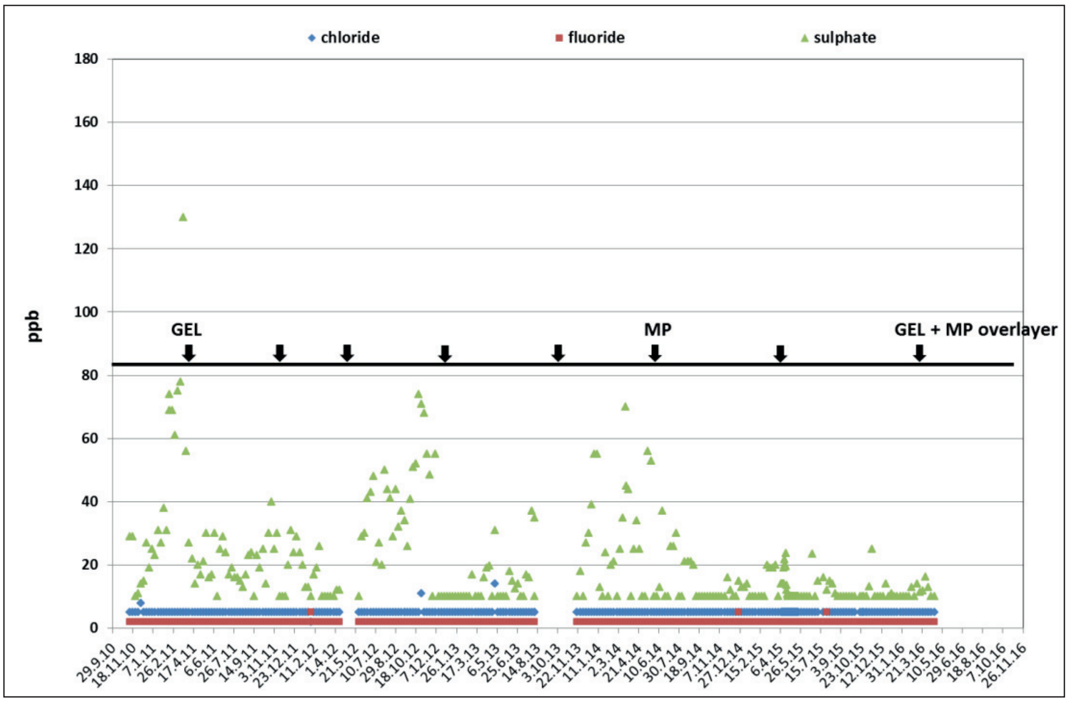

Figure 2. Impurity ion concentrations in SFP (arrows represent resin replacements)

