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Technical Note

Utilization of EPRI ChemWorks tools for PWR shutdown chemistry evolution modeling

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ABSTRACT

Shutdown chemistry evolution is performed in nuclear power plants at each refueling outage (RFO) to establish safe conditions to open system and minimize inventory of corrosion products in the reactor coolant system (RCS). After hydrogen peroxide is added to RCS during shutdown chemistry evolution, corrosion products are released and are removed by filters and ion exchange resins in the chemical volume control system (CVCS). Shutdown chemistry evolution including RCS clean-up time to remove released corrosion products impacts the critical path schedule during RFOs. The estimation of clean-up time prior to RFO can provide more reliable actions for RCS clean-up operations and transients to operators during shutdown chemistry. Electric Power Research Institute (EPRI) shutdown calculator (SDC) enables to provide clean-up time by Co-58 peak activity through operational data from nuclear power plants (NPPs).

In this study, we have investigated the results of EPRI SDC by shutdown chemistry data of Co-58 activity using NPP data from previous cycles and modeled the estimated clean-up time by EPRI SDC using average Co-58 activity of the NPP. We selected two RFO data from the NPP to evaluate EPRI SDC results using the purification time to reach to 1.3 μCi/cc of Co-58 after hydrogen peroxide addition. Comparing two RFO data, the similar purification time between actual and computed data by EPRI SDC, 0.92 and 1.74 h respectively, was observed with the deviation of 3.7–7.2%. As the modeling the estimated clean-up time, we calculated average Co-58 peak concentration for normal cycles after cycle 10 and applied two-sigma (2σ, 95.4%) for predicted Co-58 peak concentration as upper and lower values compared to the average data. For the verification of modeling, shutdown chemistry data for RFO 17 was used. Predicted RCS clean-up time with lower and upper values was between 21.05 and 27.58 h, and clean-up time for RFO 17 was 24.75 h, within the predicted time band. Therefore, our calculated modeling band was validated. This approach can be identified that the advantage of the modeling for clean-up time with SDC is that the primary prediction of shutdown chemistry plans can be performed more reliably during shutdown chemistry. This research can contribute to improving the efficiency and safety of shutdown chemistry evolution in nuclear power plants.

1. Introduction

Calculating the activity released from RCS (Reactor Coolant System) during shutdown and cool down of the reactor requires significant effort from nuclear power plant staff. Shutdown chemistry control impacts the critical path schedule during refueling outages. Chemistry personnel should have a good understanding of the potential impacts of released corrosion products in order to make the best decisions with shutdown chemistry, including hydrogen peroxide addition evolution. Moreover, the plants that are adding zinc during initial cycle mostly experience an increase of radio-cobalt activity peak during shutdown chemistry evolutions [1,6] (see Table 1 and 2).

The EPRI SDC is designed to simplify the calculation demands necessary to quantify the amount of released radioactive species, thereby allowing chemistry personnel to devote their resources on evaluating the data for further optimization of activity removal [8]. EPRI has developed the SDC, but systematic studies have not been

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Table 1
NPP system configuration.

Parameter (unit)	value
Number of steam generators (Number)	3
Number of RHR system (Number)	1
Unit has Loop Stop Isolation Valves?	Yes
Volume of water in one steam generator (m^3)	40
Volume of water in reactor (m^3)	108
Volume of water in CVCS (m^3)	8
Volume of water in one RHR system (m^3)	70
Total volume of the pressurizer (m^3)	40
Total volume of RCS water (m^3)	346

Table 2
NPP outage milestones.

Parameter	RFO 16(Date)	RFO 17(Date)
Initial Timestamp(of the first data point)	2009-02-22 17:00	2010-08-27 10:00
Timestamp of the opening of the RHR system	2009-02-24 05:00	2010-08-29 11:30
Timestamp of steam generation isolation	2009-02-27 22:49	2010-08-31 15:00
If oxidation occurs after reactant coolant pumps are secured, then set the timestamp to RCP secured time.	N/A	N/A
Timestamp of the isolation of the PZR	2009-02-24 6:09	2010-08-21 20:00
Timestamp of the opening of the PZR	2009-02-26 3:00	2010-09-01 15:00

performed on the application of the SDC at NPPs using actual plant data.

To minimize the inventory of corrosion products at RCS in nuclear power plants, prior to refueling outage, we perform shutdown chemistry. There are several chemistry control methods to maximize corrosion product release and removal to support core design and operational chemistry goals during shutdown chemistry [2].

