

PRESSURIZED WATER REACTOR PRIMARY CHEMISTRY INITIATIVES AND IMPACT ON PLANT DOSE RATES

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ABSTRACT

Pressurized water reactor (PWR) primary system dose rates are impacted by several factors including materials, core design, cycle operations and chemistry controls. Plant chemists are continually challenged to support rapid shutdowns for refueling, optimized core designs, and major component replacements. This requires an understanding of the behavior of a complex mixture of corrosion products that are released from in-core and ex-core surfaces.

The application of primary side zinc injection in PWRs is one of the tools a plant chemist can employ that continues to show a positive impact of dose rate reduction. PWR zinc injection is applied in approximately 68 plants world-wide and over 80% of the plants report injecting zinc as part of an overall source term management program. The remaining plants report injecting for benefits related to primary water stress corrosion cracking (PWSCC) or corrosion product management program.

The benefits obtained from zinc injection during power operation are relatively well characterized while optimized shutdown chemistry evolutions provide a different set of challenges to the chemist. Coolant chemistry is transitioned from a slightly alkaline reducing condition to an acidic oxidizing condition in a short period of time. These changes can result in significant release of corrosion products that, if not managed correctly with sufficient cleanup scheduled, can adversely impact plant dose rates for plant workers. The application of well planned and executed shutdown chemistry evolutions coordinated with outage planning prepares the plant for refueling without adversely impacting plant dose rates.

This paper provides an overview of the EPRI PWR Zinc Application Program and correlates data collected as part of the EPRI Chemistry Monitoring and Assessment and Standard Radiation Monitoring Programs and several complete shutdown chemistry profiles with the impact on plant dose rates.

1. INTRODUCTION

PWR dose rates are impacted by several factors, not one single factor can be discounted for long term success in managing plant dose rates. [1]

There are two defining areas for site personnel to consider and evaluate: dose rate impacts and dose impacts. The differences are significant and present different challenges for plant personnel. The dose impacts are culture, work control, training, and application of human performance tools and will not be discussed in this paper. The factors impacting dose rate or source term and the primary chemistry impacts will be the focus of this paper.

Figure 1 provides an overview of the complexity related to evaluating plant dose rates and dose to plant conditions. The overall purpose of Figure 1 is not to show a complete story but to show the many components and the complex nature of the factors impacting plant dose rates. Figure 1 also shows that not one area can be approached from a source term / dose perspective but an integrated approach provides the best opportunity for improvements.

