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AN OVERVIEW OF ZINC ADDITION FOR BWR DOSE RATE CONTROL

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ABSTRACT

This paper presents an overview of the BWRs employing feedwater zinc addition to reduce primary system dose rates. It identifies which BWRs are using zinc addition and reviews the mechanical injection and passive addition hardware currently being employed. The impact that zinc has on plant chemistry, including the factor of two to four reduction in reactor water Co-60 concentrations, is discussed. Dose rate results, showing the benefits of implementing zinc on either fresh piping surfaces or on pipes with existing films are reviewed. The advantages of using zinc that is isotopically enhanced by the depletion of the Zn-64 precursor to Zn-65 are identified.

INTRODUCTION

Beginning in 1982, analysis of historical BWR radiation buildup data, sponsored jointly by the Electric Power Research Institute (EPRI) and GE Nuclear Energy, identified a correlation between low primary system dose rates and the presence of ionic zinc in the reactor water. Several BWRs were found to have zinc in the reactor water because they had a brass condenser and a powdered condensate treatment system. The brass provided a source of zinc which was not totally removed by the powdered resin condensate system. This resulted in reactor water soluble zinc concentrations of 5 to 15 ppb. These plants were dubbed 'natural zinc' plants and served as the foundation of the correlation. This correlation was hypothesized to be the result of a corrosion inhibition effect of zinc for stainless steel. Subsequent laboratory testing confirmed that ionic zinc is strongly incorporated into the protective oxide film which forms on stainless steel surfaces and that this film is more protective to the base metal than films formed without zinc present. As a result, a thinner layer of oxide is sufficient to curtail the corrosion process. Figure 1 shows the relationship between oxide film thickness and the concentration of ionic zinc in the water for laboratory tests conducted at BWR conditions of temperature and pressure.

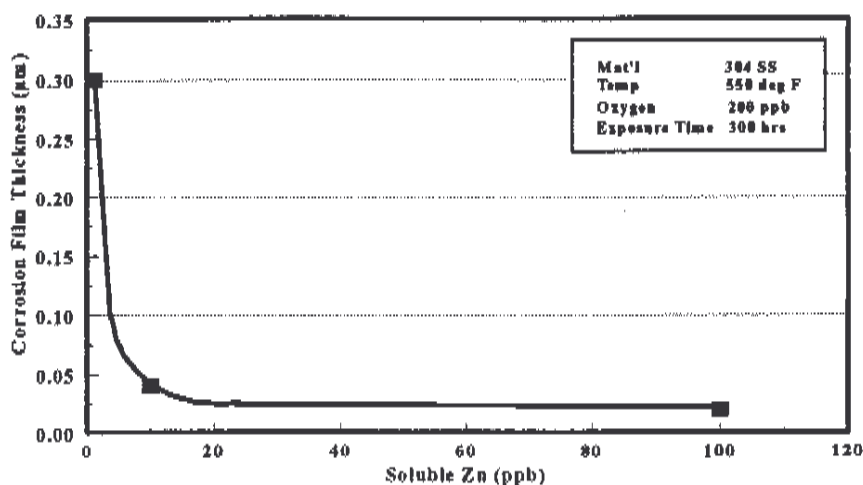


Figure 1. Effect Of Zinc On Stainless Steel Corrosion.

Additional testing was required to verify that the corrosion inhibition effect established by the data shown in Figure 1 would produce the reduced radiation buildup identified in the plant correlation. These tests showed that the corrosion inhibition effect of zinc did result in reduced Co-60 buildup on stainless steel under either normal BWR water chemistry (150-200 ppb oxygen) or hydrogen water chemistry (<15 ppb oxygen). Some of the data from these tests are shown in Figures 2 and 3.

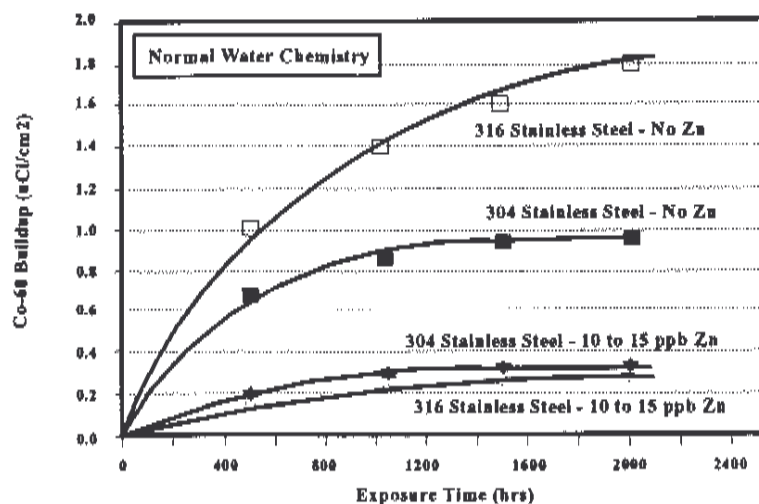


Figure 2. Effect Of Zinc On Radiation Buildup Under Normal Water Chemistry.

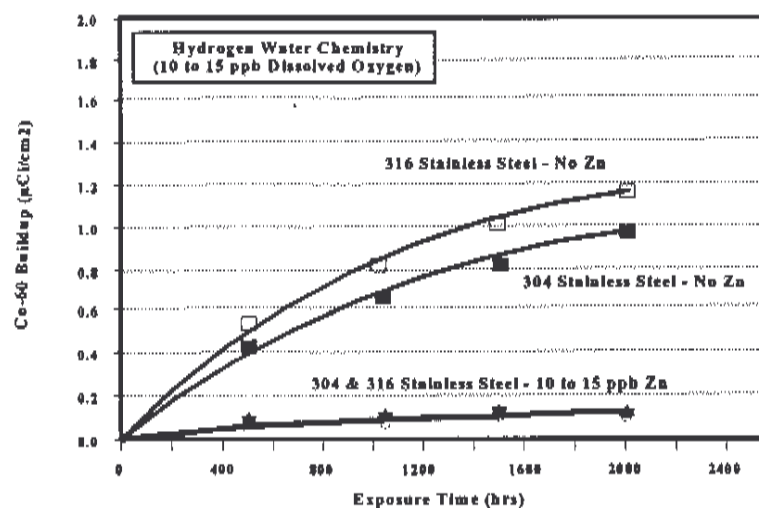


Figure 3. Effect Of Zinc On Radiation Buildup Under Hydrogen Water Chemistry.

The data analysis and laboratory testing described above have been documented in published reports^{1,2,3} and resulted in the development by GE Nuclear Energy of systems for the addition of zinc to the BWR primary system under the registered trademark of **GEZIP**.

BWRs USING GEZIP

In the Fall of 1986, Hope Creek became the first BWR to intentionally add zinc to the primary system. At this time, there are a total of fourteen BWRs which have implemented GEZIP and several additional

plants which are currently evaluating implementation. Figure 4 provides a list of the plants using GEZIP and a time line reflecting the implementation calendar.

