Optimization of Reactor Coolant Shutdown Chemistry Practices for Crud Inventory Management

B. FELLERS, J. BARNETTE, J. STEVENS, and D. PERKINS, All TXU ELECTRIC

Abstract

This report describes reactor coolant shutdown chemistry control practices at Comanche Peak Steam Electric Station (CPSES, TXU-Generation, USA). The shutdown evolution is managed from a process control perspective to achieve conditions most favorable to crud decomposition and to avoiding re-precipitation of metals. The report discusses the evolution of current industry practices and the necessity for greater emphasis on shutdown chemistry control in response to Axial Offset Anomaly and growth of ex-core radiation fields during outage conditions. Nuclear Industry experience with axial offset anomaly (AOA), radiation field growth and unexpected behavior of crud during reactor shutdowns has encouraged the refinement of chemistry control practices during plant shutdown and startup. The strong implication of nickel rich crud as a cause of AOA and unexpected crud behavior has resulted in a focus on nickel inventory management. The goals for Comanche Peak Steam Electric Station (CPSES) include maintaining solubility of metals and radioisotopes, maximizing nickel removal and effective cleanup with demineralizers. This paper provides results and lessons learned from long term efforts to optimize the shutdown process.

Comanche Peak is a relatively new plant with slightly more than eight cycles of operation on Unit 1 and nearly six full cycles on Unit 2. There have been both the opportunities to benefit from early industry experience and the challenge of being in the category of higher temperature plants where changes in core crud characteristics and behavior could be expected. Integration of multiple, and sometimes conflicting, outage objectives through inter-departmental teaming and coordinated outage planing are essential. These opportunities and challenges have been met with dedicated efforts to improve crud management practices during shutdown and plant restart while recognizing other outage goals.

This paper includes results of both diagnostic and multi-variable analysis techniques to elucidate previously unreported findings and conclusions. Perhaps the most significant of these is the confirmation of environmental requirements for reductive decomposition of nickel oxide for both in-core deposited crud and tramp ex-core crud. These conclusions are known to conflict with existing theories and but the basis of conclusions have been carefully researched and established. The critique and feedback from peers serves as impetus for the paper.

The results of CPSES shutdown chemistry control practices are as different as the process techniques are, in comparison to conventional practices. The control of dissolved oxygen in RCS fills sources and coordination of shutdown steps to maximize the benefit of radiolytic reactions in the core are key examples. The behavior of metals and radioisotopes has been assessed through application of materials and surface science principles. Some findings clearly indicate where improvements are needed to predictive models, especially for shutdown radiolysis effects on core and RCS electrochemical potential environments.

The benefits to improved shutdown practices include reduction in outage radiation dose, lower susceptibility to AOA, lower radwaste cost, and more efficient outages due to less spreadable contamination. Whether this is judged to be cost effective depends primarily on the reduction of principles for success to a process that effectively interfaces with total outage planning. Minor trade-off in outage schedules may be required to assure reliable plant performance and optimization of operating cost, such as optimized core designs.

There is more to be learned that will likely alter the future approach to shutdown chemistry control, for both plant specific strategies on crud management and tools to address anomalous crud behavior at outages. Industry collaboration on sharing of data and application of diagnostic techniques are examples of opportunities for future improvements.

HISTORICAL REVIEW AND EVOLUTION OF CURRENT SHUTDOWN PRACTICES

Early philosophies of shutdown chemistry practices were directed primarily at reduction of radiation field growth. Much of the shutdown cleanup was by filtration of particulate with limited consideration of cleanup in the soluble phase. To some extent the behavior of crud was more predictable than during the early evolution of new shutdown practices. These changes fostered the concepts of early boration and chemical oxidation as two major steps toward the goal of controlled shutdown chemistry.

Many of the historical improvements in shutdown chemistry control were a direct result of operating experience rather than structured research programs. The latest shutdown results and lessons would guide the next innovations for improvement. One major contribution came with improved ability to predict environmental requirements for decomposition of mixed oxides such as nickel ferrite. This progress led to a greater need for understanding the conditions required to maintain solubility of the higher iron concentrations to avoid co-precipitation of the iron and isotopes. EPRI guidelines, technical reports and workshops [1-3] serve to reflect and record industry best practices for shutdown chemistry.

Progress with shutdown techniques was coincident to greater emphasis on other outage processes and goals. Reduction of the outage schedule and rapid shutdown became a higher priority with potential compromise to shutdown chemistry goals. For example, one time saving measure was to reduce coolant dissolved hydrogen to relatively low concentrations (<4cc/kg) just prior to plant shutdown, although in conflict with effective decomposition of crud. Consequently, oxygen saturated boric acid additions, as well as the hydrogen dilution effects, rapidly depleted these low hydrogen concentrations at shutdown. The oxygen effect to limit effective crud decomposition required initiatives for control of the BAT atmosphere and alternatives to early removal of RCS hydrogen.

Perhaps the expectations for shutdown chemistry were set too high, resulting in disappointment in results and less commitment to improve practices. For example, it was once speculated that shutdown chemistry would effect substantial ex-core crud decomposition and reduce radiation fields, but this expectation would not be realized. In parallel, the modern and high temperature plant introduced some new issues in crud behavior and particularly for plants with lead core duties. The fuel economy of low neutron leakage core designs with higher sub-cooled boiling heat transfer would alter the crud characteristics and behavior during the cycle and during shutdown. As more plants experienced AOA, unexpected growth in ex-core radiation fields, and large inventories of high specific activity crud during outages, it was time to re-visit and improve shutdown practices.

Many PWR's experienced the need to replace their steam generators due to various modes of stress corrosion cracking of tubes. The large inventory of metals introduce to the RCS from on-line conditioning of such major surfaces would become a new challenge during subsequent shutdowns. The metals inventories had unwanted effects including radiation field growth, increased susceptibility to AOA, enhanced radwaste cost from filtration, and extension of outages. The experiences would once more highlight the importance of shutdown chemistry to mitigate the impact of unexpected circumstances.

OVERVIEW OF CPSES SHUTDOWN AND STARTUP CHEMISTRY

Introduction to Shutdown Chemistry: CPSES shutdown chemistry program is an aggressive high temperature nickel ferrite decomposition/dissolution process. Plant chemistry is transitioned from an alkaline-reducing environment to acid-reducing and finally to acid-oxidizing conditions following hydrogen peroxide additions. The use of higher hydrogen, low pH(t) and RCS temperature to drive the decomposition/dissolution process optimizes shutdown chemistry and outage goals with minimal schedule impact.

Alkaline-Reducing to Acid-Reducing: On shutdown the RCS is borated to shutdown boron concentrations, typically from < 10 ppm to >2400 ppm and RCS lithium is removed from the system. This process transitions the system from an operating pH(t) of approximately 7.2 to 5.3 and is complete prior to cooldown <500F. The step is in preparation for the nickel-ferrite decomposition and dissolution of iron compounds.