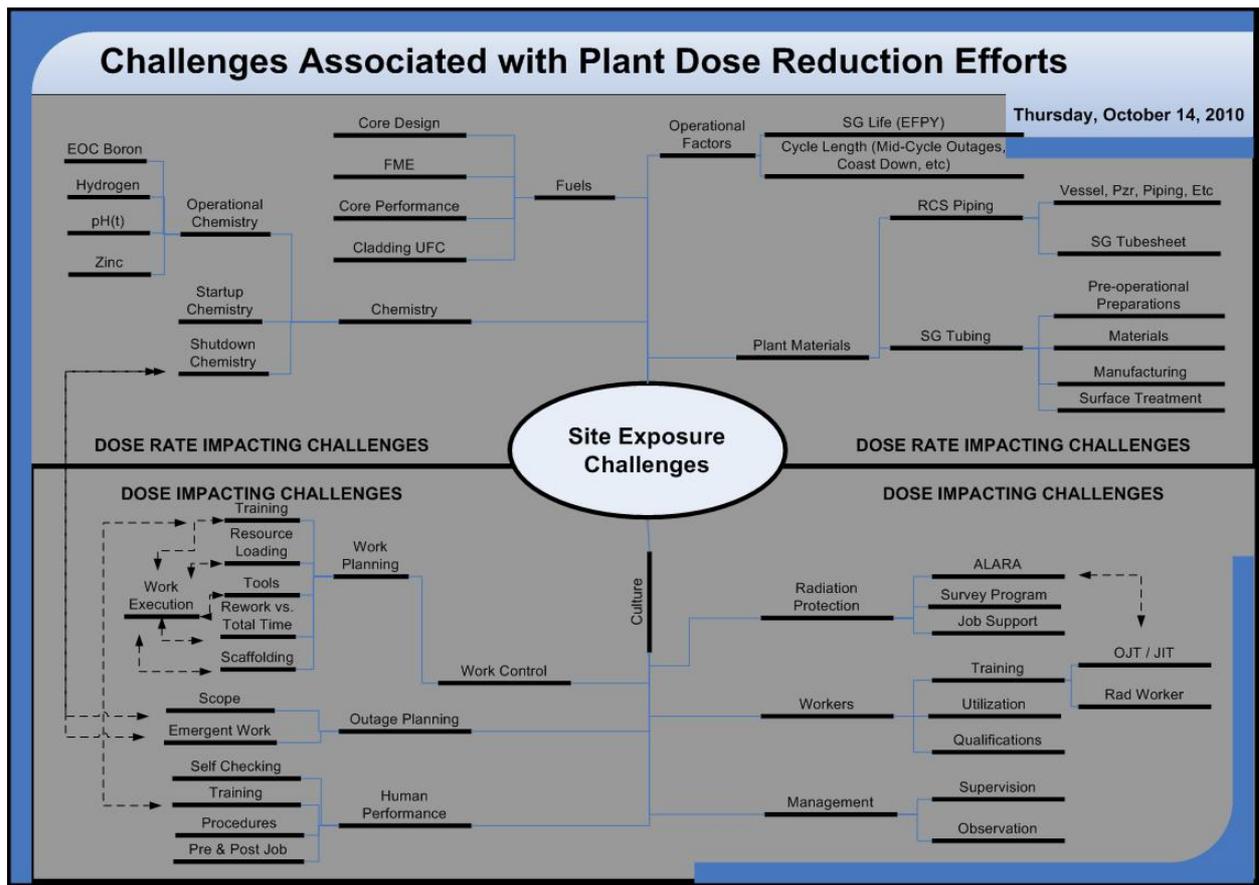


Figure 1
Challenges Associated with Plant Dose Reduction Efforts

EPRI continues to correlate and trend plant chemistry, radiation monitoring, fuel related through various programs. When this data collection and monitoring is combined with specific analyses, these results have provided the necessary input into comprehensive EPRI reports on the impact to plant dose rates. In 1997, EPRI established the SRMP to collect and analyze dose rate related data from Westinghouse plants. The database has expanded in recent years to cover Westinghouse, Combustion Engineering (CE) and Babcock and Wilcox (B&W) designs and currently has over 1000 cycles of SRMP information.

In 2007, the Chemistry Monitoring and Assessment (CMA) database was created and modeled after the highly successful boiling water reactor (BWR) database and as of today has over 350 cycle of detailed chemistry information. The SRMP data has also been incorporated into this database to facilitate assessment of chemistry program impacts on dose rates. [2]

Coupling the chemistry and SRMP data with the Fuel Reliability and Steam Generator Degradation Databases provides potentially the most comprehensive review of plant materials, fuel and chemistry impacts on plant dose rates.

2. FACTORS IMPACTING PLANT DOSE RATES

Corrosion products are generated from out-of-core surfaces, transported to in-core surfaces which in turn results in activation and followed by subsequent release or transport of these products to ex-core surfaces. Several authors have attempted to quantify the amount of corrosion products (i.e., nickel and iron) released during each cycle and the results vary from 9 to 55 kg of crud which is available for deposition on fuel surfaces. [3, 4, 5] Though the numbers vary considerably the amount of corrosion products available for deposition and considering the impact of letdown systems on the ability to cleanup and remove the corrosion products a significant inventory is still available for activation contributing to plant surface contamination.

A brief summary of the impact of fuel, plant materials and operational challenges on dose rates is provided in Section 2. Chemistry impacts on plant dose rates will also be discussed in detail in Section 2.

2.1 Fuels

Utilities continue to optimize fuel designs and economics. With increases in fuel duty, fuel cladding surface evaporation rates (i.e., sub-cooled nucleate boiling) and temperature increases can be observed and have major impacts on corrosion product deposition and activity transport. It is expected and has been observed, that with increased boiling rates the magnitude of deposition is increased in the upper regions of high duty plants. [1] Core design changes should always be considered when assessing or predicting dose rates.