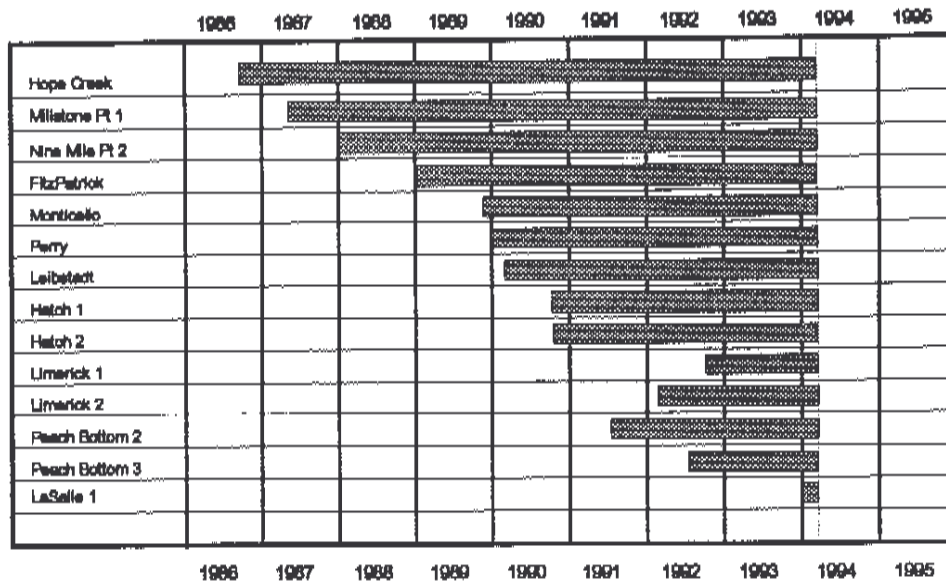


Figure 4. BWR Implementation Chart For GEZIP.

ZINC ADDITION SYSTEMS

As might be expected, the design of systems for adding zinc to the BWR have evolved since the first unit was installed at Hope Creek. This first unit used a low flow, positive displacement pump to inject a zinc oxide suspension into a recirculation loop around the final feedwater pump. Subsequent enhancements to this design yielded an improved, higher flow rate injection system which injected directly into the feedwater pipe and, thus, required no recirculation loop. Further innovation has yielded a passive design with no moving parts. The designs used in each of the GEZIP plants is provided below.

Table 1. GEZIP Equipment Application By Plant

Low Flow Pump	High Flow Pump	Passive Addition
Hope Creek	Monticello	Leibstadt
Millstone Pt 1	Limerick 1	Perry
Nine Mile Pt 2	Limerick 2	Hatch 1
FitzPatrick	Peach Bottom 2	Hatch 2
	Peach Bottom 3	LaSalle 1*

* - LaSalle 1 is temporarily using a High Flow Pump system until their Passive System is ready.

Simplified flow schematics and descriptions for these systems are included in the following sections.

Mechanical Injection

Figure 5 presents a schematic of the original, skid mounted, Low Flow Pump System for zinc injection. In this system, two, redundant, diaphragm pumps inject zinc oxide suspension from the continuously agitated supply tank into a recirculation pipe which takes suction on the downstream side of the final

feedwater pump and returns it to the upstream side of the final feedwater pump. The injection pump flow rate is approximately 30 ml/min and the recirculation loop flow rate is approximately 50 gal/min.

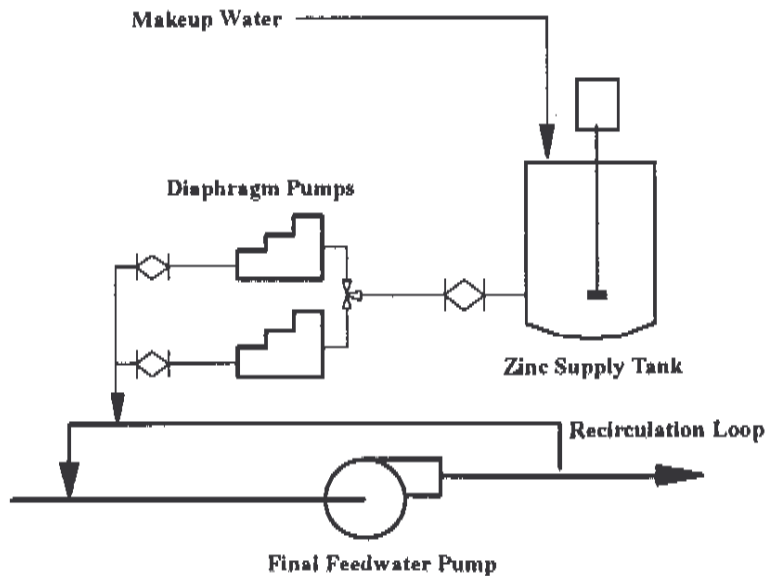


Figure 5. Low Flow Pump System for zinc injection.

Figure 6 presents a schematic of the High Flow Pump System for zinc injection. In this system dilution condensate is provided at the suction side of the injection pumps to improve flow characteristics and permit the use of larger pumps (approximately 300 ml/min) which have inherently larger components and provide improved performance. With this increased pump output, the recirculation loop around the feedwater pump is not needed. Thus the injection pump output is fed directly into the feedwater pipe on the suction side of the final feedwater pump.

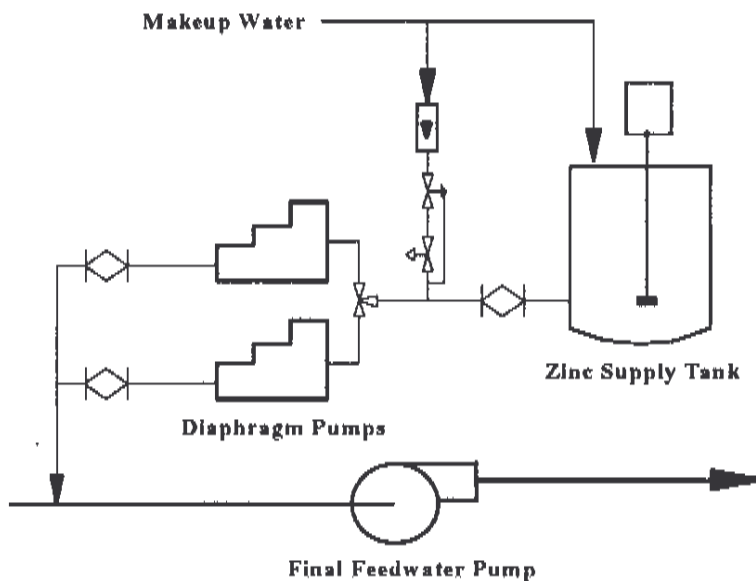


Figure 6. High Flow Pump System for zinc injection.

Passive Addition

The passive system was developed so that the operating and maintenance requirements of zinc addition would be minimized. The schematic for this system is shown in Figure 7.

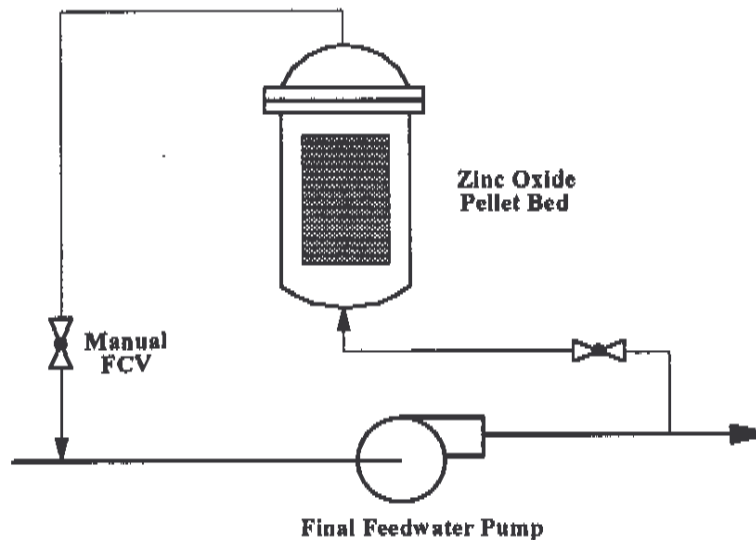


Figure 7. Passive zinc addition system.

In this system, a bed of sintered zinc oxide pellets is contained in a small pressure vessel. A bypass stream of less than 100 gpm is taken from the discharge side of the final feedwater pump, passed through the pellet bed and returned to the suction side of the feedwater pump. Sufficient zinc is dissolved from the pellets to maintain the desired concentration of zinc in the reactor water. The pellet bed is designed such that it will last at least one complete fuel cycle without requiring additional pellets. By virtue of its having no moving parts, this system provides a zinc addition option with essentially no maintenance and requiring minimal operator attention.