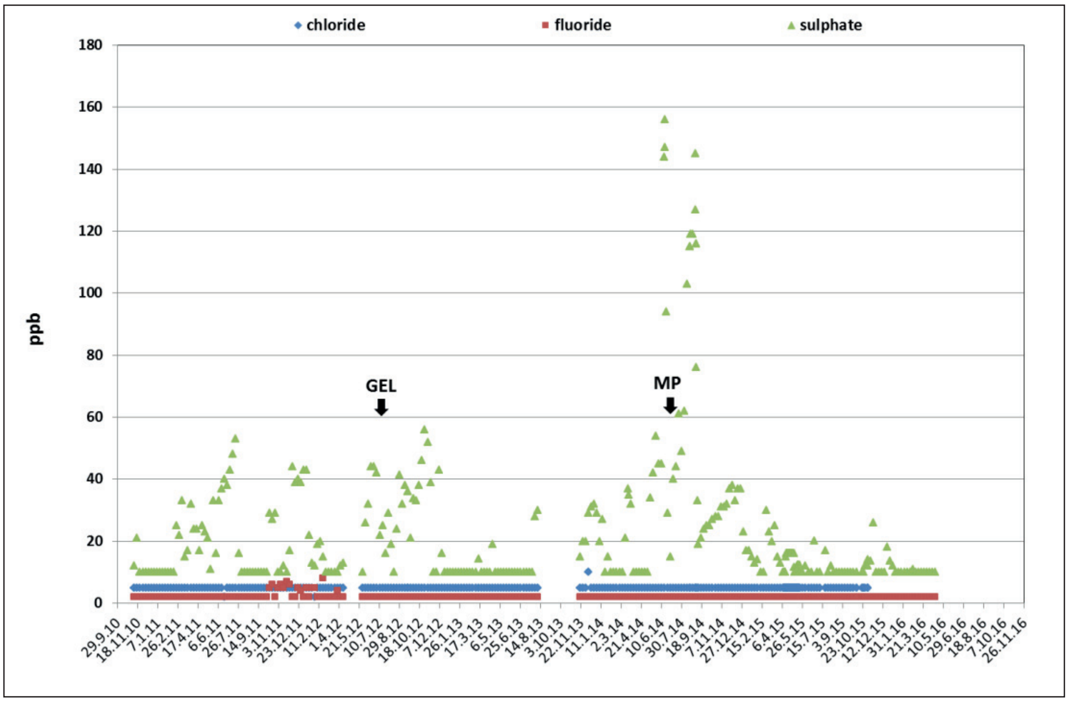

Figure 3. Impurity ion concentrations in RWST

Resin efficiency of WS demineralizer for radionuclide purification during online operation was not evaluated because of inconstant data. Operating time of demineralizer is non-continuous, variable and generally too short.

Specific activities of several radionuclides in SFP media during on line operation are shown on Figures 4 and 5 (OL25 - OL28). Good removal of soluble fraction of Ag-110m, Cs-137 and Co-58 is observed with both resins, gel and MP (Figure 6).

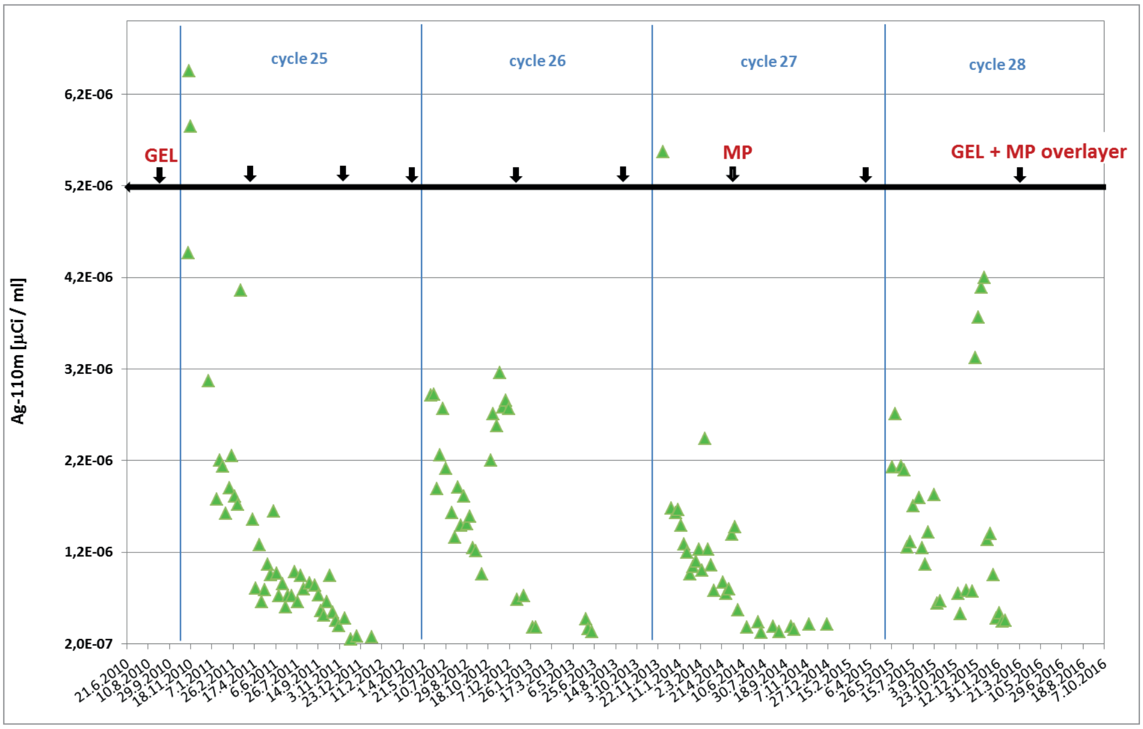

Figure 4. Specific activities of silver-110m in SFP (RFO data excluded)