Many utilities are considering, and several have implemented, ultrasonic fuel cleaning as part of an overall core crud mitigation strategy, but the overall impact related to dose reduction is limited. Though the benefits of fuel cleaning related to core deposit removal and dose rate impacts are difficult to define at this time, it is clear that removal of crud from fuel surfaces reduces the crud burden on reload fuel which may have additional benefits related to axial offset anomaly (AOA) mitigation.

2.2 Plant Materials

The steam generator (SG) surface areas can exceed 50% of the overall wetted primary surfaces and in many cases with replacement SGs this number can approach 70% of the total wetted surface area. In reviewing the EPRI sponsored Steam Generator Degradation Database (SGDD), replacement SGs have increased surface area from 225,000 ft² to over 300,000 ft². [6] Considering the release estimates discussed in section 2.0, these replacements can produce a significant increase in corrosion products during the first 2 cycles of operation following replacement. Reference [1] attempted to review and normalize ⁵⁸Co shutdown releases to tubing surface area and system volume for Westinghouse plants. The results are shown on Figure 2, but as noted in Reference [1], the material factor alone does not account for the behavior entirely.

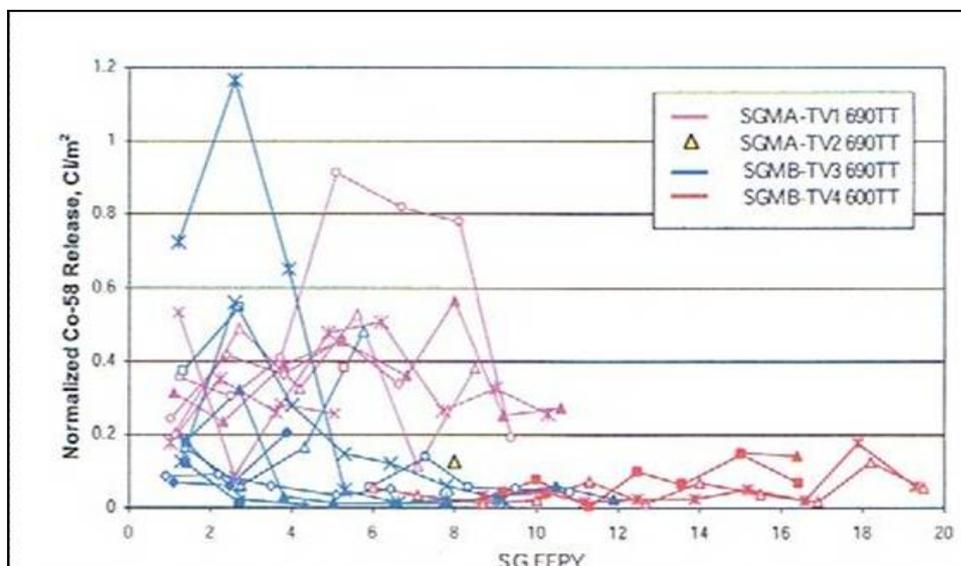


Figure 2
⁵⁸Co Normalized Release Following Peroxide Addition (Westinghouse Replacement SG)

It is important to understand the impact of all the component replacements in the primary system especially related to ⁶⁰Co and dose impacts. Site cobalt reduction programs must maintain diligence during the procurement process or dose rates will be impacted from ⁶⁰Co activity transported in the system. A general industry rule of thumb or estimate is that 1 gram of ⁶⁰Co is approximately equivalent to 1132 curies of radioactivity. Deposition across the system may not result in a significant

change to dose rates dependant on piping size and thickness, but deposition in lower flow areas or where an accumulation of corrosion products could occur could significantly change the local dose rates.

2.3 Operational Factors

There are many operational factors that can significantly impact dose rates. The impacts of mid-cycle outages and/or trips on subsequent shutdown releases are difficult to predict. Plant shutdown close to refueling outages that required plant cool down have resulted in increased dose rates. These shutdowns should be carefully planned and consideration on the refueling outage impact should be part of the outage planning. EPRI has several ongoing projects to evaluate these impacts.