Decomposition is based on hydrogen and temperature in accordance with the following equations [1]:

$$\mathrm{Ni_xFe_{3\text{-}x}O_4(s)+4x/3H_2 = xNi^0(s)+(1\text{-}x/3)Fe_3O_4(s) + 4x/3H_2O}$$

Dissolution of the magnetite product occurs according to the following reactions:

$$\mathrm{(1\text{-}x)\{FeO{\cdot}Fe_2O_3 + 2H^+ + 1/3H_2\} \leftrightarrow (1\text{-}x)\{Fe^{+2} + 4/3H_2O + 2/3Fe_3O_4\}}$$
$$\mathrm{(1/3)Fe_3O_4 + (2\text{-}b)H^+ + 1/3H_2 \leftrightarrow Fe(OH)_2{}^{(2\text{-}b)}+ + (4/3 - b)H_2O}$$

These reactions represent the largest challenge that Chemistry has to deal with on shutdown. The release of soluble iron and addition of small amounts of dissolved oxygen can lead to significant deposition of material throughout the reactor coolant system. Iron(III) hydroxide can and will precipitate from the introduction of oxygen and co-precipitate cobalt-58 and other isotopes, creating localized hot spots and deposition throughout the plant. This is minimized by boric acid tank deoxygenation prior to the outage but small amounts of oxygen will overcome the residual hydrogen and drive the precipitation process. At low plant temperatures, approximately 325 °F, it is extremely difficult to overcome the addition of oxygen and recover from this precipitation and every effort should be made to minimize the amount of oxygenated water introduced. RCS hydrogen is maintained as high as possible during plant cooldown to support decomposition. CPSES has repeatedly shown that >22 cc/kg is needed to recover iron solubility at ~325 °F [2,3].

Hydrazine that is added to the RHR system prior to the outage is an example of minimization of oxygen introduction. The filling of the pressurizer solid at 325 °F creates a significant challenge for chemistry to maintain an acid-reducing condition. On-going evaluation of chemistry data, Fe and Ni, are used for indicators of potential problems during this time frame and are used for the decision on whether to cooldown or hold for additional time. The current strategy is to flush the RHR to waste prior to placing into service.

Acid-Reducing to Acid-Oxidizing: The transition from acid-reducing to acid-oxidizing occurs with the addition of hydrogen peroxide to the reactor coolant system. This addition also is used for chemically degassing the reactor coolant system.

Hydrogen peroxide is added to the RCS to begin chemical degassing and oxidation of the nickel metal and cobalt. This promotes a rapid oxidation of the metal and release from core surfaces. The oxidation reaction for the nickel metal and release (Cobalt-58 behavior is expected to match nickel) is as follows:

$Ni^0 + 2H^+ + ½O_2 = Ni^{+2} + H_20$

Startup Chemistry: CPSES philosophy for startup chemistry is to reduce dissolved oxygen concentration as quickly as possible with hydrazine. After RHR is secured for the last time, lithium hydroxide is added to raise pH above pH neutral and hydrogen is subsequently placed on the volume control tank (VCT). This philosophy allows for a transition from acid–oxidizing to alkaline–reducing as quickly as possible and begins the stabilization of crud and filmed surfaces as quickly as possible [2,3].

CPSES SHUTDOWN OPTIMIZATION INITIATIVES AND PROCESS OBJECTIVES

Approach to Process Control: The fact that multiple chemistry parameters are interactive and must be managed according to both a timeline and specific plant conditions provides the distinction of process control. The key principles for success are defined and carefully planned to avoid conflicts with other outage objectives and toward optimization of results. The bases for these principles are derived from fundamental science and diagnostic evaluations of both industry and CPSES experience. The close monitoring of chemistry results and other indicators enables mitigating actions for unexpected results during the shutdown.

- **Preplanning and Training**
  Preparation for each outage begins with capturing and incorporating lessons from the most recent outage and from industry experience. Detailed preparations of activity schedules, monitoring requirements, and training materials typically begin about six months prior to the plant outage. Appropriate training materials are prepared or revised to reflect new objectives and approaches and for each plant organization responsible for implementation. Significant revisions to prior practices may be included in plant simulator training to verify feasibility and consistency with other outage evolutions.

- **Teaming with Plant Operations and Outage Management**
  There are several aspects of teaming and coordination practiced to enhance the overall outage success, while preserving the shutdown chemistry plan objectives. For example, outage schedules are prepared to reflect key chemistry criteria after coordination with plant operations and outage planning.

- **Monitoring Results**
  CPSES has developed enhanced chemistry monitoring capabilities for timely feedback of results. For example, the installation of in-line oxygen and hydrogen analyzers provides continuous indication of these critical parameters. The addition of metals analysis by ICP provides information for key metals while reducing time and resources. Electronic spreadsheets facilitate timely access of data through the chemistry web site by support personnel and management. Outage results are trended and compared to expected conditions to facilitate mitigating actions and input to overall outage management decisions.

Effective Crud Decomposition: There are many important objectives associated with this principle. First, the potential consequences of particulate crud release and deposition on ex-core surfaces are considered unacceptable. Radiation exposure to outage personnel can be dramatically affected, spreadable contamination can impact maintenance efficiency, and outage schedule and cost are influenced by filtration requirements. The remaining ex-core crud becomes a source term for the next cycle of operation and becomes more important to plants considered susceptible to AOA. In view of these considerations, CPSES has strongly emphasized crud decomposition and nickel removal [2,3]. Some of these practices include the following;

- **High Hydrogen Concentration**

Consistent with the principle of chemical reduction of nickel to the metal as a path to decomposition and removal, CPSES adopted the practice of entering the outage with as much as 40 cc/kg hydrogen to sustain strong reducing conditions throughout the plant cooldown, Figure 1. This value was derived after compensating for the expected dilution of hydrogen with boration and consumption by introduced oxygen, while maintaining a residual >25cc/kg to sustain solubility of iron during initial cleanup. Differing modes of shutdown including solid operation at higher temperature have produced hydrogen spikes to higher values. The reduction of hydrogen below target values during cooldown produce strong contrast in results versus sustained objectives, which will be discussed later.