IMPACT OF ZINC ON REACTOR WATER Co-60

One of the impacts of zinc addition, which was impossible to anticipate prior to GEZIP, was the suppression of the reactor water Co-60 concentration. 'Natural Zinc' plants had zinc present from the first cycle of operation and, thus, there was no opportunity to know that this suppression was occurring (i.e. there was no 'before and after' available for comparison). Likewise, the first application of GEZIP was at Hope Creek, a new plant, and therefore there was no comparison basis there either. However, when zinc was introduced at Millstone Pt 1 for the first time, in April, 1987, the impact was immediately observed. It has subsequently been repeated at each BWR which has introduced zinc after operating for one or more cycles as a non-zinc plant. The marked impact observed at Millstone Pt 1, commencing with initial zinc injection, is shown in Figure 8. The comparison of total reactor water Co-60 before and after zinc addition is shown for Millstone Pt 1, FitzPatrick, Monticello, and Leibstadt in Figure 9.

Zinc acts to lower the Co-60 in two ways. First, it suppresses the corrosion release rate for in-core cobalt alloys, such as the stellite rollers and pins. Second, it is incorporated into the iron-based fuel deposits and results in an oxide which releases Co-60 at a lower rate.

This effect results in additional reduction of Co-60 buildup on primary system piping and components, as well as decreasing the curies of Co-60, and Co-58 which enter the radwaste as a result of capture in the

reactor water cleanup system. The curies of Co-60 and Co-58 released to the reactor water at shutdown are also reduced as a result of this suppression.

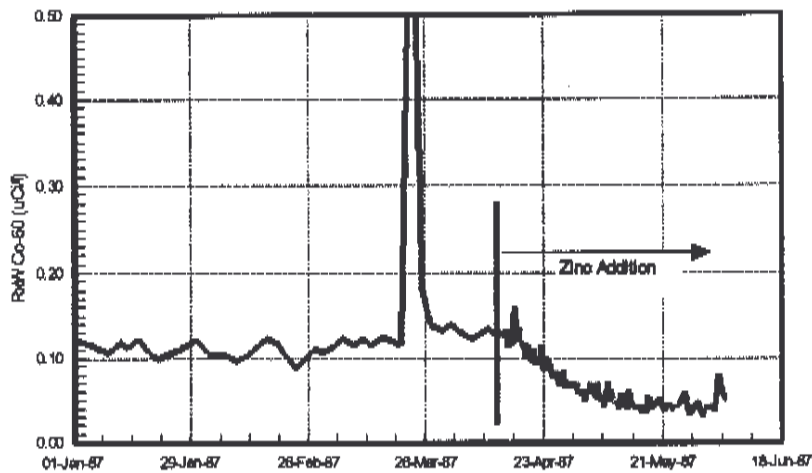


Figure 8. Suppression of reactor water soluble Co-60 by zinc addition at Millstone Pt 1.

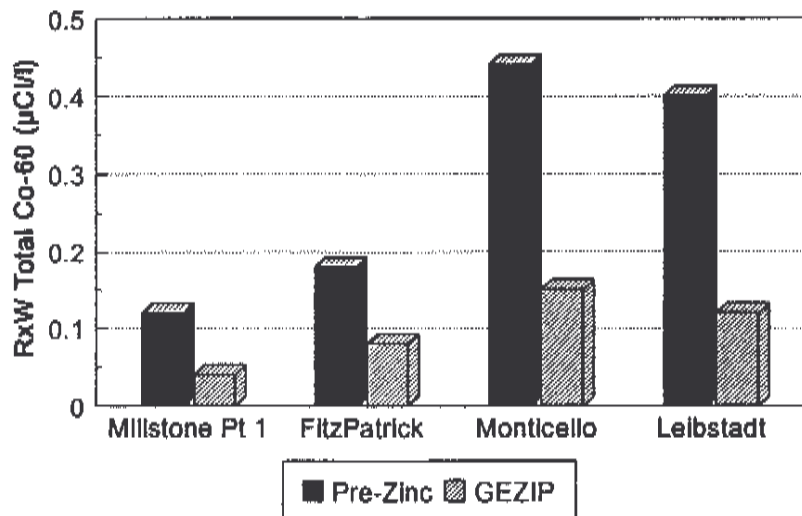


Figure 9. Reduction of reactor water Co-60 as a result of zinc addition.

IMPACT OF GEZIP ON PRIMARY SYSTEM DOSE RATES

The probable impact of GEZIP implementation at any BWR is dependent on several factors. Included in these factors are the following:

1. Was the plant a 'Natural Zinc' plant just prior to GEZIP implementation?
2. Is the plant a new plant?
3. If the plant is an operating plant, has a chemical decontamination been performed?
4. Is the plant using Normal Water Chemistry or Hydrogen Water Chemistry?

Several of the natural zinc plants identified in the original studies have since either replaced their brass condenser or added deep bed demineralizers to the condensate treatment system and thus lost their source of zinc to the reactor. Implementing zinc at these BWRs would be expected to maintain the historically low radiation buildup that they have experienced.

The expectation for pipes in a new plant at initial startup, and for pipes which have just experienced a successful chemical decontamination, are that subsequent radiation buildup should be analogous to the laboratory test data shown earlier in the report. Thus radiation buildup should be slower and equilibrium dose rates should be significantly below the average of non-zinc BWRs.

For piping systems in operating plants, which have an existing oxide film, formed during one or more cycles of operation and not subjected to a chemical decontamination, zinc can gradually alter the structure of that film so that dose rates will decrease gradually as exposure to zinc progresses.

For reference purposes, the BWRs listed above implemented GEZIP under the circumstances displayed in the table below.

Table 2. Status Of Plants Implementing GEZIP

New Plants	Non-Zinc Operating Plant w/ Chem Decon	Non-Zinc Operating Plant no Chem Decon	Nat'l Zinc Operating Plant
Hope Creek	Millstone Pt 1	Perry	Hatch 1*
Nine Mile Pt 2	FitzPatrick*	Leibstadt	Hatch-2*
	Monticello*		Limerick 1
	LaSalle 1		Limerick 2
			Peach Bottom 2
			Peach Bottom 3

* - Reactors using Hydrogen Water Chemistry.

Normal Water Chemistry (NWC)

Hope Creek and Nine Mile Pt 2

Both Hope Creek and Nine Mile Pt 2 initiated GEZIP at the start of the first cycle of operation and have operated with NWC through the period covered in this report. Figure 10 shows the radiation buildup at these reactors over the first few cycles.

During the first cycles at each of these reactors, the zinc concentration in the reactor water was maintained in the range of 5 to 10 ppb. In subsequent cycles, concern about Zn-65 has resulted in operation at approximately 2 ppb. Even with the lower than recommended zinc concentration, both plants have experienced dose rates which are well below the non-zinc BWR average of approximately 300 mR/hr.

With dose rates <100 mR/hr, Hope Creek is in the lowest group of BWRs with respect to dose rates. This reactor has recently converted to both DZO (*Depleted Zinc Oxide*, discussed later in the report) and HWC. It is expected that the impact of DZO will not be fully observed for several cycles because of the large natural zinc (i.e. Zn-64) inventory present in the reactor. HWC may result in an increase in dose rates over, at least, the next few cycles.

Nine Mile Pt 2 has higher dose rates than Hope Creek and is currently at 184 mR/hr. Niagara Mohawk is currently evaluating a switch to DZO as the zinc source material. This higher dose rate is the result of

two factors. First, and most important, the average pipe wall thickness is only 1.0 in. compared to the more typical value of 1.25 in. for BWRs. This reduces the self-shielding of the pipe and results in higher dose rates for the same surface concentration of isotopes. Correcting for this thinner pipe and normalizing to the 1.25 in. wall thickness would result in an average dose rate of ~130 mR/hr.

Nine Mile Pt 2 also has higher than average insoluble activity in the reactor water and it is believed that deposition of this particulate matter is contributing more dose rate at the pipe surface than is typical.