2.4 Chemistry

There is extensive literature on the subject of coolant chemistry and the impact on corrosion product release and deposition which will not be discussed in this paper. This paper focuses on two areas of discussion; pH_T and zinc injection.

2.4.1 Operational pH_T

In the normal range of operation, primary coolant pH_T (7.0 – 7.4) has minimal impact on corrosion and release rates of associated plant materials. According to Reference [7], the corrosion rates of Alloy 600 and Stainless Steel are defined by Equations 1 and 2.

Alloy 600 Corrosion Rate:

$$CR_{600} = 0.83 \times (10^6)^x [H^+] + 0.92 \quad \text{(Equation 1)}$$

Stainless Steel Corrosion Rate:

$$CR_{SS} = 1.7 \times (10^6)^x [H^+] + 1.84 \quad \text{(Equation 2)}$$

Primary coolant pH_T can have a significant impact on deposition of corrosion products onto fuel surfaces (in the absence of boiling) and activity incorporation on ex-core surfaces. The basic understanding is that solubility cannot exceed the equilibrium concentrations. Figure 6-1 of Reference [1] shows that as core temperature increases, and with a RCS $\text{pH}_T < 7.4$, iron is expected to precipitate on core surfaces unless plants increase RCS pH_T above 7.4. The limiting solubility of iron decreases across the core as temperature is increased unless primary pH is increased above 7.4. As precipitation occurs, the solubility at the core outlet will decrease resulting in an increased release from the steam generator tubing and piping surfaces. Though similar, nickel behavior is much more complicated and discussed in more detail in Reference 8.

The industry has progressively increased primary system pH over the last 10 years with some units starting up with lithium as high as 6 ppm and operating with a constant 7.4 pH for the entire cycle. [9]

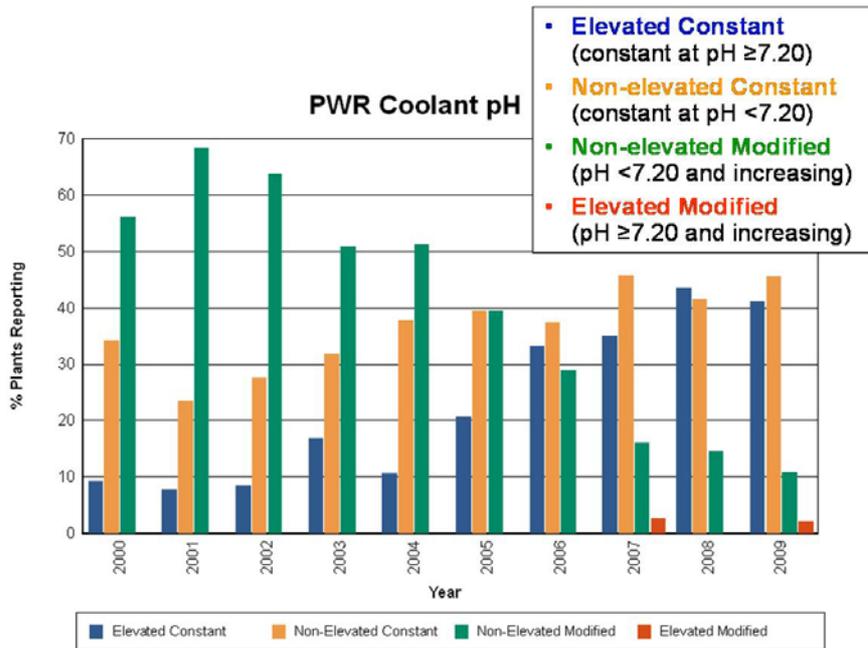


Figure 3
PWR Primary Coolant pH Trends [12]

There have been varying results with respect to dose rate reduction related to operation with elevated pH. Reference [1] states that the Ringhals and San Onofre units have shown positive benefits related to shutdown dose rates with operation at elevated pH. However, at the Comanche Peak units have not shown the same dose reduction benefits further reinforcing the concept that multiple factors may be impacting dose rates.