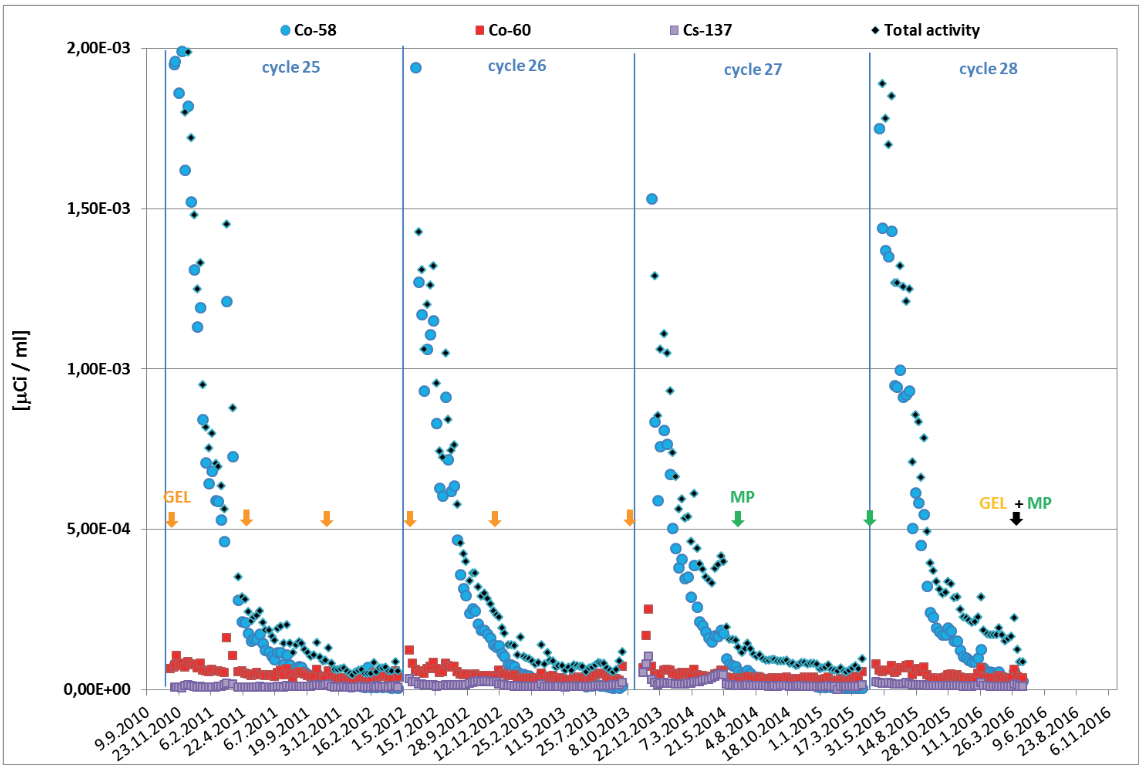

Figure 5. Specific activities of cobalt-58, cobalt-60, cesium-137 and total activity in SFP (RFO data excluded)