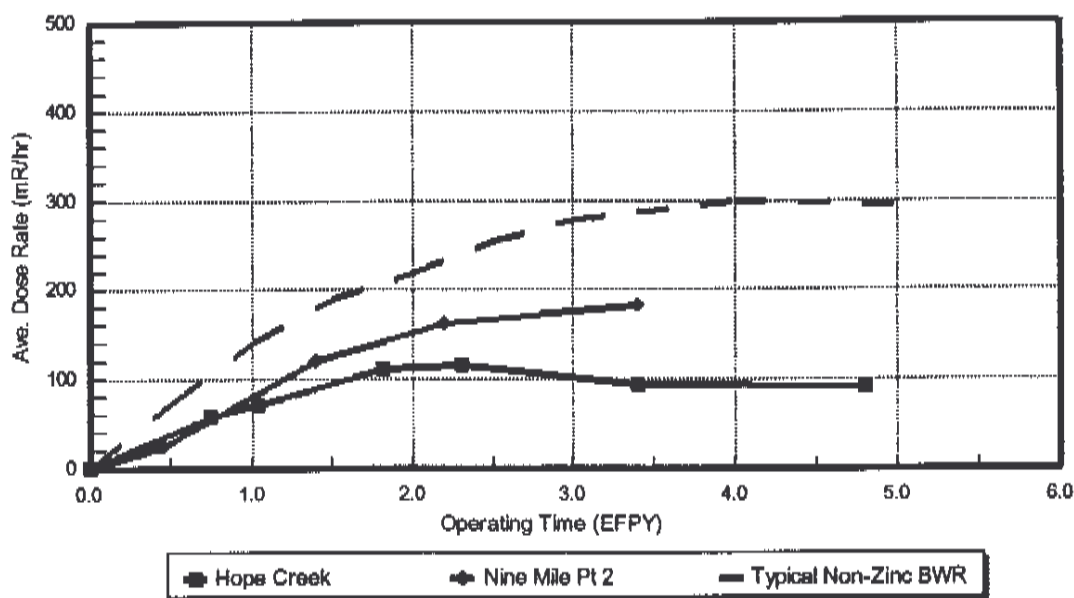


Figure 10. Radiation buildup with GEZIP at Hope Creek and Nine Mile Pt 2.

Millstone Pt 1

Figure 11 provides the history of radiation buildup at the Millstone Pt 1 reactor since they chemically decontaminated the primary system in 1984.

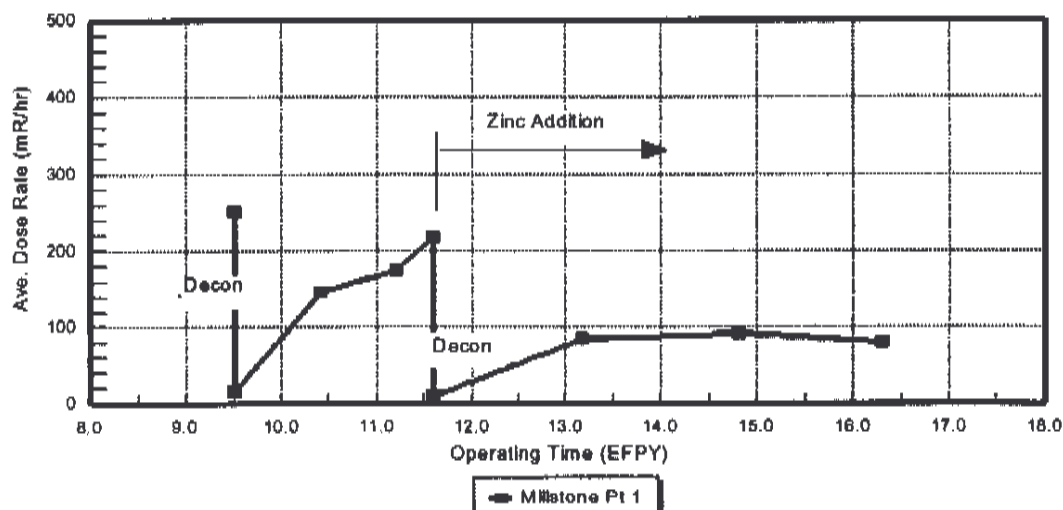


Figure 11. Radiation buildup with GEZIP at Millstone Pt 1.

Northeast Utilities implemented GEZIP on a test basis for two months prior to the refueling outage in 1987, and then continued on a permanent basis after another chemical decontamination in that outage. This gives an excellent opportunity to compare one reactor both with and without zinc addition.

In the period 1984 to 1987, doses increased from a post-decon value of ~10 mR/hr to a pre decon value of 217 mR/hr. Following initiation of GEZIP, dose rates have remained at <100 mR/hr. In the most recent cycle, Millstone has begun using DZO. Again, the inventory of natural zinc created over two cycles of operation will dictate that the impact of DZO will be obscured for a few cycles.

LaSalle 1

The LaSalle 1 reactor began GEZIP operation, using DZO, in January, 1994 at the end of their current cycle. A chemical decontamination will be performed during the Spring refueling outage. The impact of GEZIP at LaSalle 1 will not be known until, at least, 1995.

Perry

The Perry plant implemented GEZIP after one full cycle of operating as a non-zinc reactor. The radiation buildup for this plant is shown in Figure 12. The average dose rate reached 100 mR/hr in the cycle prior to GEZIP and has since increased to 173 mR/hr. Recent data received from plant personnel indicate that dose rates have leveled off at 200 mR/hr. While this average dose rate is still significantly below the non-zinc BWR average, it is somewhat higher than might be expected. A review of the reactor water chemistry data for this period indicates that the insoluble Co-60 concentration is varying between 0.2 and 2.0 $\mu\text{Ci/l}$. This is one to two orders of magnitude higher than the typical BWR (normally 0.02 to 0.05 $\mu\text{Ci/l}$) and suggests that insoluble deposition may be playing a greater role in the buildup at Perry. Perry continues to use natural zinc as the feedstock and maintained a reactor water zinc concentration of 4 to 6 ppb over this period.

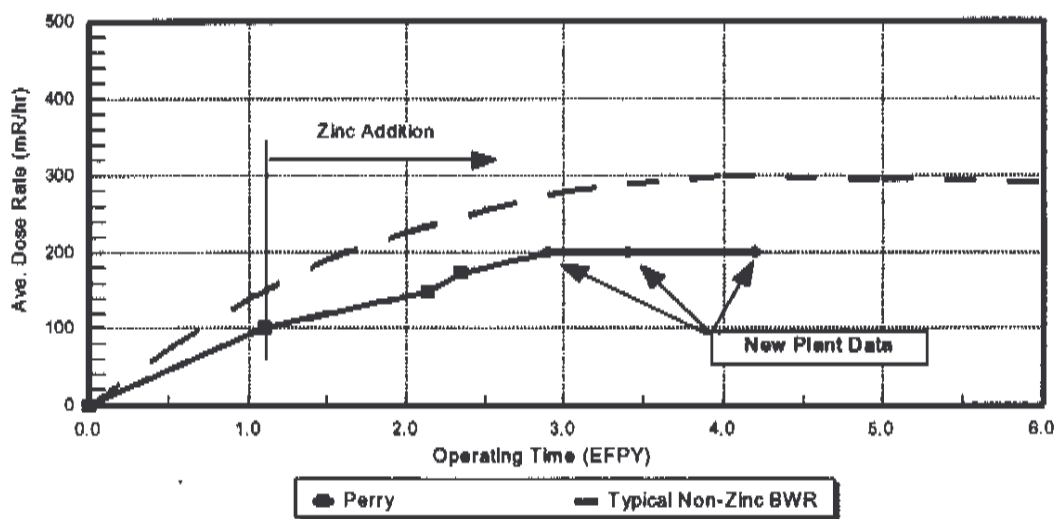


Figure 12. Radiation buildup with GEZIP at Perry.