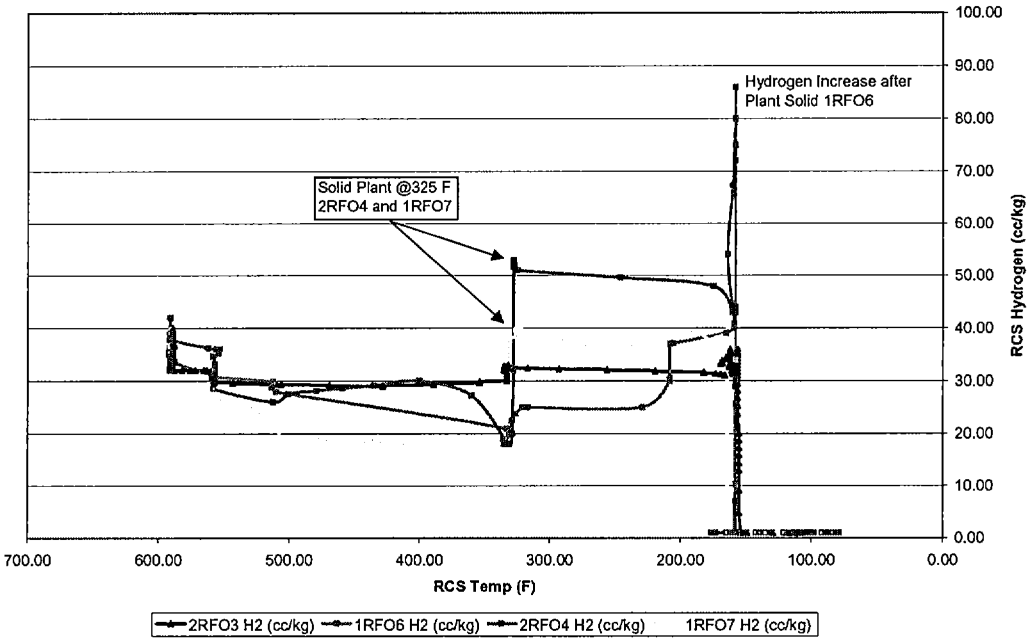

Figure 1
Comparison of Hydrogen to Temperature by Outage

- **Rapid Boration and Lithium Removal**

The timeline for boration has been compressed to support cooldown and to optimize recovery of strong reducing conditions while the plant is at higher temperature and core gamma radiation flux is at it's peak. The initial shutdown gamma flux at the core and high temperature facilitates a strong reducing environment consistent with crud decomposition requirements [4]. It has been observed that the time and temperature at which initial crud decomposition occurs can be accelerated to about one hour following end of boration. Variations in shutdown pH with rapid boration practices for CPSES are shown in Figure 2. This objective supports not only decomposition but also solubility of metals and is more easily controlled than hydrogen concentration during the cooldown. The following discussions attempt to distinguish the decomposition of nickel oxide from nickel ferrite type compounds and from in-core and ex-core locations, based on chemistry and radiochemistry data obtained during CPSES shutdowns.

- **De-oxygenation of Residual Heat Removal (RHR) Loops**

The primary purpose of this initiative is to reduce the ingress of oxygen. Oxygen in sufficient quantity causes oxidation of iron to the insoluble trivalent state, which force precipitation with co-precipitation of radionuclides. CPSES developed a method of hydrazine addition to the RHR in advance of the outage to scavenge oxygen. Also, excess hydrazine was found beneficial to mitigate oxygen introduction from areas not influenced by the hydrazine dosing. CPSES has recently adopted a procedure for flushing the RHR with reactor coolant prior to placing into service.

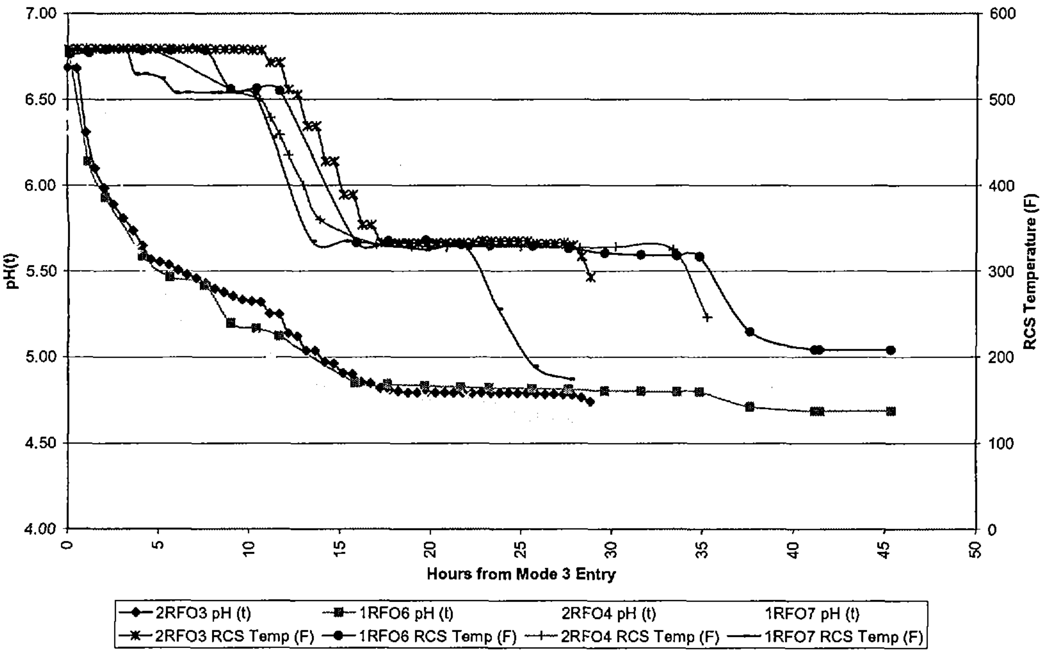

Figure 2
Comparison of pH(T) of Comanche Peak Outages

- **De-oxygenation of Boric Acid Tanks (BAT)**

  CPSES has long recognized the benefit of this practice and installed a temporary provision of nitrogen introduction to displace BAT oxygen just prior to shutdown. This practice has improved shutdown results but not to the desired level due to limitations of the temporary nitrogen sparge method. Permanent modifications have been designed for BAT de-oxygenation and will be implemented to optimize oxygen control for both shutdown and operating objectives.

Maintaining Solubility of Metals and Isotopes During Cooldown: Effective crud decomposition enhances the requirement to maintain iron solubility until initial cleanup is achieved, prior to the oxidation phase, as reflected in Figures 3-6. The CPSES-1RFO8 outage chemistry conditions produced effective decomposition and only a minor precipitation of iron at 325 °F plateau, which was promptly recovered, Figure 3. The co-precipitation of cobalt isotopes and their recovery with re-solubilization of iron, was evident for even this limited example of iron response to temporary oxidizing conditions, Figure 4. It is unacceptable to have major plate-out of large inventories of radioisotopes that will remain insoluble under acid-oxidizing conditions. The removal of the insoluble material by filtration can slow the outage schedule while increasing disposal cost and radiation exposure. CPSES-RFO6 data, Figure 5, reflect a good example of the relative magnitude of the potential issue when iron dropped from ~700 ppb to ~200 ppb at a typical point in the shutdown process.

- **Recovery of Precipitated Iron**

  The final requirements for introduction of borated water occur after partial cooldown and crud decomposition. Also, the RHR is placed in service and can be a source of oxygen. Both the cause of iron precipitation and recovery are shown in Figure 6. The major drop in iron coincides with placing RHR in service and filling the pressurizer. Re-solubilization of iron occurred promptly after reduction in filling by oxygenated water and recovery of hydrogen concentration above ~22cc/kg. The amount of hydrogen required to recover iron solubility and the time for recovery depend on the oxygen content of the fill water, magnitude of fill, RCS temperature, and decay of core gamma flux. CPSES has repeatedly confirmed the minimum concentration to be > 22cc/kg for a typical shutdown. The consequences of the iron precipitation, if uncorrected, can be major increases in outage radiation dose. The consequences of iron and isotopic recovery include an impact on time for iron cleanup and overall outage schedule, therefore every effort should be made to eliminate the oxygen in the RHR and borated fill waters.