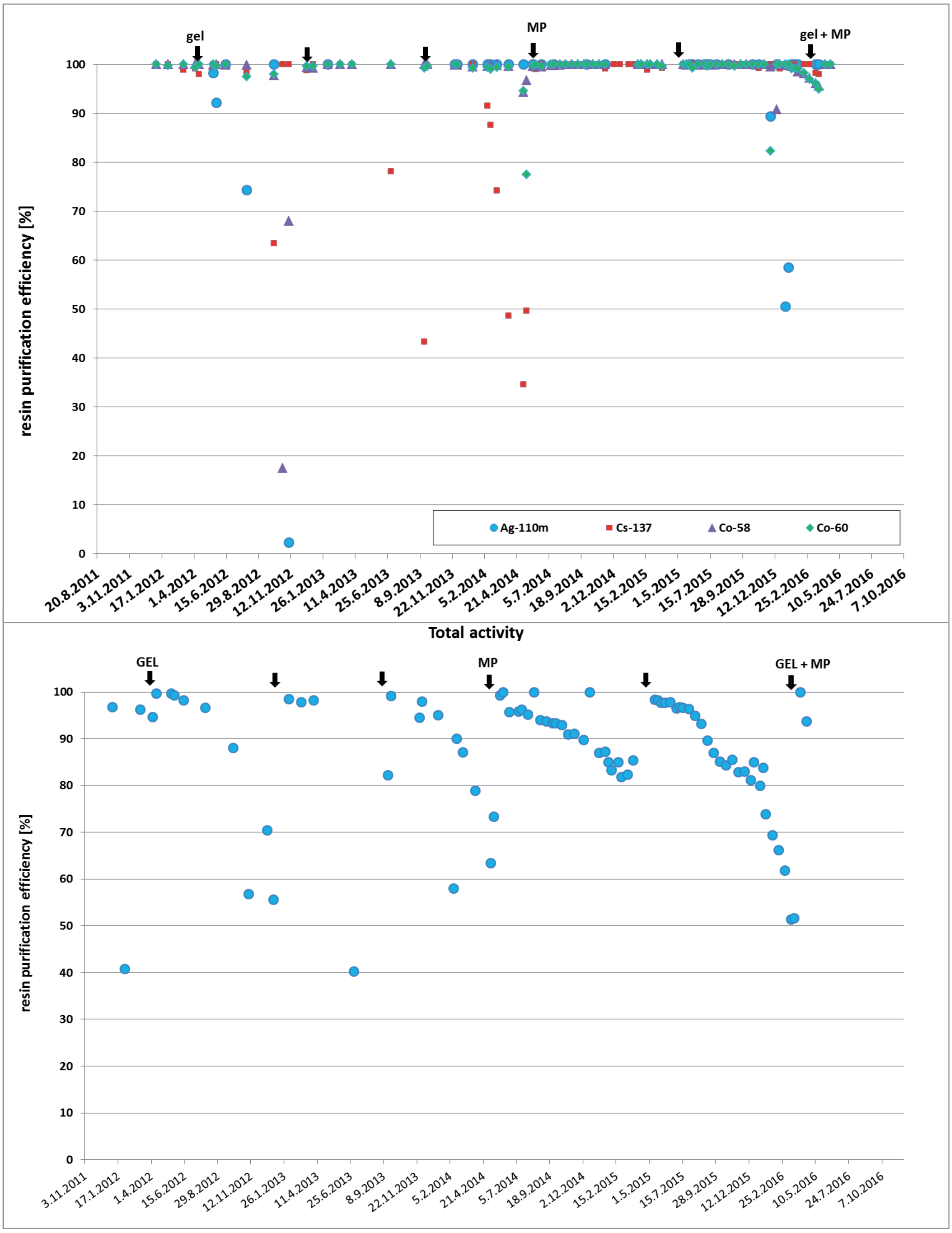

Figure 6. Purification efficiency of SFP demineralizer during on line operation (OL25-28)

Figure 7 presents comparison of the two resins, gel and macroporous, applied in SFP demineralizer (the last four replacements i.e. the last two operational cycles). Specific activities of several radionuclides (Co-58, Cs-137, Ag-110m and total activity) are observed during resin online operation. No significant differences in performance are observed from cycle to cycle or from resin to resin operation time. At the beginning of cycles radioactivities are generally higher and they decrease towards the end.