Leibstadt

The Leibstadt plant installed GEZIP in the middle of fuel cycle 6 and, consequently, started zinc addition with no chemical decontamination. This was the first BWR to use the passive zinc addition system.

Wishing to minimize the impact of Zn-65 on the plant, Leibstadt has elected to maintain zinc concentrations in the reactor water in the 2 to 3 ppb range. This has undoubtedly impacted the rate of dose rate reduction observed. Figure 13 shows the steady decrease in the average dose rate obtained, even with the lower than recommended zinc concentration. At the most recent refueling outage in August, 1993, the measured dose rate appeared to show a slight increase from 196 to 203 mR/hr. The gamma scan data taken during this survey provided information that explained the dose rate data. The Co-60 loading on the pipe had continued to drop at a significant rate (~11%), as shown in Figure 14, but deposited fission products (Ru-103, Zr-95, and Nb-95) from a failed fuel bundle contributed 16% to the dose.

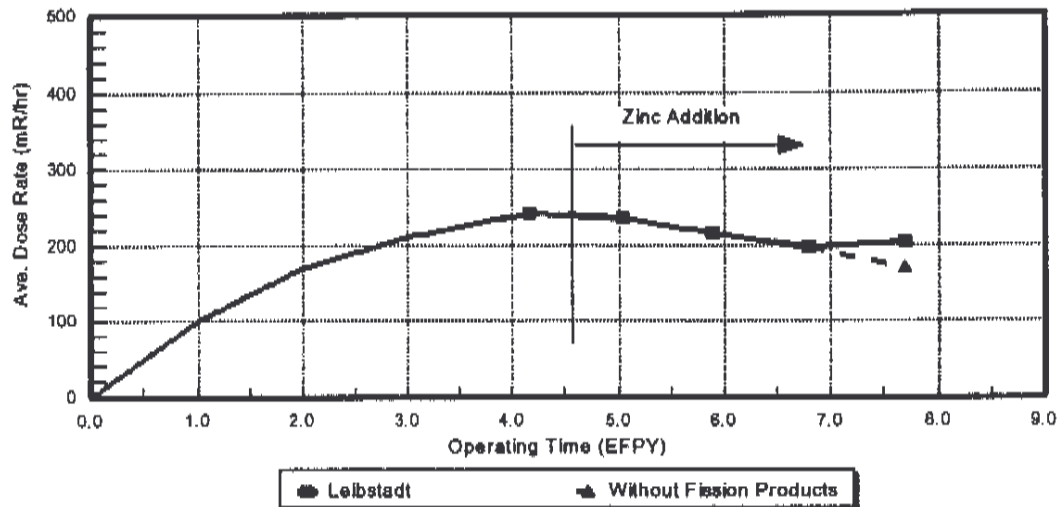


Figure 13. Radiation buildup with GEZIP at Leibstadt.

Figure 13 shows a calculated data point for the 1993 dose rate of 170 mR/hr which is based on subtracting the fission product contribution.

Leibstadt used DZO for this past fuel cycle and will continue to do so.

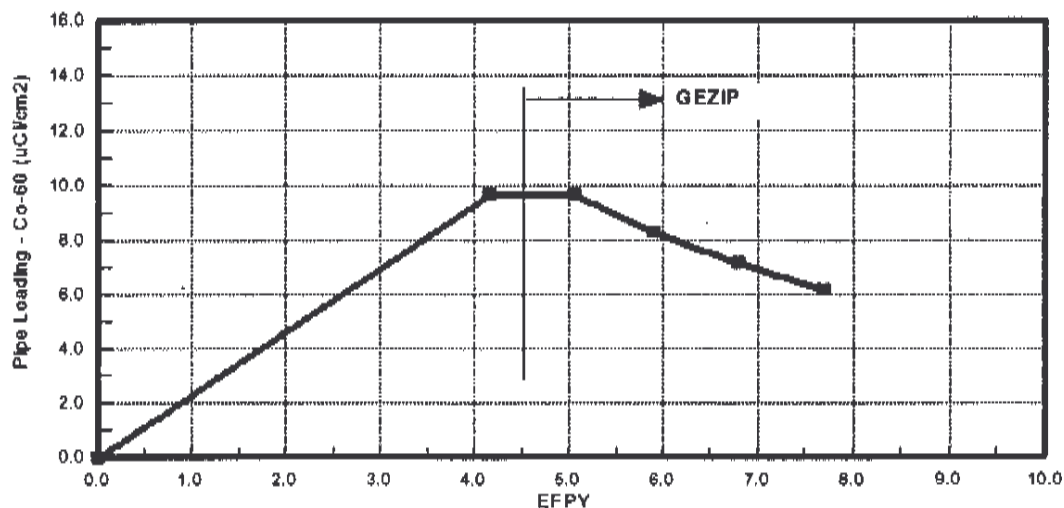


Figure 14. Decrease in Co-60 on Leibstadt piping with GEZIP.

Limerick 1 and Limerick 2

Limerick 1 and 2 were initially in the group of 'Natural Zinc' plants but they have added deep bed demineralizers to the condensate system and this has virtually eliminated the original source of zinc. They have implemented GEZIP to retain the dose reduction effect of zinc and appear to be continuing on the low dose rate track. Reactor water zinc concentrations have generally been maintained at less than 5 ppb.

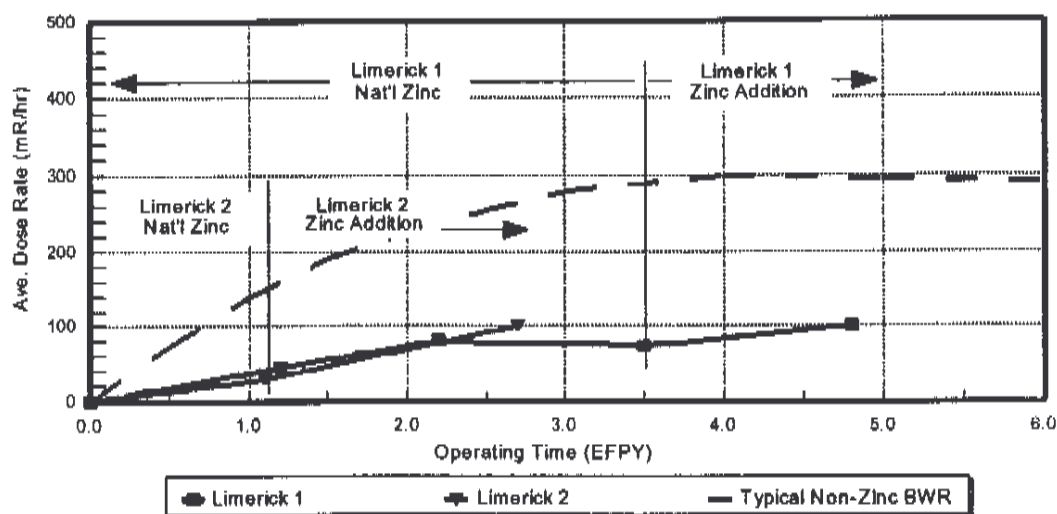


Figure 15. Radiation buildup at Limerick 1 and 2 with GEZIP.

Peach Bottom 2 and Peach Bottom 3

The Peach Bottom units were also 'Natural Zinc' plants initially but have replaced their brass condensers with titanium. To replace the lost source of zinc, Unit 2 implemented GEZIP in 1991, and Unit 3 in 1992. GE does not have subsequent dose rate measurements at this time.

Hydrogen Water Chemistry

FitzPatrick

At the end of 1988, and prior to the start of fuel cycle nine (8.5 EFPY), the FitzPatrick plant performed a chemical decontamination of the primary system as a prelude to beginning both HWC and GEZIP. They are currently in the middle of fuel cycle eleven. The radiation buildup experience for this period is shown in Figure 16.