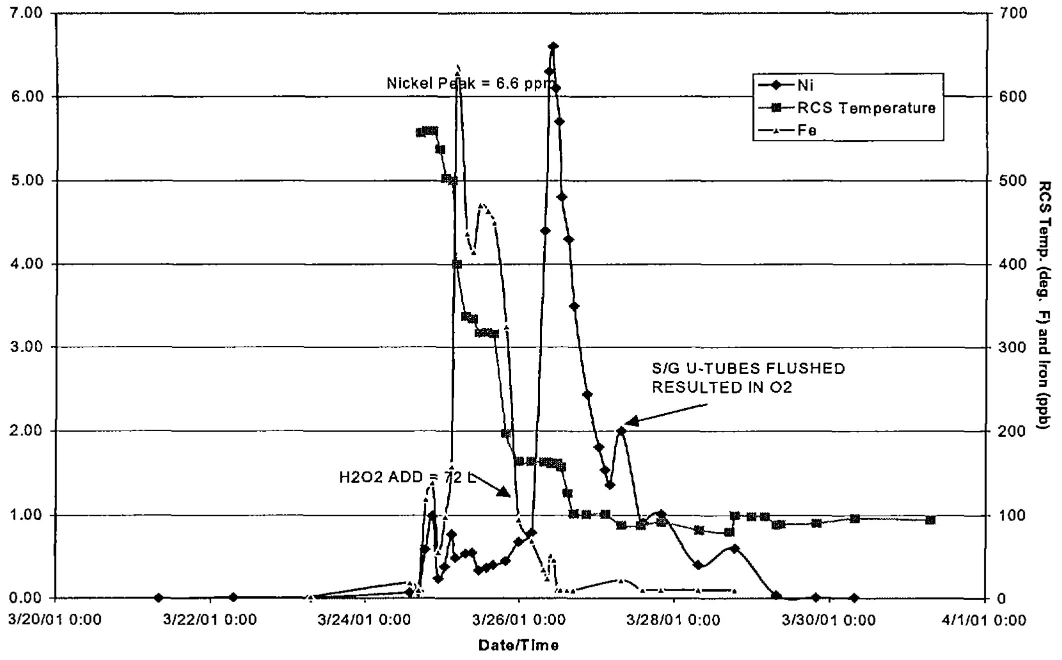

Figure 3
1RFO8 Shutdown Metals

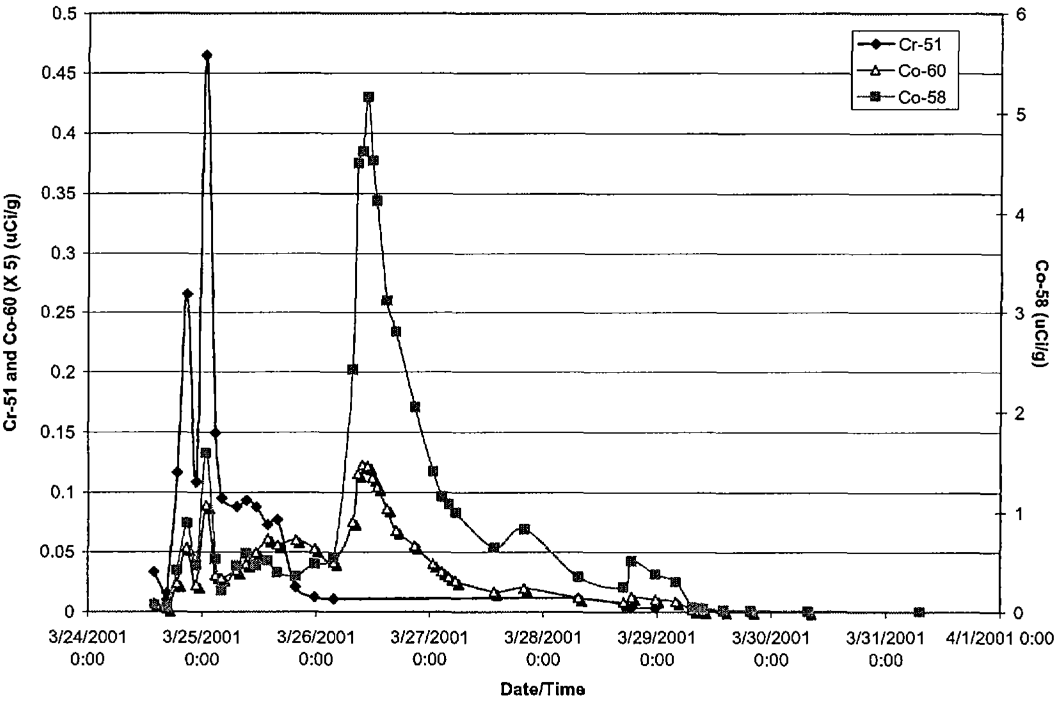

Figure 4
1RFO8 Shutdown Co-58, Co-60, & Cr-51

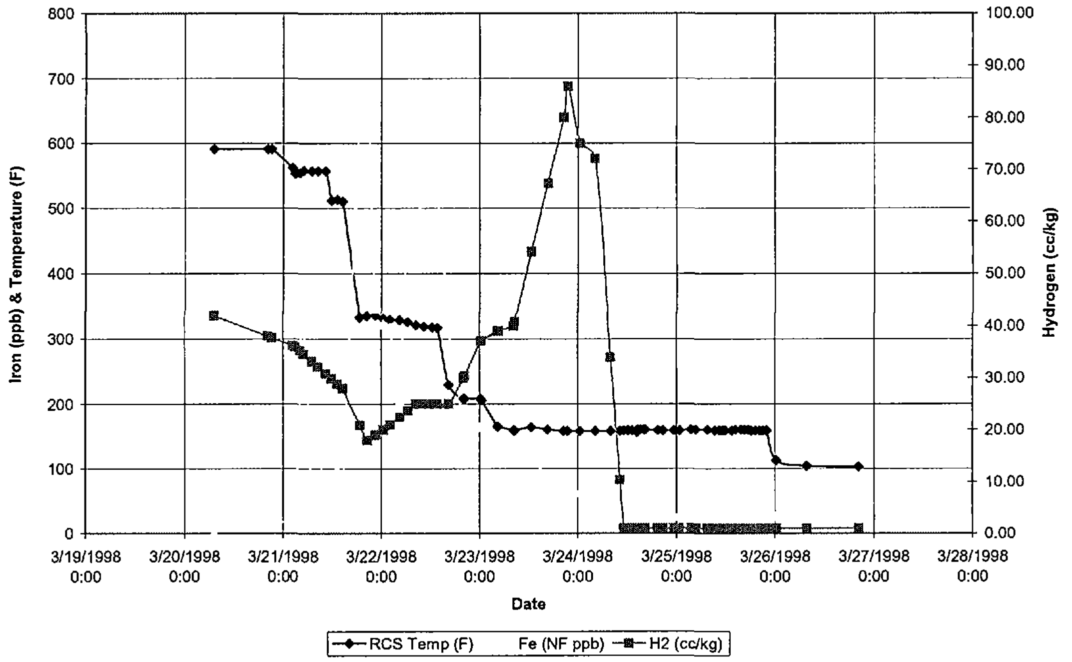

Figure 5
1RFO6 Temperature to Hydrogen

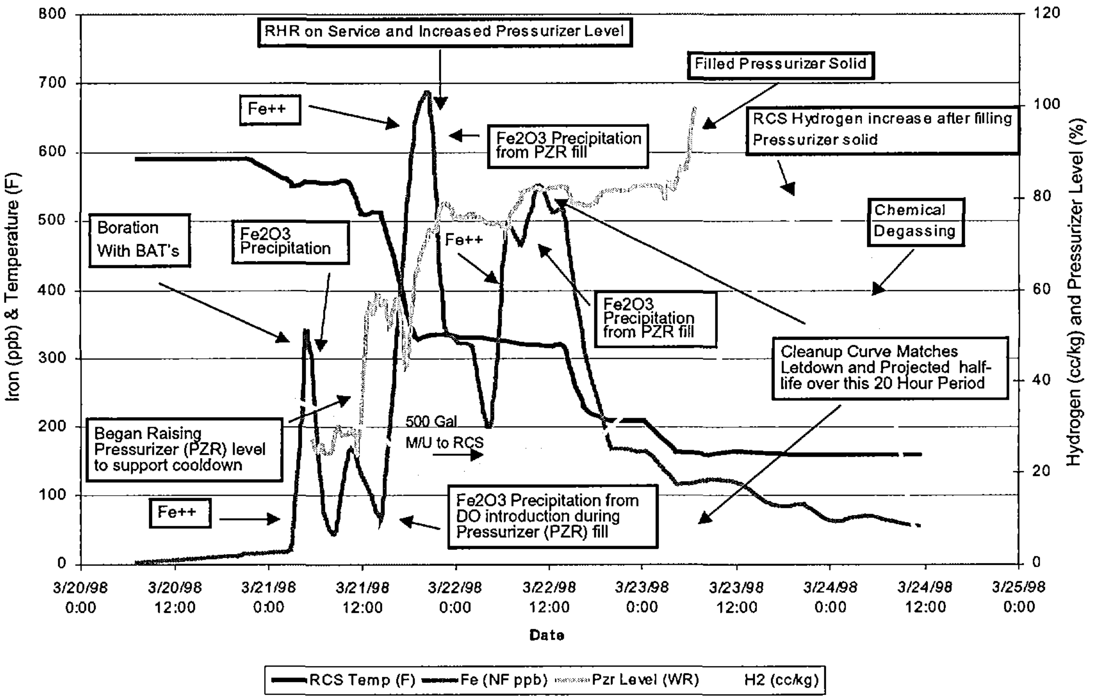

Figure 6
1RFO6 Iron Solubility and Cleanup Considerations

Timely and Effective Cleanup: Removal of radionuclides resulting from crud decomposition is limiting to the outage schedule and impacts radiation exposure to workers in the vicinity of these systems. Therefore, the highest purification rates and removal efficiencies are desired throughout the shutdown process.

- **Dedicated Clean-up Demineralizers**

  CPSES personnel recognized the conflict in using demineralizers in the RCS letdown system to serve both operating and shutdown needs. The limited use of boron thermal regeneration system (BTRS) demineralizers provides resolution for this limitation through dedication of two BTRS vessels for shutdown use. This required a minor modification to letdown piping to access the larger vessel and accommodate effective treatment of higher letdown flow rates. The larger resin volume and optimized resin ratio facilitate excellent removal efficiencies and resin utilization.

DISCUSSION OF CPSES SHUTDOWN AND STARTUP RESULTS

General Observations: Based on comparison to industry data [2,3] and outage dose rates, the current approach is a highly successful process for CPSES, although more improvements are pending. The amount of nickel removed is among the highest in the industry as reflected in Figure 7, ~2 times industry average [2,3]. The amount of Co-58 removed is also well above average and the positive trend of lower isotopic to nickel ratios for most recent outages is a reflection of increasing BOC pH [5,6], which will be increased in future cycles [7]. CPSES has successfully reduced filter usage for shutdown chemistry from > 20 to <5 filters per outage while actually increasing metals removed. Most recently the number of filters has been 2 or less. Shutdown dose rates, specifically refueling bridge dose rates, are < 5 mr/hr and this corresponds to lower dose rates in the overall plant. Spreadable contamination is typically very low with soluble conditions for metals. These combined factors contribute to lower outage dose and to enhance outage efficiency due to favorable work environments.