2.4.2 Zinc Injection

The impact of zinc is subject to continued research within the industry. EPRI published the EPRI *Pressurized Water Reactor Zinc Application Guideline* in 2006 to support industry efforts related to zinc injection. [10] This document is currently undergoing revision to address the large increase in industry experience and to provide further documentation for strategically decision making related to zinc addition.

The mechanism by which zinc addition to the reactor coolant lowers dose rates is a topic of some debate. At the time of publication of the Zinc Application Guidelines in 2006, the accepted mechanism was two-fold. Zinc had shown to have a similar preference to cobalt in the inverse spinel oxide structure on RCS surfaces. Based on a 5 ppb RCS zinc concentration, which is an atomic concentration of approximately 10^6 times an average RCS cobalt concentration, preferential incorporation of into RCS oxides was to be expected. Additionally, it was hypothesized that zinc atoms would displace other divalent cations, for example radio-cobalts and nickel from the RCS surface oxide as zinc ions were more thermodynamically favored in the inverse spinel structure. [10] The incorporation of zinc into the oxide in lieu of cobalt also contributes to the reduction of plant radiation fields. The exact mechanism by which RCS zinc addition impacts mature RCS surface oxides is still under investigation.

In laboratory data, zinc uptake into fresh surface oxide formation has also shown to reduce the corrosion rate and release rate of stainless steel, Alloy 600, and Alloy 690 materials as shown in Table 1. [10]

Table 1
Effect of Zinc on Approximate Corrosion and Corrosion Release Rates @ 3.5 Months (mg/dm²/mo)

Material	Corrosion		Corrosion Release	
	With Zinc	Without Zinc	With Zinc	Without Zinc
304 SS	1.1	3.5	0.1	1.3
316 SS	1.3	3.5	0.1	1.4
600 MA	1.5	2.6	0.3	0.8
600 TT	0.5	2.1	0.2	0.9
690 TT	0.2	1.3	0.1	0.6
X-750	0.6	2.6	0.2	1.2
Stellite	0.4	14.7	0.1	12.0

By reducing corrosion rates and corrosion product release rates, corrosion product generation and transport to the core is reduced and serves as a key component to a source term mitigation strategy.

Figure 3 is documented in the EPRI *PWR Primary Water Chemistry Zinc Application Guidelines* and shows that with increasing zinc exposure (ppb-months), plant dose rates will be lower. [10] The trends are divided based on Alloy 600, 690 and 800 plants as well as depleted and natural zinc.