There are two controlled phases such as acidic reducing and acidic oxidation conditions for shutdown chemistry. Boric acid is added into RCS to the refueling boron concentration (more than 2400 ppm) to achieve acidic reducing conditions. Dissolved hydrogen is reduced from 45 cc(STP)/kg to 5 cc(STP)/kg to reach acidic oxidation conditions [4]. Maximizing time in both two phases would lead to proper dissolution of nickel and activated cobalt (Co-58 and Co-60) from oxide layers [1,2]. When hydrogen is removed to less than 5 cc/kg in the reactor coolant, hydrogen peroxide would be added to the RCS in order to release corrosion products from oxide layers until co-58 concentration peak is detected. The purification letdown flow rates maintain at maximum level and through filters and ion exchange resins in the Chemistry and Volume Control System (CVCS), released corrosion products are removed [3].

The main purpose of this paper is to review and demonstrate the application of the EPRI SDC at NPPs and develop effective ways to use it as a planning tool for shutdown chemistry control regarding the phase of hydrogen peroxide addition based on calculation results from the EPRI SDC, using plant shutdown data at KHNP's NPPs.

2. Experimental methods

2.1. EPRI ChemWorks tools – PWR shutdown calculator

The RCS is composed of five main components: reactor vessel, steam generator, pressurizer, CVCS and the residual heat removal (RHR) system. In the considered systems, the CVCS is the only location where water can be removed or injected in the primary circuit. The purge is located at the entry of the CVCS system (letdown of the RCS loop). Then, the water goes through the filtration system and arrives in the volume control tank (VCT) where pure water can be added into the circuit. Finally, the water goes back into the primary loop through the charging pumps [7,8].

The concentration is considered homogeneous in all the subsystems. Two other concentrations are considered for the calculations, the concentration of the water added to the VCT and the concentration of the effluent of the CVCS before entering the VCT. If a subsystem is isolated, its concentration at the time of the isolation is stored. The RHR system is initially isolated and closed at the beginning of the shutdown, the steam generators can be isolated during the shutdown if the system includes two loop stop isolation valves (LSIV). The pressurizer can be isolated and reopened at any time depending on the needs [8].

The shutdown calculator performs mass balance calculations as to the inventories released and removed for each chemical species of interest. In order to accurately perform the mass balance calculation, the data required for input includes bulk RCS water chemistry, bulk RCS radioisotopes, bulk RCS soluble and insoluble fractions of activated corrosion products, as well as the respective items for the CVCS demineralizer effluent. Given the data, the shutdown calculator can derive accurate amounts of each chemical specie released from the reactor core to the coolant, as well as the species removed via the CVCS system, for each interval of time, as well as cumulative amounts for each interest species [7,8].

Removal half-life calculation is based on non-filterable Co-58 concentration after maximum level using the equation:

$$\frac{C}{dt} = -\left(\frac{Q_{purification}}{V_{RCS}}\right) C_0, \mathrm{C} = C_0 e^{-\left(\frac{Q_{purification}}{V_{RCS}}\right)t}$$

$$\ln(\mathrm{C}) = ln(C_0) - \left(\frac{Q_{purification}}{V_{RCS}}\right) t$$

where C and C_0 are Co-58 concentration in RCS (GBq/m^3) at times t and 0, respectively. $Q_{purification}$ represents CVCS purification flow rate (L/min). V_{RCS} is RCS total volumes (m^3) and t is purification time (s).

2.2. SDC modeling for shutdown chemistry clean-up

To evaluate SDC as it is utilized for predicting the shutdown clean-up period for next activities, we have analyzed results with SDC from performed data in the NPP with SDC to clarify the certainty of using SDC for shutdown clean-up time prediction [9]. Entire data of shutdown clean-up were included to see the difference between SDC and actual performed data in plants. Additionally, creation of modes was attempted in order to see how SDC results can be utilized to estimate shutdown clean-up time to expected limits for certain radio nuclides.

2.2.1. Assessment of SDC results with actual data from NPPs

We used shutdown chemistry data from one of KHNP NPP to evaluate reliability of SDC results (see Table 1 and 2). The plant data include: 1) starting to add zinc into reactor coolants systems to evaluate SDC results with normal shutdown and 2) shutdown data with zinc injection since it is known that zinc injection into RCS occur shutdown release and leads to changes in corrosion product transport [5]. Shutdown chemistry data including pre-zinc injection, RFO 16 and post zinc injection, RFO 17 from the same plant are

used for assessment of SDC. The EPRI SDC system configuration and outage milestones can be seen in Figs. 1 and 2 below.