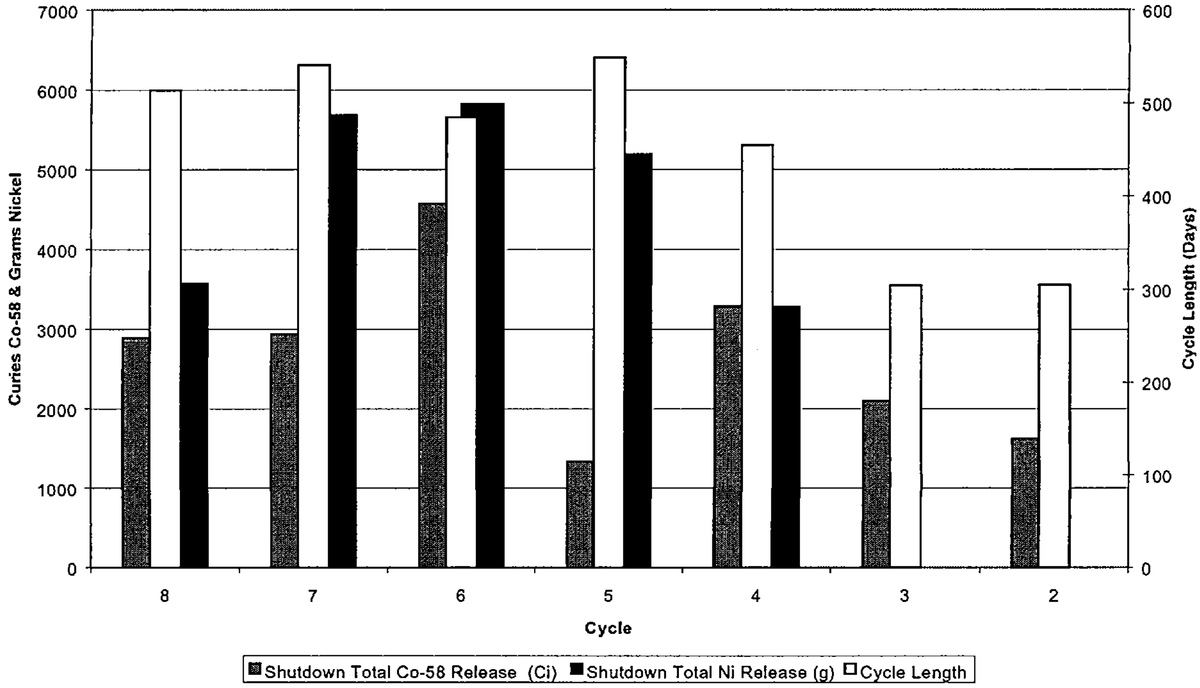

Figure 7
Unit 1 Shutdown Results

CPSES has improved operating chemistry to limit crud issues while maintaining the philosophy of nickel management during shutdown. These complementary initiatives have contributed to reduction of susceptibility to AOA and avoidance of anomalous crud behavior during outages. The latter achievement is due, in part, to shutdown processes that could compensate for core crud that had been released prior to shutdown, such as EOC release characteristic of AOA cycles. The characteristic of such crud is different to non-AOA cycles and much more likely to release at EOC or prior to decomposition during shutdown, especially with a unit trip. The key process elements responsible for this success are discussed below. Plant wide ownership and teaming on related initiatives is most responsible for successfully meeting these goals.

- **Crud Decomposition and Solubility of Iron**

The shutdown of a plant results in major changes to radiolysis reactions and particularly the production of molecular oxidants from high LET radiation produced by neutron reactions is reduced. The initial gamma flux predominates to maintain strong reducing conditions, driven by the core produced radical's [4]. Therefore, the local environment at the crud layer is more reducing than ex-core areas to explain the contrast in decomposition between in-core and ex-core crud deposits [8]. Also, the higher axial position of the core is most affected due to lowering of pH from operating conditions such that the stability of previously formed crud layers and species are challenged. This includes lowering of pH as result of temperature reduction and absence of concentration processes by SNB within crud layers. This core area can be most influenced by production of molecular oxidants as influenced by SNB and high surface concentrations of boron, a major contributor to molecular oxidants [9-11], as shown in a theoretical model [9], a part of which is shown Figure 8. These environmental conditions have been show to change the composition and morphology of crud such that decomposition by conventional shutdown chemistry processes is unknown.