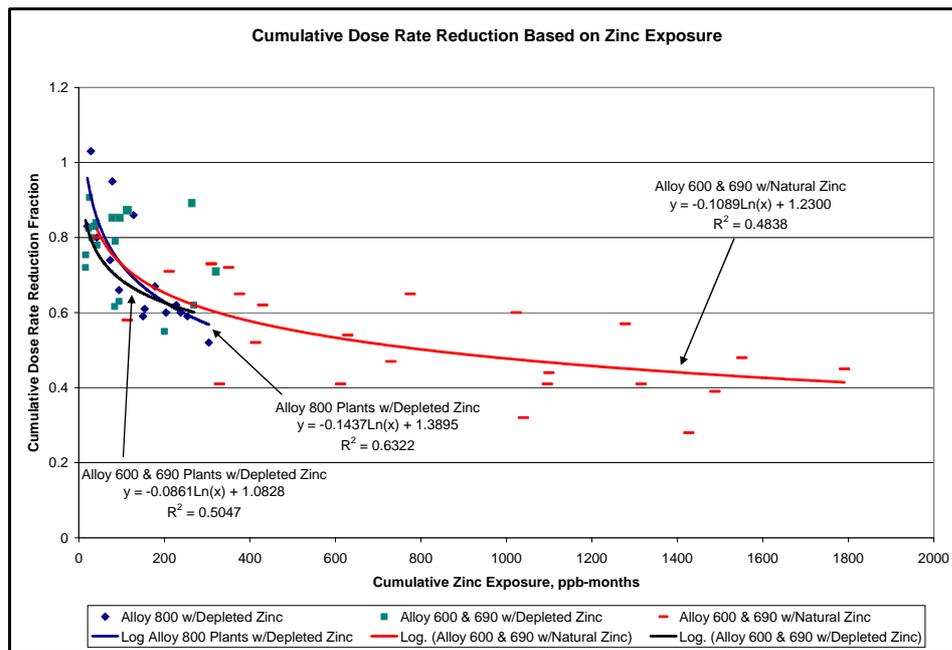


Figure 4
Dose Impact from Zinc Injection

A significant amount of additional data has been collected since the publication of the Zinc Application Guidelines and the trends shown in Figure 4 are being revised to incorporate the additional industry experience. Additionally, alternative predictive tools are being investigated.

2.4.3 CVCS Demineralizer Operation

A common subject of discussion related to demineralizer resins is the impact of macro-porous resins on RCS chemistry, especially related to colloid or particulate activities. The data contained within the EPRI data set is inconclusive related to the impact of macro-porous resins on plant dose rates. There are several factors that must be considered when using various resins.

The key challenge for utilities is the impact of particulate activity. Particulate activity is different from soluble activity in several ways. Particulates are of varying sizes, not uniformly distributed in solutions, typically have an associated charge, may or may not be attracted to plant surfaces, and have inertia. In order for letdown systems to remove particulates with either filters or specialty media, the reactor coolant system liquid must have a sufficient particulate inventory, activity must reach the filters, and the particles are removed either by filtration or charge based driving force [11].

Particle size in reactor coolant systems are difficult to quantify with any accuracy as noted above. According to Reference [11], the particle count is proportional to the diameter of the particle:

$$N = c(d_p)^p \quad (\text{Equation 3})$$

Where,

N = number of particles in a measured sample

d_p = particle diameter

C, p = empirically derived constants

The data shown in Table 2 from Reference [11] show the results of calculations used to estimate the particle mass distribution.

Table 2
Parameters Used to Estimate the Distribution of Particulate Sizes

Particle size distribution (lower-upper in microns)		Harmonic Mean Diameter (cm)	Particle Count %	Mass Fraction	Nickel Mass (g)	Co-58 Curies	Cum mass percent	Cum Co-58 Curies
2.5	5	3.33E-04	0.0000%	0.163	30.9	38.61	100.0%	236.88
1	2.5	1.43E-04	0.0002%	0.164	31.2	38.94	83.7%	198.26
0.45	1	6.21E-05	0.0024%	0.166	31.4	39.27	67.3%	159.32
0.25	0.45	3.21E-05	0.0175%	0.167	31.6	39.53	50.7%	120.05
0.1	0.25	1.43E-05	0.2015%	0.168	31.9	39.85	34.0%	80.53
0.01	0.1	1.82E-06	99.7783%	0.172	32.5	40.68	17.2%	40.68
Total				1	189.5	236.88		

This information is based on data provided to EPRI for the 2004 EPRI Shutdown workshop. The calculations were based on an average 0.5 ppm insoluble nickel concentration (average of data reported), a system volume of 100,000 gallons, spherical particles, nickel density of 8.0 g/cm³, activation of 1.2 Ci ⁵⁸Co/g Ni and a particle size distribution from 0.01 to 5 microns.

2.4.4 Shutdown Chemistry

Utilities continue to optimize shutdown and cool down activities for refueling outages supporting outage durations of less than 30 days and in some cases less than 20 days. The industry continues to review plant shutdown strategies including a rapid shutdown and cool down that allows utilities to enter Mode 5 in ≤ 6 hours from Mode 3 entry. This reduction in time requires chemistry, operations and outage work groups to evaluate and optimize their site specific shutdown strategies to meet the new time requirements.