Table 3 shows the listed plant information and RCS data in the input conditions and data category. Although all available data obtained from the plant were included in the table; however, there are blanks in the table where data were non-reliable or absent. As the 'Plant Information' tab includes the most critical data, reliable input data (temperature, letdown flow rates, etc.) should be listed to obtain accurate results.

2.2.2. SDC modeling for shutdown chemistry clean-up before shutdown

The milestone is essential to estimate and optimize RFO periods before start-up. Normally, the previous experience for shutdown

Table 3
EPRI SDC Plant chemistry information.

Parameter	Unit	RFO 16	RFO 17
Reactor Power	%	0–100	0–100
O_2	ppm	0	0
H_2O_2	ppm	0–2	0–2
H_2	cc/kg	0–48	0–48
Reactor Temperature	°C	60–304	60–296
Pressurizer Level	%	100	100
CVCS Charge Flow Rates	L/min	283.3–450	266.7–450
CVCS Letdown Flow Rates	L/min	283.3–450	266.7–450
Li	ppm	0.24–1.21	0.19–0.51
B	ppm	57–2311	89–2198

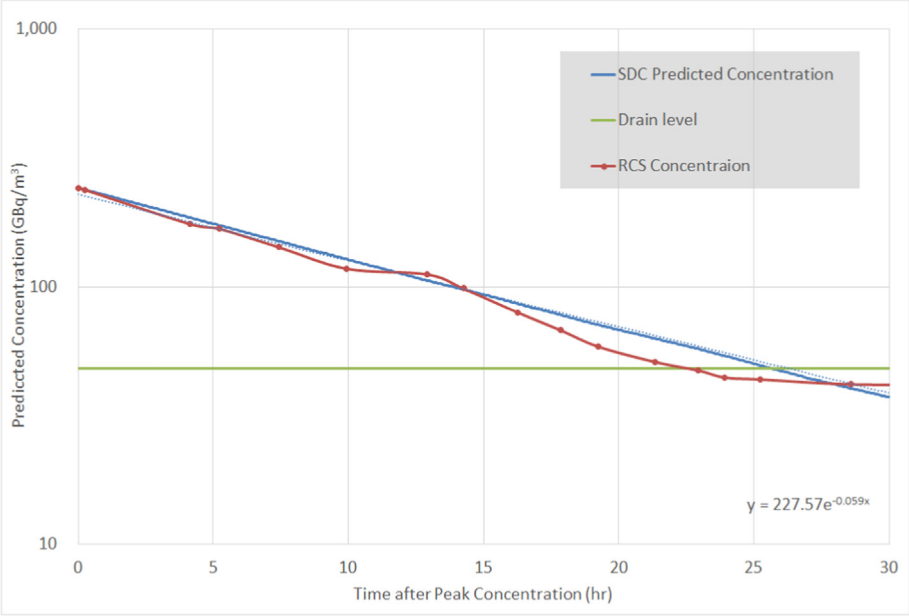

Fig. 1. EPRI SDC predictions of Co-58 for RFO 16.