Crud decomposition during shutdown is influenced by changes in stability domain of oxides and mixed oxides with temperature reduction, loss of core gamma flux with time and temperature, hydrogen concentration, and introduction of oxygen from external sources. Typically, the pH is consistent with the near absence of lithium and much more predictable than ECP, Figure 2.

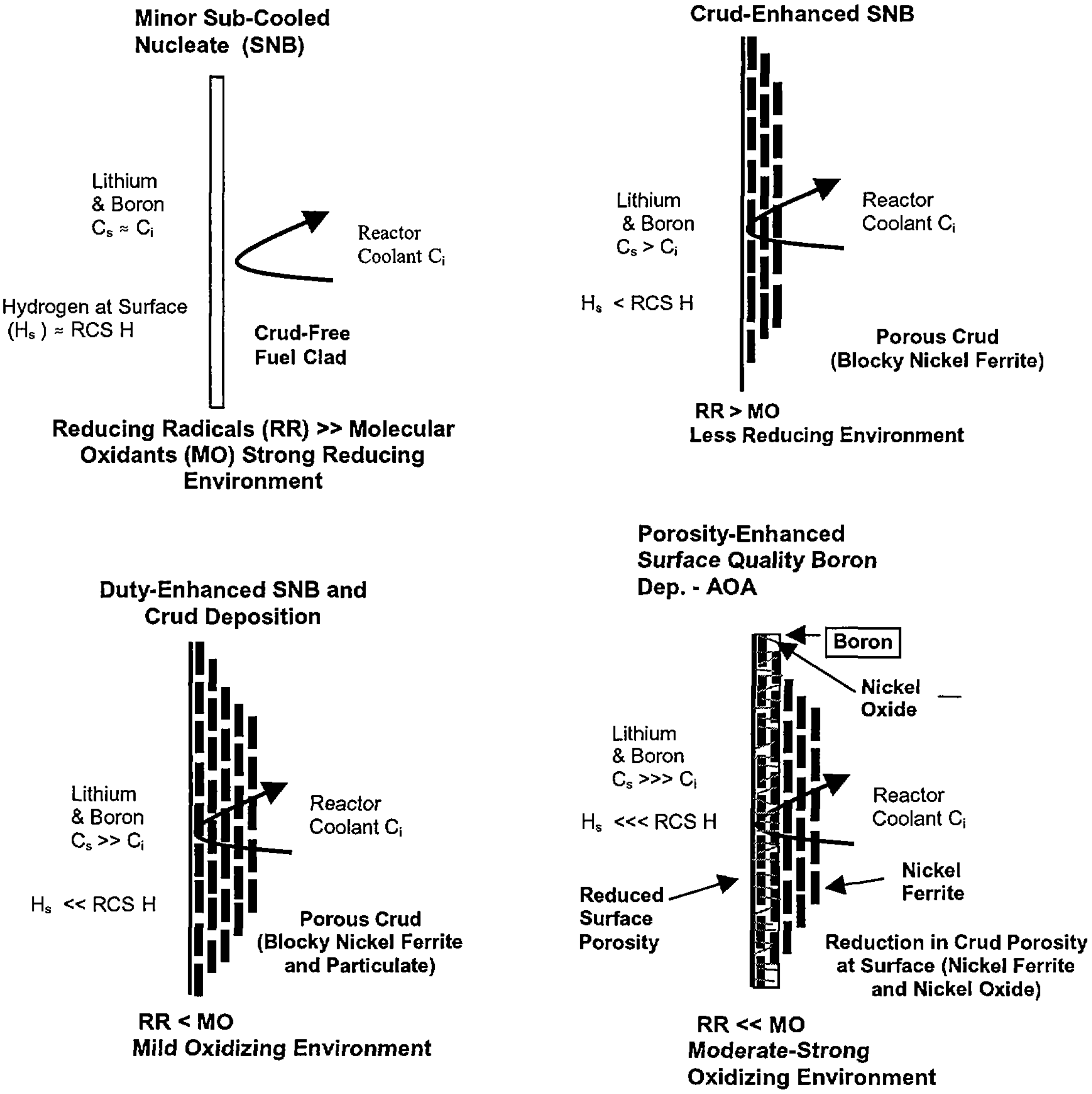

Figure 8

Effect of Hydrogen Stripping & High LET Reaction on Local Net Radiolysis

- **Shutdown Nickel Management and Cobalt-58 Removal Trends**

The high priority for nickel management at CPSES has produced results that require some explanation and challenge existing theories. First, the amount of nickel released and removed is often *three times as much* as other plants and typically twice industry averages [2,3]. The following discussions will address the amount of nickel removed, specific activity, Co-58/Co-60 ratios, indicators of the source and oxide form, and relationship to operating chemistry. Finally, a theory is offered to explain these results and observations in the hope that others may contribute to future nickel management strategies through their experience and insight.

According to one assessment [6] the amount of nickel removed at CPSES may be a significant fraction of that released and deposited on the core for the preceding cycle. Assuming the conventional idea that the release is primarily from decomposition of nickel ferrite, suggest that the amount of iron removed should proportionally increase. This data from CPSES clearly show greater iron removal but this or other industry data reflect a proportionality consistent with the mixed oxide.

Examination of reactor crud for several plants [12] reflect an increasing nickel/iron ratio, confirm significant amounts of nickel metal toward the core inlet and nickel oxide toward the core outlet. However, it is often assumed that nickel oxide may be thermodynamically stable under shutdown chemistry conditions [4,6,13]. This position may not fully consider the extreme low ECP that may exist at initial shutdown or the combined effect of high hydrogen and low oxygen to maintain the ECP during rapid boration and cooldown. Indeed, the stability diagram for nickel and nickel oxide does support the possibility of decomposition during this process. The exact timing of decomposition is less certain than for nickel ferrite since other parameters may not rise as iron does in the latter case. The nickel does not rise for in a strong reducing environment from either case due to kinetics for reduction to the metal.

The shutdown trend of C0-58 released for several cycles is shown in Figure 9, and one observation is the sometimes unusual spiking during initial boration and cooldown. Similar trends can be seen for iron in Figures 3-6 above. These trends are consistent with strong reducing conditions at higher temperatures and after boration. The quick recovery of these spikes have been evaluated along with metals and isotopic data, resulting in the conclusion that a high specific activity release may be shortly followed by a relatively low specific activity release. Also, the behavior of metals and isotopes is not typical of nickel ferrite decomposition.