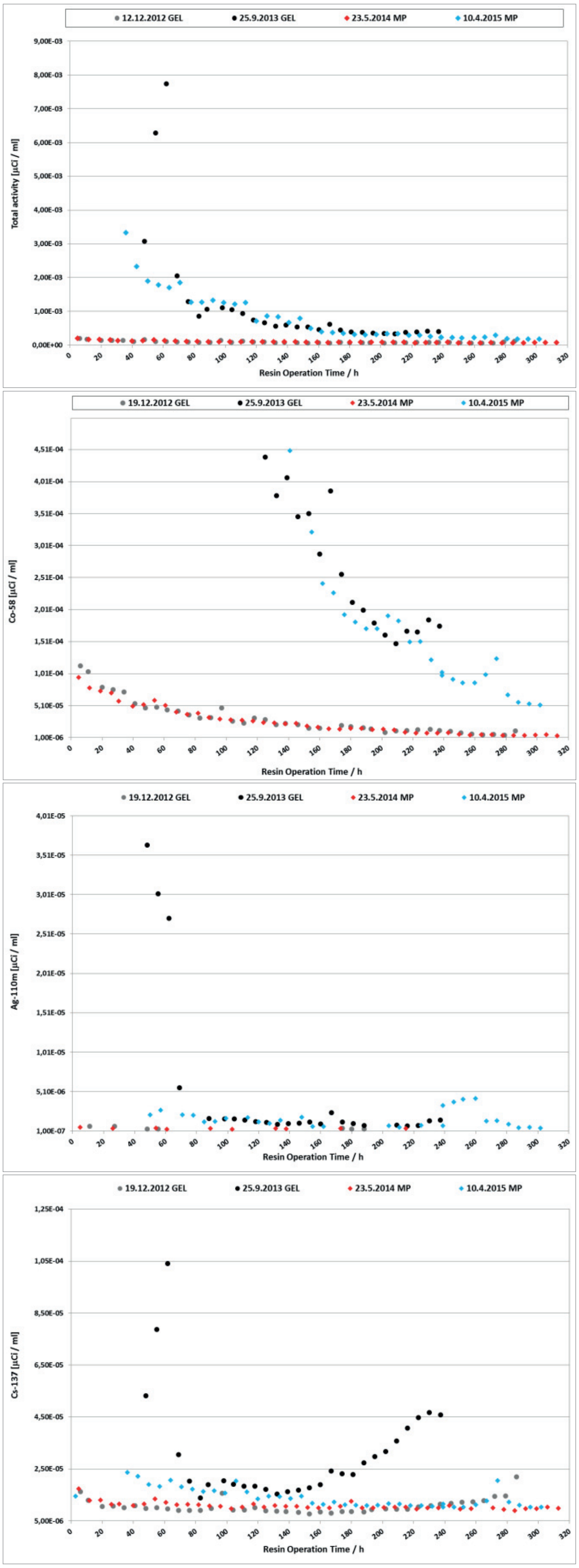

Figure 7. Comparison of specific activities in SFP media during operation time of resins, gel and macroporous: total activity, cobalt-58, silver-110m and cesium-137

Shutdown CSMB resin purification efficiencies during RFO2012, 2013 and 2015 are presented in Figures 8 - 10. It is too early to make any reliable conclusions (few more cycles and resin change outs should pass) but CVCS shutdown purification seems more stable and more efficient with MP resin overlay in comparison with gel type resins; efficiency factors are generally higher and less scattered. Removal of Ag-110m from primary coolant is performed much better with MP resins. Unfortunately no matter what resin type is used, a slight decrease of removal efficiency is observed for some radionuclides at start up (Cr-51, Mn-54, Co-60, Cs-137). It looks like non-continuous operation, temperature and flow changes, have effect on shutdown CSMB performance.