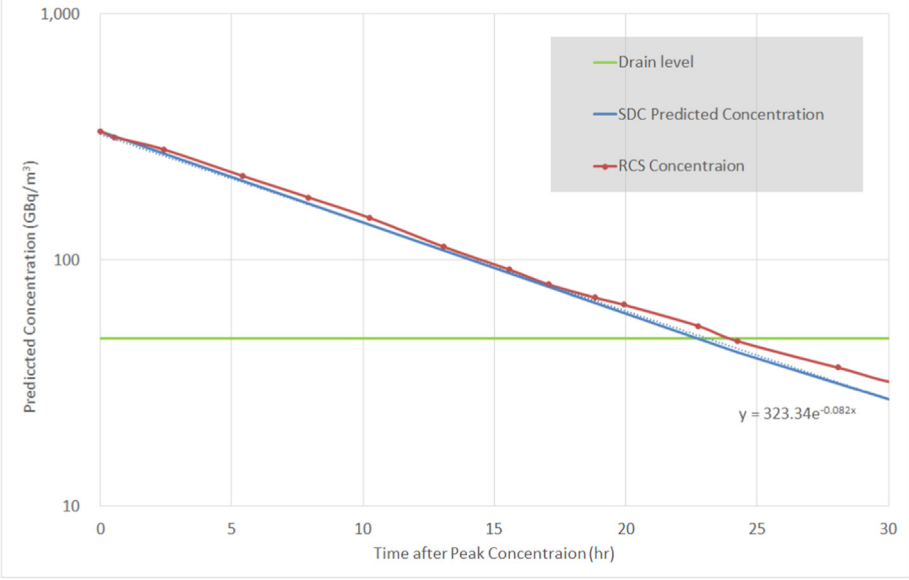

Fig. 2. EPRI SDC predictions of Co-58 for RFO 17.

cleaning periods without the criteria were used, but could use SDC as the standard for the expected clean-up time during RFO.

In order to get reliable data, we should consider the standard data for modeling. Every plant has different trends for clean-up, so a decision for standard data should be selected upon careful consideration of plants' circumstance. Several methods are reviewed as follows, but the standard data suitable for each plant should be developed with own consideration in advance.

For initial cycles after commercial operation, the circumstances of corrosion condition are different in operated NPPs. For instance, the peak data of initial 10 cycles are likely to be lower than normal operations after cycle 10.

Moreover, due to some of transient situation, the peak of concentration could increase abnormally and for some reason the peak could be very low. For those reasons, to get reliable standard data, we need to consider the proper methodology to get the average data.

SDC is eligible to make prediction for clean-up time to set up the schedule of RFO milestone in advance of shutdown cleaning operation. Average data for entire cycles is not representative due to the influence of Co-58 releases of operational conditions and transients including reactor coolant pump changes and fuel defects. Therefore, average data for selected cycles is more reliable when we used sufficient shutdown data more than 10 cycles.

3. Results and discussion

After inputting the actual plant data, we calculated the prediction results of SDC. As shown in Fig. 1, the red dots represent actual plant data and the blue line is predicted data by EPRI SDC. The plant's clean-up limits mostly depend on plant's standards and regulatory requirements. However, mostly Co-58 concentrations are used to decide the time to drain and open S/G manway for next activities of RFO. Therefore, we assumed the clean-up limits as Co-58 1.3 μCi/cc (48.1 GBq/m^3).

Fig. 1 shows the calculation results of EPRI SDC for Co-58 clean-up time for RFO 16. The blue line in Fig. 1 represents estimated clean-up time to reach an acceptable Co-58 concentration level of 1.3 μCi/cc, and the red line represents actual shutdown clean-up data for RFO 16.

It took 23.93 h after the Co-58 peak concentration to reach 1.3 μCi/cc (48.1 GBq/m^3) of Co-58 from the shutdown chemistry data for RFO 16, whereas EPRI SDC predicted a clean-up time of 25.67 h. The difference between the actual and predicted results was 1.74 h. The SDC prediction of clean-up time was similar to the actual results with deviation of 7.2%.

Fig. 2 shows the calculation results of EPRI SDC for Co-58 clean-up time for RFO 17. The blue line in Fig. 2 represents estimated clean-up time to reach the Co-58 concentration level of 1.3 μCi/cc, and the red line represents actual shutdown clean-up data for RFO 17. Plant information and normal RCS operation data, identical to those of RFO 16, were used in the calculation of the EPRI SDC. The clean-up trends were calculated with EPRI SDC by inputting shutdown chemistry data of RFO 17.

It took 24.75 h after the Co-58 concentration peak to reach 1.3 μCi/cc (48.1 GBq/m^3) of Co-58 from the shutdown chemistry data for RFO 17, whereas EPRI SDC predicted a clean-up time of 23.83 h. The difference between the actual and predicted results was 0.92 h. The SDC prediction of clean-up time was similar to the actual results with the deviation of 3.7%.

As modeling for prediction of clean-up time with SDC, we used average peak concentration after cycle 10 (see Fig. 3). Normally, before cycle 10, the peak concentration is lower than stabilized operation. Standard normal distribution band from previous RFO data to predict the possibilities prior to shutdown chemistry if extraordinary experiences are not present such as initial zinc injection into RCS, failed fuels and etc. Even if plants have special transients, more consideration for the band shall be taken.

To compare the results, we used the average peak data excluding the RFO 12 due to short operation period until RFO 16 to analyze actual results RFO 16 which were used above.