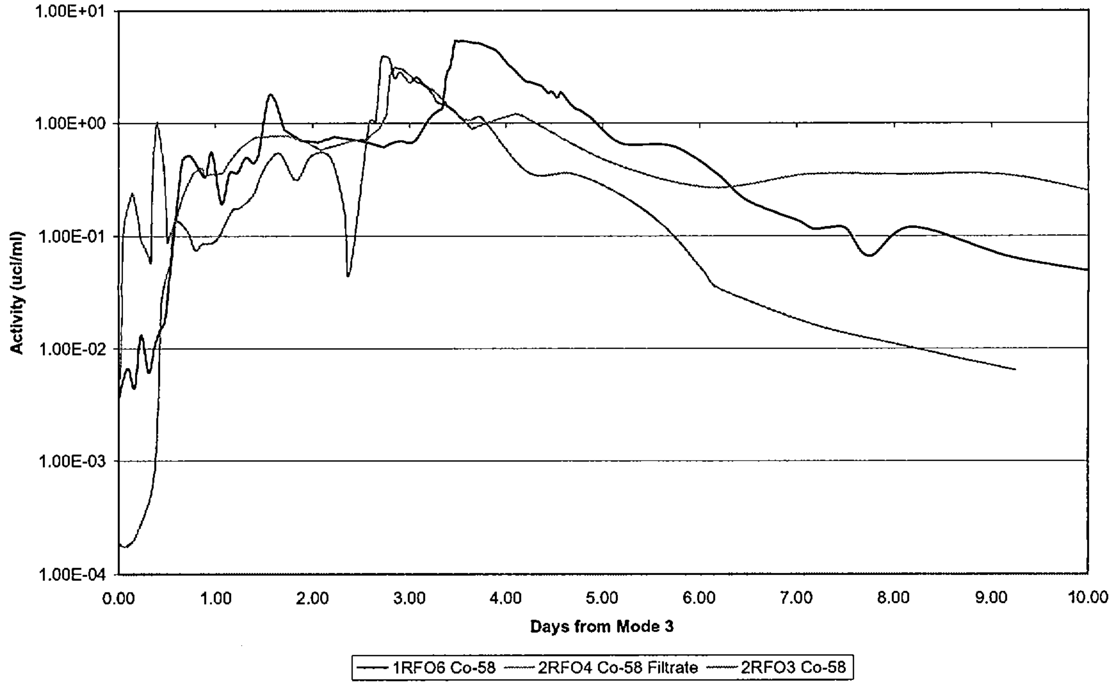

Figure 9
Co-58 Comparison for Outages

The CPSES shutdown data includes another major difference to typical industry results for shutdown in regard to specific activity, C0-58/Ni ratio, and in isotopic ratio or Co-58/Co-60 ratio, as reflected in Figure10. In this example, the specific activity ratio is less than one at the peak and approaches 0.01 Ci/gm at the lowest value. This compares to typical high industry values > 5 Ci/gm. It should be noted that a sustained low specific activity release occurs just prior or during peroxide addition and must include at least some high specific activity crud from in-core locations, as reflected by the isotopic ratio. Therefore, the discrete specific activity of the crud fraction giving rise to these low values would be much less than typical reactor crud [3] and more likely from an ex-core location. If true, this suggests that nickel oxide is being decomposed both in-core and ex-core.

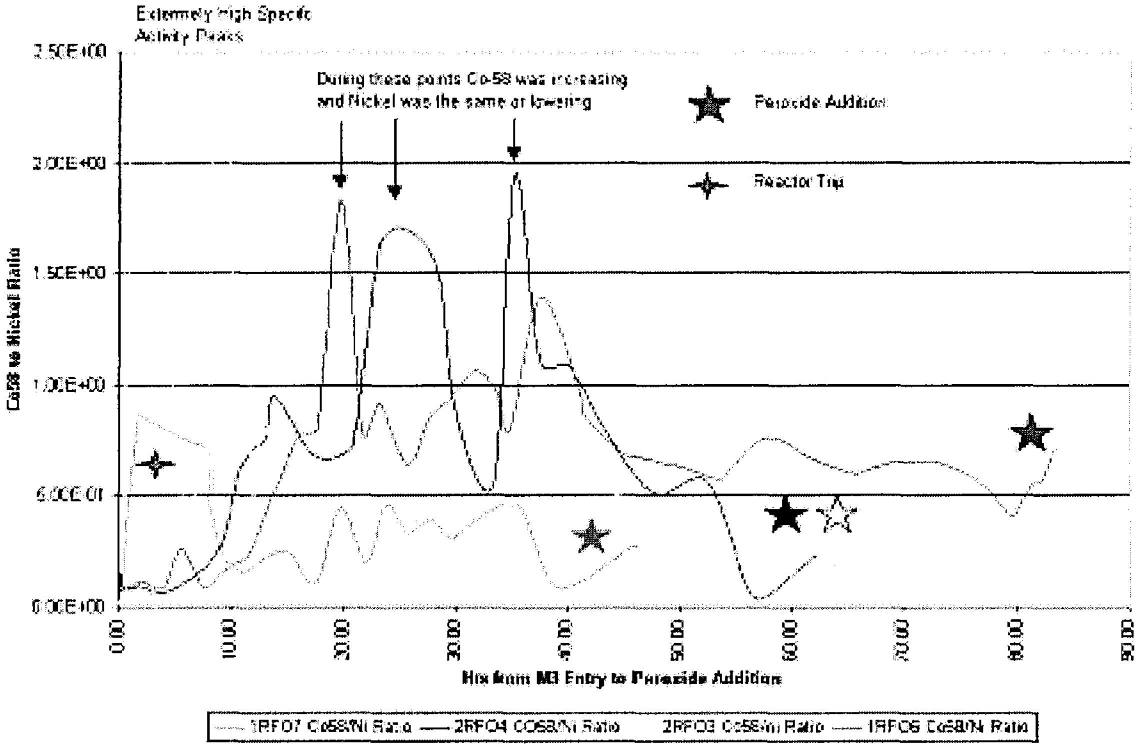

Figure 10
Co-58to Nickel Ratio Comparison by Outages

After considering all of the metals and isotopic data in this diagnostic manner, it is concluded that strong at-temperature acid-reducing conditions during shutdown result in decomposition of nickel oxide. This occurs first for the in-core location where the lowest potentials arise first, followed by similar ex-core decomposition as the reactor recovers loop potentials to ECP conditions necessary for reductive decomposition. The decomposition of nickel oxide occurs in-between these events and typically around 450 °F during cooldown. This is the first sustained release of substantial iron and isotopic ratios and is typical of most industry data, although some plant [3] data reflect very limited decomposition of nickel ferrite as well.

The reductive decomposition of nickel oxide does not reveal a sustained soluble concentration due to kinetics of reduction to the metal at the reactor. Therefore, the intermediate ECP consistent with solubility of nickel is not achieved until further cooldown of the reactor and gamma decay, or during chemical degas of hydrogen. During this time the same relationship between in-core and ex-core potentials is expected and evident in the data. Consulting Figure 10, we see low Co-58/Ni ratios occurring prior to peroxide injection as the ex-core loops see a slight rise in potential, substantiating the ex-core origin of the nickel. The ratio rises sharply as the chemical degas overrides local reducing conditions in the core.

The source of the ex-core nickel oxide being decomposed is believed to be primarily tramp core crud released prior to EOC, explaining the Co-58 decay and ratio to nickel. This material is highly porous as compared to the hydrothermally grown ex-core films that are not significantly decomposed by the shutdown chemistry process. Any influence on the latter would be limited to surface reactions instead of in-depth reductive decomposition and the morphology differences also play a role in their stability.