Prior to switching to GEZIP and HWC, FitzPatrick was a typical non-zinc BWR with average dose rates at the standard locations which had peaked at approximately 300 mR/hr before stabilizing and drifting down by decay processes. The switch to HWC, for IGSCC mitigation of the primary system piping, produced insoluble transport of activated isotopes and resulted in the creation of localized hot spots of 1 to 2 R/hr. However, the general buildup in the primary system has been controlled by the zinc addition and the average at the standard locations peaked at ~120 mR/hr. The hot spot problem appears to have been a transition process and has diminished significantly in recent measurements.

Like the other GEZIP plants, FitzPatrick has elected to maintain reactor water zinc concentrations at 3 to 5 ppb, well below the recommended 10 ppb, so that the effects of Zn-65 are minimized. DZO has been used for most of the current cycle, but changeover problems have also necessitated the use of some natural zinc oxide.

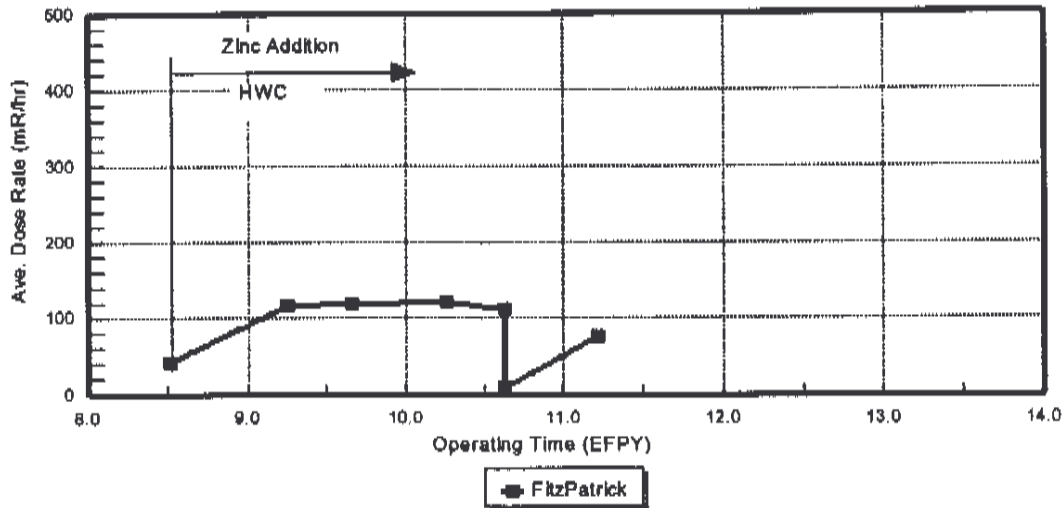


Figure 16. Radiation buildup at FitzPatrick with GEZIP and HWC.

Monticello

Monticello implemented HWC in the middle of fuel cycle thirteen, but did not start zinc addition until the beginning of fuel cycle 14. Even prior to HWC, the dose rates at Monticello had been above average. At the standard locations, the dose rates on NWC had climbed to ~400 mR/hr before the HWC switch (13.2 EFPY) and then jumped rapidly to 760 mR/hr during the last half of cycle thirteen (14.0 EFPY). During this initial HWC period, the hydrogen injection rate was limited to 15 scfm.

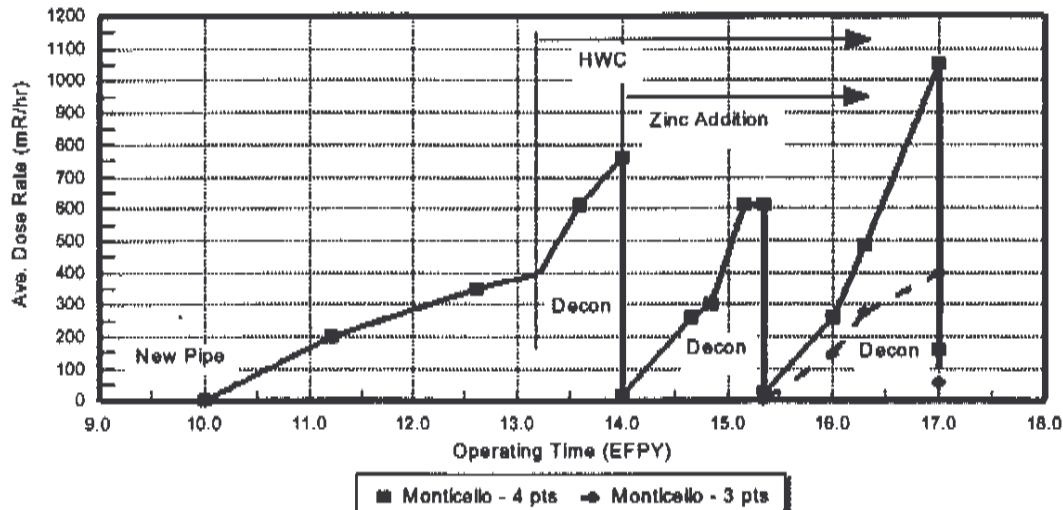


Figure 17. Radiation buildup with GEZIP and HWC at Monticello.

Shielding

Permanent and temporary shielding is an integral part of the System 80+™ Standard Design. Permanent shielding is used where possible. For instance, System 80+™ Standard Design provides shielding between redundant components of an operating system. This reduces the dose to personnel performing maintenance on one component while the other component is operating. The location and design of labyrinths are also considered in plant layout. Labyrinths are provided for entrances in all high radiation rooms.

Portable shields, such as lead blankets and pigs, will be used during maintenance activities if the total exposure, which includes exposure received during installation and removal of the shielding, is reduced. Removable/portable shielding in the form of bricks and concrete blocks will be avoided. Rigging and transport paths are also provided in the design of the System 80+™ Standard Design for the removal of the shielding as necessary.

INFORMATION MANAGEMENT SYSTEM

The System 80+™ design is provided on an Information Management System (IMS). This IMS provides an effective means of acquiring, storing, retrieving and manipulating the documents and data necessary to design, construct, startup, operate, and maintain the plant. The System 80+™ IMS utilizes an existing computer program that is in operation within Duke Power Company called PASCE as its base program. PASCE currently store two dimensional drawing data in a hierarchical database called PLANT-SCHEMA. Three dimensional drawing data is stored in a hierarchical database call PLANT-VIEW. The System 80+™ plant layout is currently provided on the three dimensional graphics/data model within PASCE PLANT-VIEW. This model can be used in future plant operations for entering and developing three dimensional dose maps (See Figure 7). These dose maps can be generated within PASCE which integrates the plant layout graphics with specific area information, such as dose rate and source location(s) measured and entered by health physics personnel. This information can be readily used by health physics personnel to estimate the dose, as well as by personnel in the field to effectively implement the ALARA principles of time, distance, and shielding during maintenance activities. In addition the three dimensional model can be utilized for maintenance personnel in preplanning their maintenance activities and locating electrical and service connections. This allows pre planning without entering the radiation protection area, thus reducing occupational dose.

Duke Power has modeled their McGuire and Catawba Nuclear Stations on PASCE and currently utilize PASCE for developing three dimensional dose maps and for maintenance and outage planning. PASCE also interfaces with a program called PASSPORT which allows work request to be developed including the dose information for the area, dress out and dosimetry requirements. Duke Power Company experience has found that PASCE has considerably reduced the time personnel spend in the radiation protection zone for visual inspection for planning purposes and thus has reduce operation dose.

DOSE ASSESSMENT

Many design features which reduce operation exposure have been discussed above and implemented into the System 80+™ design. The two most important features which will reduce the annual exposure and allow the EPRI ALWR goal of 100 person-rem/yr to be meet are source term control through the reduction of cobalt and the steam generator material, fabrication, maintenance and inspection improvements that have been incorporated into the System 80+™ design.