The average peak data of Co-58 was identified to be 7.04 μCi/cc with standard deviation (sigma, δ) of ±0.78. Using this information, we applied a probability density function in the below equation with 2δ, 95.4%, to create a time band that predicted to upper and lower values for Co-58 peak concentration compared to the average data (see Table 4). The equation used for this analysis takes into account the average value (μ) and standard deviation (δ) to determine the probability of a certain value occurring (see Fig. 4).

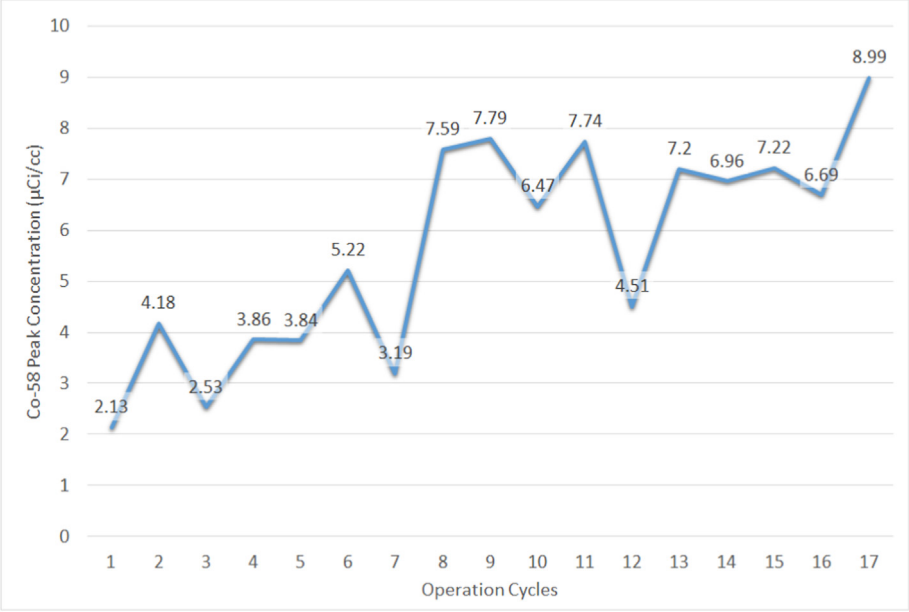

Fig. 3. Co-58 peak data during shutdown chemistry at the NPP.

Table 4
Co-58 peak data for SDC modeling.

	Average (μ)	Standard Deviation(δ)	Upper Band (μ+2 δ)	Lower Band (μ-2 δ)
Co-58 concentration (μCi/cc and GBq/m^3)	7.05 (260.85)	±0.78	8.60 (318.20)	5.49 (203.13)

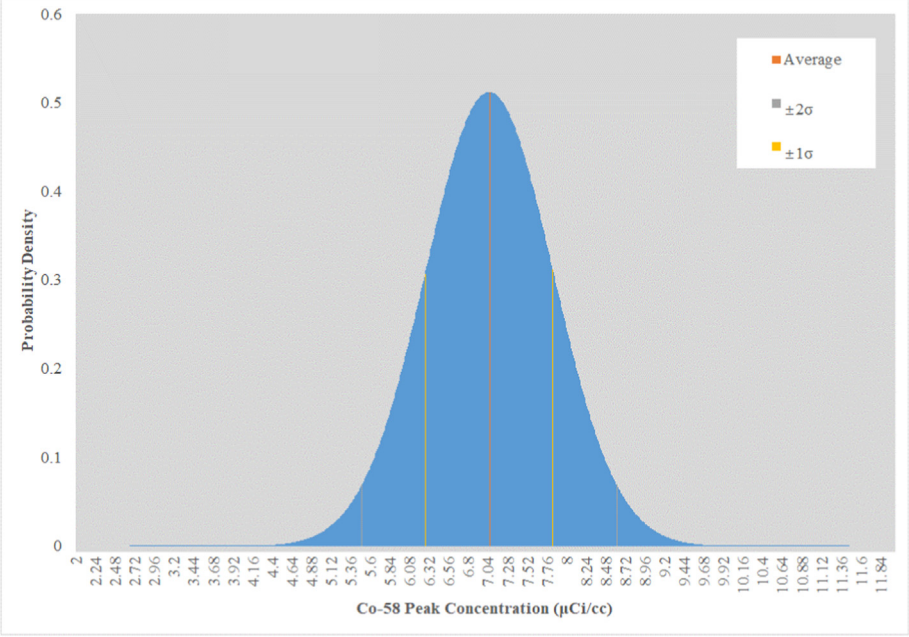

Fig. 4. Standard normal distribution for Co-58 peak data during shutdown chemistry at the NPP.