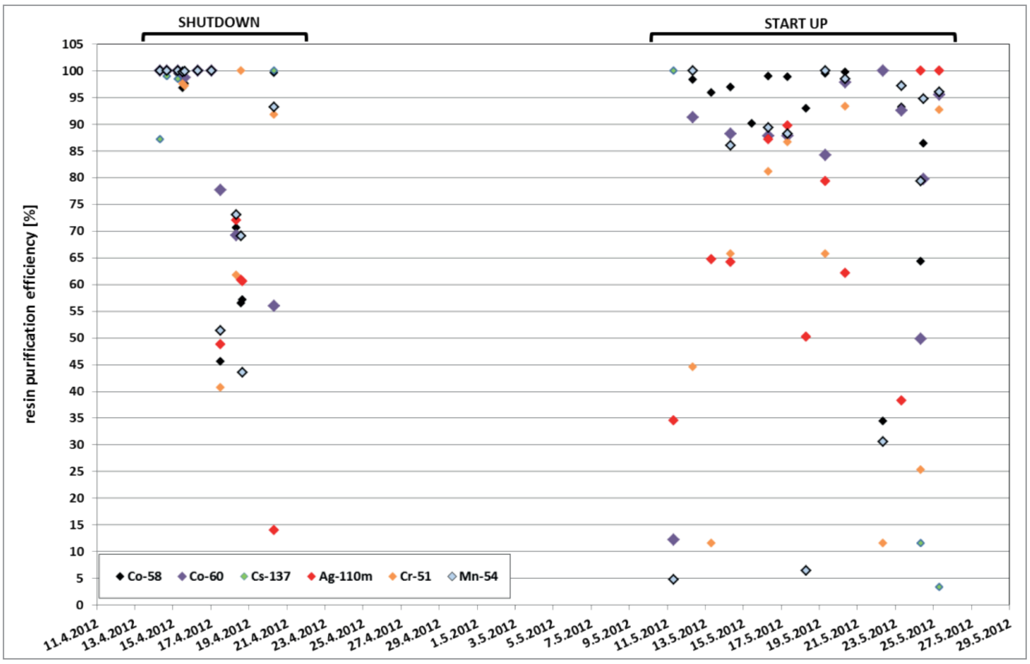

Figure 8. CVCS shutdown mixed bed resin efficiency during refueling outage 2012

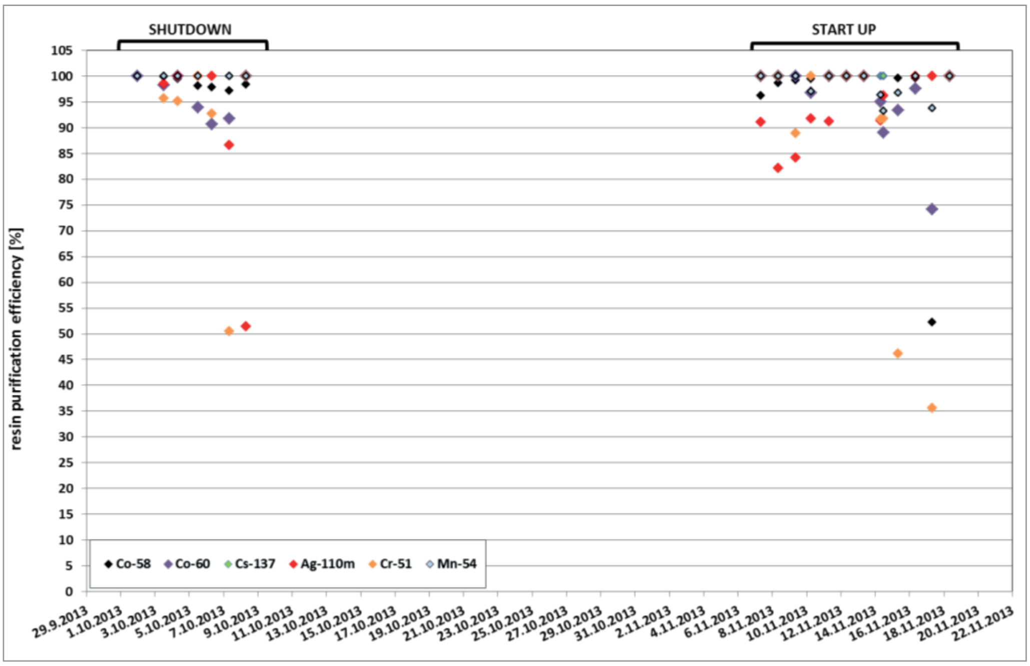

Figure 9. CVCS shutdown mixed bed resin efficiency during refueling outage 2013

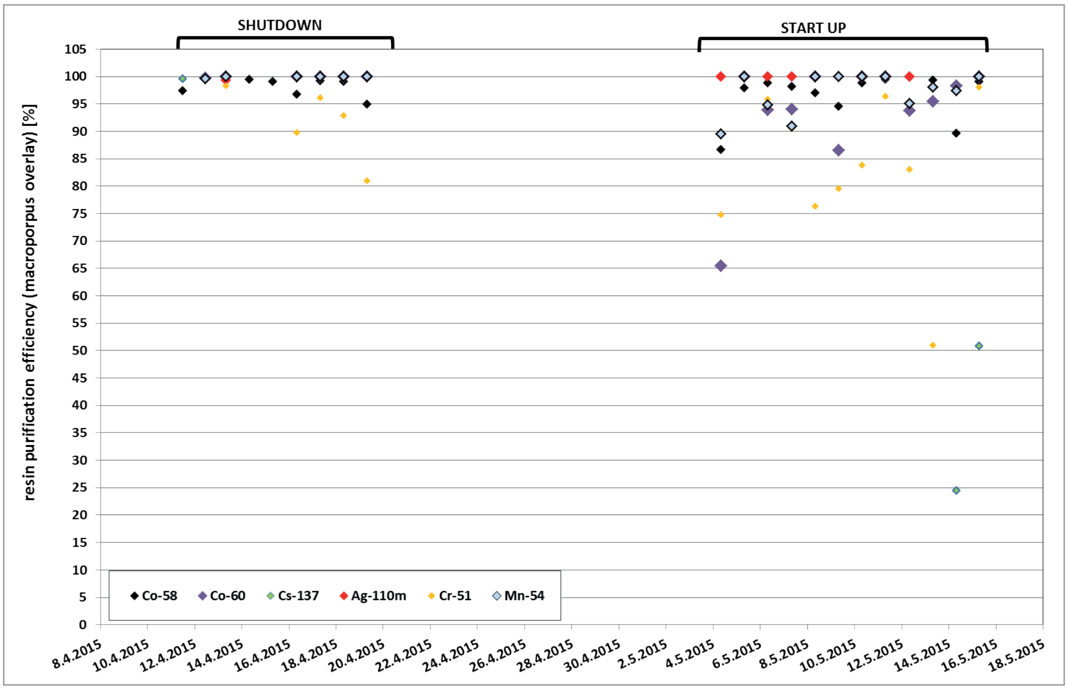

Figure 10. CVCS shutdown mixed bed resin efficiency during refueling outage 2015

3 CONCLUSION

Some NPPs use specialty resins which have more effective means of particulate removal. Layering of macroporous resin in clean up beds and in spent fuel and radwaste has become common practice. Macroporous (MP) resins were implemented in the primary circuit demineralizers of NPP Krško during OL27 and RFO2015. It is too early to make any reliable conclusions (few more cycles and resin change outs should pass) but some observations about macroporous resins could be indicated:

- MP resins are fulfilling their function and are efficiently purifying the primary media. Similar performance is observed for removal of radionuclides in SF media with both, gel and MP resins.
- Removal of sulfates is good and seems like the resin itself is more resistant to peroxide than gel type. SFP MP resin mixed bed has longer lifetime than average (over 300 days).
- During outage periods purification with MP resins seems more stable with macroporous resin in comparison with gel type resins; resin efficiency factors for different radionuclides are generally higher and less scattered.
- Generally, certain stability is noted in behaviour of Ag-110m after the MP resin implementation.

Unfortunately no matter what resin type is used, a slight decrease of removal efficiency is observed for some radionuclides at start up: non-continuous operation, temperature and flow changes effect shutdown CSMB performance.

Additionally, price of MP resin is similar to gel type resins previously used in SF/WS/CS demineralizers and better removal efficiency of MP resins would be certain cost benefit.

In the future an additional evaluation of operation of the primary ion exchangers (SF, WS and CS) is planned (approximately at a beginning of the 30th cycle) and final conclusions about the (further) use of macroporous resin will be drawn.

Lately, development of new resins is in progress. Improvements of the performance and selection characteristics of the ion exchange resins lead to the increased resin bed life, higher superior capacity, and increased selectivity (removal of target ions with a good efficiency in the presence of other ions or under harsh operating conditions) and high crush strength.

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