The annual exposure at Duke Power Company's seven Pressurized Water Reactors (PWRs) for 1989 is shown in Table 1. This results in an annual average exposure of 235 person-rem per unit. This table also shows the percentage of annual exposure resulting from each major maintenance task.

Laboratory testing by GE has demonstrated that the cycling between HWC and NWC causes accelerated buildup rates which are significantly worse than steady operation under either chemistry⁴. HWC/NWC cycling laboratory data for 304 SS is shown in Figure 18.

Monticello is the lone GEZIP plant which has experienced high radiation buildup. The reasons and mechanisms causing this result are still ill-defined and will require continued monitoring and examination before remedies can be known with confidence.

Hatch 1 and Hatch 2

The Hatch reactors were 'Natural Zinc' initially but replaced the brass condensers and thereby lost their source of zinc. GEZIP was implemented at both units in 1990. Hatch 1 began using HWC to protect primary system piping in 1987, while Hatch 2 did not start adding hydrogen until 1991. Both units have been gradually increasing the hydrogen addition rate over 1993 to reach the level which will protect the vessel internals. At Hatch, this rate is 35 scfm.

Hatch 1 reached the 35 scfm addition rate in January, 1994 and maintains a reactor water zinc concentration of approximately 5 ppb using natural zinc oxide as a feedstock. A switch to DZO is planned for later in 1994. Figure 19 shows the radiation buildup experience at Hatch 1 from its initial operation as a 'Natural Zinc' plant, through its transitions to HWC and GEZIP. The average dose rate increased ~100 mR/hr following the onset of HWC but has returned to pre-HWC dose rates of 100 mR/hr in the most recent measurements at the beginning of 1994.

This experience is in direct contrast to the high buildup at Monticello. Even though the hydrogen addition rate has been steadily increased and is now protecting core internals, dose rate buildup is very low. Georgia power has made a concerted effort to minimize the cycling of hydrogen and maintains an availability for HWC of greater than 90%.

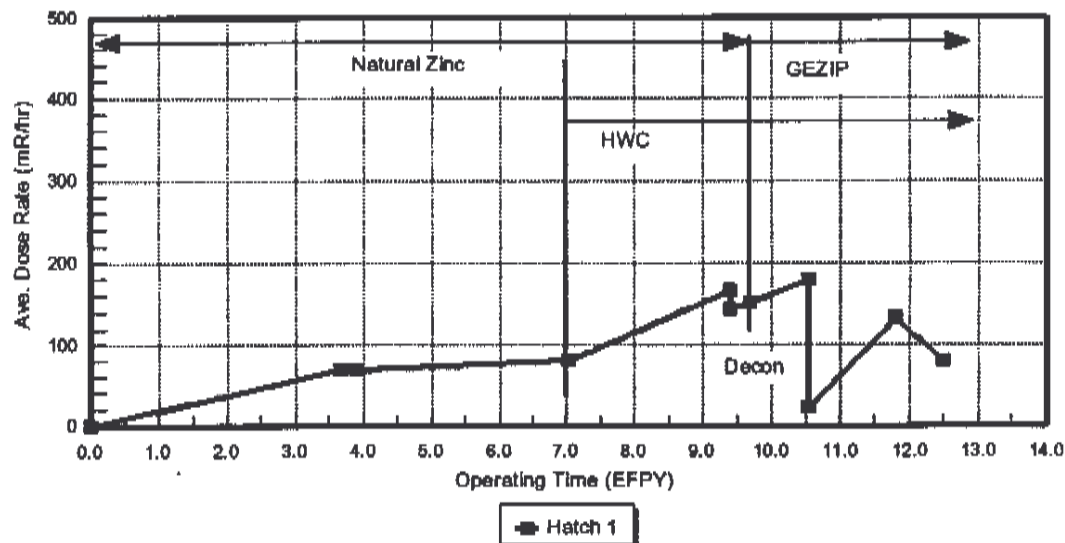


Figure 19. Radiation buildup with GEZIP and HWC at Hatch 1.

Hatch 2 is currently operating at 20 to 25 scfm of hydrogen addition while system and instrumentation adjustments are made which will permit them to operate at the 35 scfm needed for full protection. Reactor

water zinc is maintained at 5 ppb using DZO as the feed material. Figure 20 shows the radiation buildup history for Unit 2.

Again, a minimal increase from an NWC dose rate of 150 mR/hr to an HWC transitional level of 210 mR/hr was observed. The most recent measurements suggest that dose rates are decreasing to the range experienced under NWC.

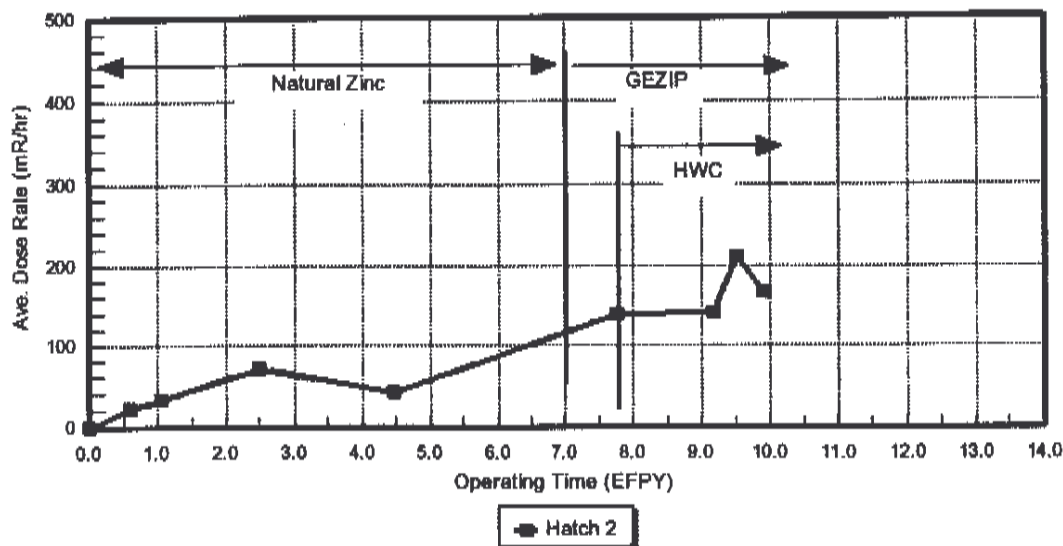


Figure 20. Radiation buildup with GEZIP and HWC at Hatch 2.

RELATED ISSUES

DZO (Depleted Zinc Oxide) and Zn-65

While it was known that the presence of zinc in the BWR primary system results in activation on the fuel surface and distribution of Zn-65 through the plant, experience in 'Natural Zinc' plants had not indicated that this was a significant problem. However, at the first refueling outage for Hope Creek it became clear that some fundamental differences existed between the 'Natural Zinc' plants and the first plant to implement GEZIP. At that refueling, Zn-65 was released from the fuel deposits to the reactor water at a high rate and resulted in a peak concentration of approximately 200 $\mu\text{Ci/l}$ in the reactor water and a total release of approximately 3000 Curies of Zn-65 to the radwaste system. These unexpectedly large quantities of Zn-65 caused difficulties in handling and disposal for plant personnel and made it clear that actions were needed to understand and deal with the problem that Zn-65 could cause in GEZIP plants.

After review, it was determined that the important difference between the 'Natural Zinc' plants and Hope Creek was the amount of iron entering with the feedwater. The powdered resin condensate systems in the 'Natural Zinc' plants are excellent particulate filters and typically result in less than 2 ppb iron in the final feedwater. Conversely, the deep bed demineralizers in plants such as Hope Creek are less efficient particulate filters and result in higher iron inputs. In the case of Hope Creek, the iron input averaged approximately 12 ppb over the first cycle. This iron incorporates 5% to 15%, by weight, zinc and carries this zinc to the fuel surface, where over 80% of the iron is deposited. Thus, the inventory of zinc and Zn-65 on the fuel was much higher at Hope Creek and would be expected to be at any plant with higher iron input than the typical 'Natural Zinc' plant.