The suggestion of nickel oxide decomposition and especially at ex-core locations will provoke much interest and challenge to the analysis of the data, which is the desire of the authors. This is a critical piece of information to demonstrate alternatives for nickel management strategies and reduction in risk of AOA due to nickel inventory carryover from cycle to cycle. While it will not totally remove the iron rich compounds from EOC release, the removal of cobalt is beneficial to the same outage dose. This has substantial implications for AOA cycles where dose rates have substantially increased due to tramp core crud deposition on SG tube surfaces. Issues include interference with ECT inspections, maintenance of RCS components, and high activity spreadable, soot like, crud. The CPSES data provides valuable insight to define environmental conditions consistent with nickel oxide decomposition and the relationship of multi-variable parameters to create the desired condition. Perhaps pending improvements to oxygen control at CPSES will result in sufficiently low ex-core potentials necessary to effect decomposition of nickel ferrite in the tramp deposits. It is quite interesting to compare the CPSES experience with other plants that reported large amounts of low Co-58/Ni transport at the next BOC.

- **Relationship Between Operating Conditions and Shutdown Results**

Plants operating with low and constant pH are known to form considerable nickel metal deposits near the core inlet [12]. The introduction of the modified chemistry regime appears to promote some release of this inventory with subsequent deposition as nickel oxide toward the core outlet [9]. The additional influence of modern core designs with higher SNB appear to accentuate this condition, giving rise to more localized enrichment of nickel, as nickel oxide, as boiling peaks near the core outlet [9,12]. This behavior is considered in a proposed theoretical model [9] that seeks to integrated pH and potential effects to explain crud morphology and corrosion observations at shutdown for modern plants.

- **Startup Chemistry and Nickel Management**

CPSES philosophy for startup chemistry is to reduce dissolved oxygen as quickly as possible with controlled amounts of hydrazine and after RHR is secured for the last time add lithium hydroxide [2,3]. Sufficient lithium is added to exceed the at-temperature neutral pH prior to introducing hydrogen on the VCT. This philosophy allows for a prompt transition from acid-oxidizing to alkaline–reducing and begins the stabilization of the crud and surface films as quickly as possible. This approach is based on the concept that further decomposition of crud would result in a small fraction of the released nickel being removed unless the startup was delayed and ECP controlled consistent with nickel solubility, just below the hydrogen evolution line. In the absence of this provision, which is prohibited by startup schedule, crud decomposition would primarily result in an RCS inventory of "tramp" nickel metal that would be highly susceptible to oxidation, transport and redistribution on the core feed fuel assemblies during the beginning of next cycle as shown through a diagnostic multi-variable analysis [14]. In fact, a survey of plants with AOA experience reflected a strong correlation with use of crud decomposition conditions during startup. The evaluation for CPSES reflected this to be a high risk factor in view of the limited amount of nickel removed by these practices and possibly even greater risk for plants with less effective decomposition of crud during shutdown, as the inventories of reducible nickel oxide would be high.

SUMMARY & SUGGESTIONS FOR FUTURE IMPROVEMENTS

- Preplanning, training and teamwork are essential to conduct of an effective shutdown chemistry process. For example, it is important to integrate chemistry changes/steps into Operations procedures to ensure control room awareness of critical steps.
- Oxygen control on BAT's and RHR loops area critical requirements to effect high temperature decomposition of nickel oxide phases both in-core and ex-core.
- Hydrogen levels during shutdown must be based on multi-variable analysis of radiolysis conditions and chemistry requirements to achieve desired reducing conditions for both crud decomposition and maintenance of soluble iron.
- CPSES results and their evaluation suggest need for improvements to shutdown radiolysis predictive models.
- Achieving an at-temperature pH of <5.3 is critical during cooldown and is readily achieved compared to ECP conditions.
- The use of diagnostic methods to evaluate both operating and shutdown data strongly complement research results to predict the state, morphology, and behavior of metals and their oxides. This is essential to enable more reliable predictions and manage radiation fields; risk of AOA and other crud related issues. This approach provides insights beyond the typical "anecdotal" distinction given to field data and takes advantage of results that are not often replicated in research experiments.
- CPSES shutdown chemistry results reveal a pathway and process means to address major issues with nickel rich crud deposits found in modern cores, to minimize nickel carryover due to nickel oxide for both in-core deposited and ex-core tramp crud, and reduce tramp crud impact on outage dose goals.
- Future improvements in shutdown chemistry processes are expected to provide more tools and alternatives for plants to achieve their specific goals and as contingencies for unexpected circumstances.

REFERENCES

1. PWR Primary Water Chemistry Guidelines: Volume 1, Revision 4, EPRI, Palo Alto, CA: 1999, TR-105714-V2R4
2. Proceedings: PWR Primary Startup/Shutdown Chemistry Workshop, EPRI, Palo Alto, CA: 2000. 1000689
3. PWR Shutdown Chemistry Practices, EPRI, Palo Alto, CA: 1998. Report TR-109569
4. K. Garbett, et al., "Hydrogen, Oxygen and Nickel Behavior in PWR Primary Coolant", Proceedings of the Axial Offset Anomaly (AOA) Science Workshop, Report 1000137, EPRI, Palo Alto, CA: 2000
5. Evaluation of Dose Rate and Chemistry Data from Plants Operating with Increased BOL pH Chemistry Control, EPRI, Palo Alto, CA: Interim Report July 2000
6. Impact of PWR Primary Chemistry on Corrosion Product Deposition on Fuel Cladding Surfaces, EPRI, Palo alto, CA: Final Report November 1997, TR-108783
7. B. Fellers, et al., "Elevated-Constant pH Control Assessment at TXU's Comanche Peak Steam Electric Station", Paper 155, SFEN-CHIMIE 2002, Avignon, Fra., April 2002
8. K. Burrill, B. Fellers, "The Role of Water Radiolysis in changing Local Water Chemistry during Subcooled Nucleate Boiling and Influence on Iron Oxide Deposits", Proceedings of the Axial Offset Anomaly (AOA) Science Workshop, Report 1000137, EPRI, Palo Alto, CA: 2000
9. B. Fellers, "Prediction of Local pH and Radiolysis Influence on Metals and Their Oxides at Temperature", Robust Fuels WG 1 Meeting, New Orleans, LA, December 14, 2001
10. B. Fellers, " Radiolysis Influence on Fuel Crud Deposition for PWR Sub-Cooled Nucleate Boiling Environments", EPRI Robust Fuel WG1 Meeting, Washington, DC., December 1999
11. K. Burrill, B. Fellers, "Using a Simple Validated Mathematical Model to Predict Iron Oxide Deposit Weights on Fuel Sheaths during Boiling in a PWR Core", Proceedings of the Axial Offset Anomaly (AOA) Science Workshop, Report 1000137, EPRI, Palo Alto, CA: 2000
12. W. Byers, J. Partezana, "Characteristics of Crud from Cores with and without AOA", Proceedings of the Axial Offset Anomaly (AOA) Science Workshop, Report 1000137, EPRI, Palo Alto, CA: 2000
13. S. Sawochka, et al., "Oxide Solubility and Phase Stability", EPRI 6151-12, Robust Fuels Working Group 1, Orlando Fla., February 19, 1999
14. J, Bosma, B. Fellers, "The integration of In-Core Data, Core Design and Chemistry as a Diagnostic Approach to Crud Deposition and Release Modes in PWRs with Subcooled Nucleate Boiling", Proceedings of the Axial Offset Anomaly (AOA) Science Workshop, Report 1000137, EPRI, Palo Alto, CA: 2000