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}, -\infty < x < \infty$$

where μ represents average value and δ represents standard deviation.

The blue line in Fig. 5 shows the result of clean-up time for upper predicted concentration data from average data (7.05 μCi/cc = 260.85 GBq/m^3). The estimated time to reach 1.3 μCi/cc (48.1 GBq/m^3) was about 27.58 h from upper predicted Co-58 peak concentration, 318.20 GBq/m^3. Moreover, the red line in Fig. 5 is the result of clean-up time for lower predicted concentration data from the averages. The estimated time to reach 1.3 μCi/cc (48.1 GBq/m^3) is about 21.05 h from lower predicted Co-58 peak concentration, 203.13 GBq/m^3. Shutdown data for RFO 16 were used to obtain these estimates.

Therefore, according to our predicted modeling, RCS clean-up time band for next RFO is between 27.58 and 21.05 h. For the RFO

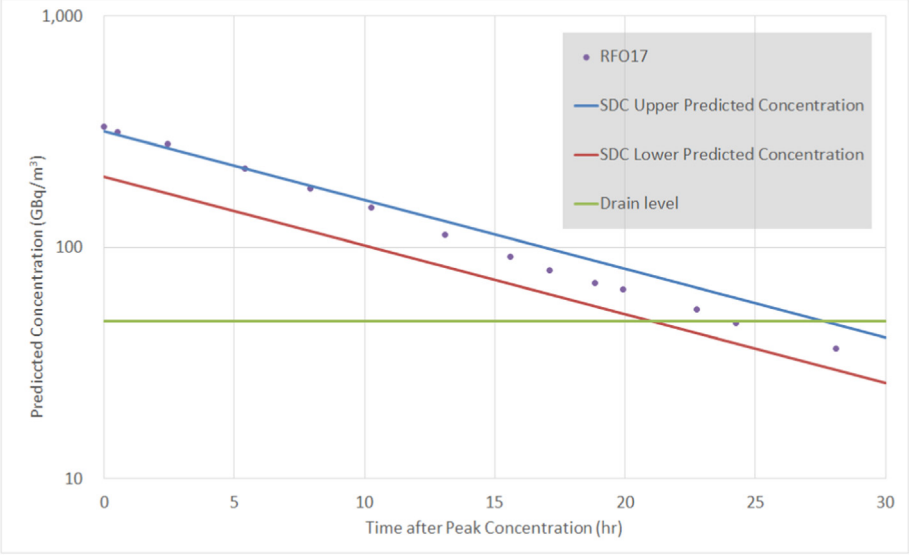

Fig. 5. EPRI SDC predictions of Co-58 concentration band.

schedule, using the more conservative value, 27.58 h is more flexible to arrange RFO schedules of the clean-up time. To compare with actual plant data, it took 24.75 h as we simulated the modeling for shutdown clean-up time for RFO 17 as above. Therefore, it is within our calculated bands.

The modeling approach using EPRI SDC for predicting RCS clean-up time is a useful tool that can improve the planning and execution of shutdown chemistry during RFOs. By establishing purification time bands, the plant can ensure that the RFO schedule is optimized and that the necessary chemical treatments are performed efficiently and effectively. However, it is important to continuously review and improve the modeling approach to account for abnormal cycles and unexpected events, as these can significantly impact the clean-up time and shutdown chemistry plans. By leveraging data and implementing modification factors, the modeling approach can be further refined and optimized for future RFOs.

4. Conclusion

Shutdown chemistry evolution is an important process in nuclear power plants to ensure safe operation and minimize corrosion products in the reactor coolant system. EPRI SDC is a tool that provides estimated clean-up time for RCS based on Co-58 activity data. In this study, we evaluated EPRI SDC results using actual plant data and modeled the estimated clean-up time using average Co-58 peak concentration during normal cycle. The results showed that EPRI SDC provided reliable estimates of clean-up time and modeling can be used to predict shutdown chemistry plans more accurately. This research can contribute to improving the efficiency and safety of shutdown chemistry evolution in nuclear power plants.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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