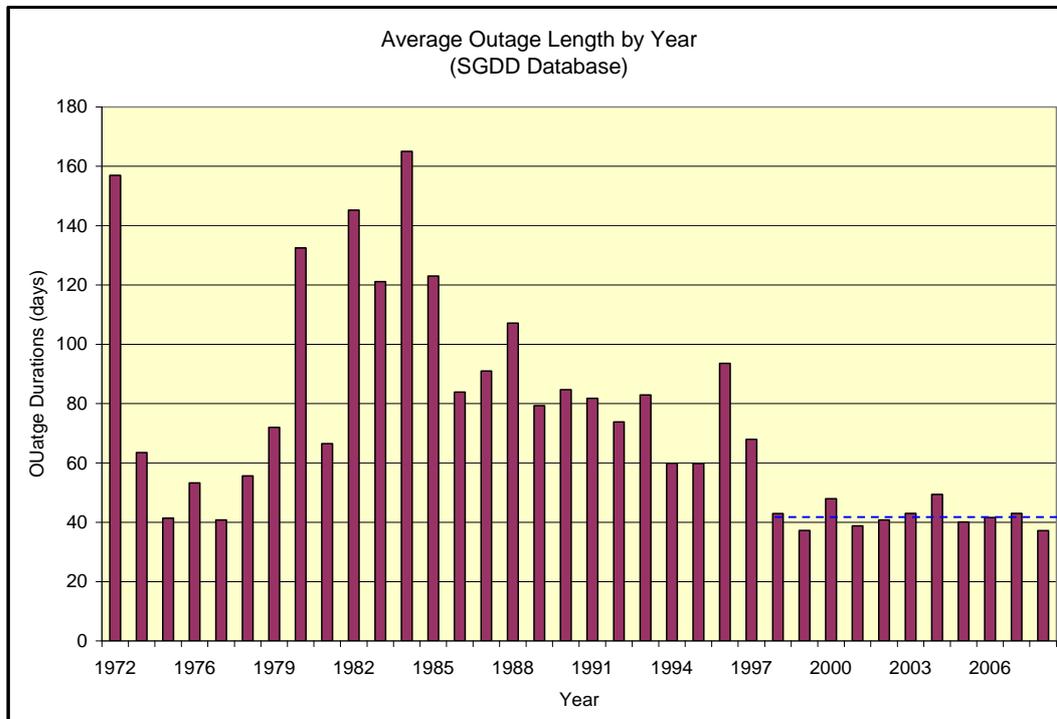


Figure 5
Industry Average Outage Durations Since 1972

Figure 5 captures the average outage duration by year from the Steam Generator Degradation Database. [6] As shown since 1998, outage durations are in general approximately 40 days in duration. This number can be misleading due to the number of steam generator replacements. Accounting for the steam generator replacements the number is closer to 33 – 35 days. The impact on primary chemistry controls and especially shutdown chemistry can impact these duration windows and for extremely short refueling outages (i.e., < 25 days) failure to properly prepare can impact outage scope, schedule and dose.

In addition, plant personnel are constantly being challenged to lower site dose and are looking into various source term reduction strategies. Various industry reports have placed a premium on shutdown chemistry, resins and material replacement programs to reduce site dose. While each of these is integral to an overall site strategy, it is important to understand the limitations of each process and the impact on overall site dose.

Chemistry personnel are challenged on shutdown chemistry to accomplish site dose reduction goals by station management, yet at most the overall impact to dose may be a 2 – 3% improvement on outage dose rates [12]. A failure to adequately plan, optimize and perform a controlled plant shutdown and cool down with the correct chemistry controls could result in a significant particulate release adversely impacting dose rates.

The basic function of shutdown chemistry is to manage the process for refueling. Each site should develop an overall source term reduction program aligned and focused on all aspects of source not a single component.

Another common misconception is that shutdown chemistry is related to a chemical decontamination process that is considered part of the source term reduction program. When in fact shutdown chemistry is better defined as a means to:

“Prepare the plant for a refueling or mid-cycle outage in as short a time as possible without negatively impacting on shutdown dose rates or particulate contamination levels and associated contamination events.” [12]

Reference [12] further states that factors such as operating chemistry, the extent of core steaming and the specific steam generator material and post-replacement operating history must be considered when evaluating variations in metal and activity releases since these factors control the overall deposition and activity formation process. *It is very difficult to perform plant to plant comparisons due to these varying factors and when benchmarking with other plants it should be done with an understanding of each of these factors and differences associated with each plant benchmarked.*

Reference [1] discusses the changes or increases in ^{58}Co and nickel concentrations and removal totals following peroxide addition at various plants and in general, plant dose rates are not expected to be impacted with the high flow areas. In the case of particulate releases, plant dose rate increases may be observed in low flow areas and these releases, in some cases, have resulted in significantly higher dose rates. EPRI has completed numerous research efforts in attempts to correlate releases to various time or durations of key events during refueling shutdown controls and unable to correlate specific events and shutdown time lines.