Interim approaches to minimizing the problems associated with Zn-65 have been identified and communicated to those BWRs using GEZIP. These recommendations include the following:

1. Reduce feedwater iron input with a goal of 0.1 to 0.5 ppb. Optimize condensate treatment system performance with improved resins and/or addition of new filters.
2. Use 'soft' shutdown procedures contained in GE Nuclear Energy's Service Information Letter (SIL) #541. These procedures attempt to minimize the hydrodynamic turbulence, associated with shutdown, that is believed to promote isotopic release.
3. If using HWC, minimize the cycling on and off of the hydrogen.

The best resolution to the concerns about Zn-65 is to use DZO (*Depleted Zinc Oxide*) as the feedstock for GEZIP. DZO has been isotopically engineered to reduce the concentration of the Zn-64 precursor of Zn-65 from the naturally occurring 48% to less than 1%. Figure 21 shows the isotopic split for both natural zinc and DZO.

The isotopic enhancement of DZO is accomplished by separation in gas centrifuges and is then converted to either zinc oxide powder or pellets as needed for the specific plant. Currently, Leibstadt, Hope Creek, Millstone, FitzPatrick, Monticello, and both Hatch units are either using or planning to use DZO. By virtue of the isotopic enrichment processing, the cost of DZO is high but it is anticipated that as experience is gained and market demand rises, the price will decrease.

For the plants mentioned, the fact that they have added natural zinc for one or more cycles means that the switch to DZO will not mean an immediate elimination of Zn-65 in the plant environment. The inventory of Zn-64/Zn-65 is expected to gradually diminish in importance over several fuel cycles. Plants using DZO from initial GEZIP operation, such as LaSalle 1, should experience no significant Zn-65 impact in the plant environment. It is strongly recommended that any BWR which implements GEZIP should plan on using DZO as the source of zinc so that the benefits are maximized.

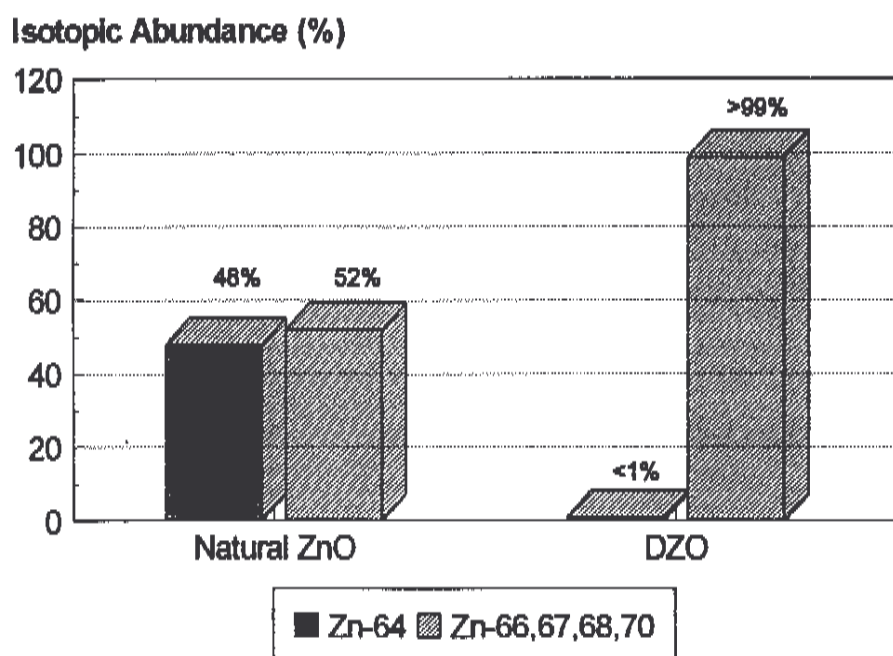


Figure 21. Isotopic concentrations for natural zinc and DZO.

IGSCC (Intergranular Stress Corrosion Cracking)

When it was verified that zinc suppresses the corrosion of stainless steel by forming an oxide film which was more protective to the base metal, it opened the possibility that zinc addition might also contribute to the suppression of IGSCC. Reviews of early BWR experience, as well as scoping tests, soon began to reinforce these additional hypothesized benefits. Two early BWRs had operated with zinc concentrations of approximately 100 ppb and reported very little IGSCC, even though some of the piping components had been fabricated from highly susceptible material. Soon controlled testing from several organizations were demonstrating the beneficial effects of zinc on IGSCC for both BWR and PWR, materials^{5,6,7}.

Extensive tests performed by General Electric, under BWR conditions, have confirmed that the presence of the zinc ion can reduce the crack growth rate of IGSCC in stainless steel and high nickel alloys, especially at the low electrochemical potentials associated with HWC. However, the beneficial effect has been found to vary from heat to heat of material. This has made it very difficult to quantify the benefit and define the role of zinc in IGSCC mitigation for the BWR.

Chemical Decontamination At GEZIP Plants

Early in the development of GEZIP, concern was expressed in the industry as to whether oxide films formed in the presence of zinc would be able to be decontaminated using the current chemical processes. In the past several years, chemical decontaminations have been conducted at Millstone Pt 1 (after two months of zinc operation), FitzPatrick, Hatch 1, Leibstadt (local), and Monticello (twice).

All but one of these decontaminations were highly successful and resulted in post-decon dose rates of approximately 10 to 20 mR/hr. The one exception is the most recent experience at Monticello. As indicated earlier, the results at this decon were non-uniform, with various locations experiencing DFs as high as 10 or as low as 2. Pending the outcome of related evaluations, it is believed that the difficulties were related to chemical process application and control.

SUMMARY

Over the last ten years, it has become possible to control dose rates in the BWR using the addition of trace quantities of ionic zinc. This technology has proceeded from the stage of hypothesis, through controlled laboratory testing, to application at fourteen BWRs. It has been applied, and been successful, in new and old plants, with and without chemical decontamination, in both non-zinc and previously 'Natural Zinc' plants, and under both NWC and HWC. This success has been attained in spite of the fact that zinc concentrations have been maintained at 2 to 5 ppb instead of the desired concentration of 10 ppb. The refinement of creating isotopically engineered zinc, DZO, offers the opportunity to eliminate Zn-65 as a concern in the application of zinc addition. Several successful decontaminations at GEZIP reactors seem to verify that the films created with zinc addition can be handled with current technology. Monticello, the lone anomaly in the fourteen plant applications for zinc addition (data reported for eleven), requires additional investigation before the mechanisms at work will be understood. However, as DZO continues to be used there, even the high dose rates at this site are expected to be greatly reduced.

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Author Biography

William J. Marble is a Principal Engineer for GE Nuclear Energy in Gilroy, California. For the past 11 years, Mr. Marble has been working on the development and implementation of zinc addition for use in controlling radiation buildup in the primary system of BWRs. Prior to his work on zinc addition, he worked in various assignments related to the development, design, and application of equipment and systems for use in the chemistry and water treatment area of the BWR. He earned a B.S. in Chemical Engineering from Cornell University in 1965.

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PAPER 1-5 DISCUSSION

- Helman:** What is the zinc contribution of that 80 to 100 mrem?
- Marble:** It varies from plant to plant how much they're putting in and how much iron they've got, but the range would be something like 15-30% or 40%, and in one case it was as high as 60%.
- Helman:** What do you expect the estimated annual cost of using zinc will be in the future, assuming that you get the price down as you are anticipating?
- Marble:** The current range would be something between \$200,000 per year and \$1 million per year, depending on the size of plant that you have. We think that we can get the price down to hopefully about half of where we are now. Depending on the size of your plant, that would be between \$100,000-\$500,000. It depends very significantly on the amount of iron you have in your feedwater. If you can also get the feedwater iron down, then you can significantly and dramatically drop your zinc costs.