Primary system activity increases significantly during plant shutdowns and can reach ^{58}Co concentrations as high as 20 $\mu\text{Ci/ml}$. These increases can result in very high localized dose rates until activity cleanup is complete. These changes can be seen in Figure 6 and show the minimal impact on plant dose rates following shutdown cleanup activities. [1]

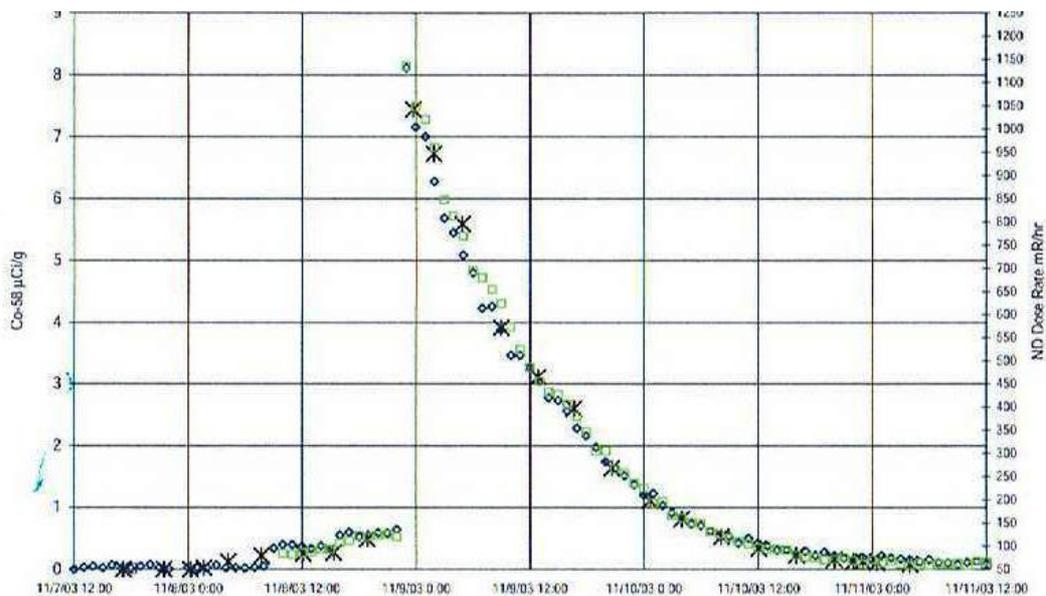


Figure 6
Dose Rate and Activity Trends During Shutdown

2.5 Conclusion

The application of a balanced primary chemistry approach with a sound technical understanding of plant materials and fuel design can have a positive impact on plant dose rates. Failure to follow industry practices related to shutdown chemistry controls can significantly impact shutdown or refueling dose rates. Some key observations from the EPRI report, *Plant Specific Recommendations for PWR Radiation Source Term Reduction*, 1019225, December 2009 and discussed in this paper: [1]

- Experience of individual plants cannot be evaluated simply by comparisons to average fleet experience.
- Zinc injection continues to show benefits related to dose rate reductions.
- Grouping by Effective Full Power Years (EFPY), zinc addition, pH_i, electropolishing and core boiling duty is expected to be necessary when assessing shutdown dose rates.
- Assessments of the impact of primary system operating and design variables on shutdown releases and dose rates must be pursued based on the expected relative importance of each independent variable.
- The effect of shutdown chemistry on shutdown dose rates should be minimal at plants where there is adherence to the EPRI Guideline recommendations for shutdown chemistry. The impact of particulate deposition should be considered when reviewing the shutdown evolution and operating practices.

2.6 References

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