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Unexpected Dose Increase at Cofrentes NPP during Refuelling Outage 14 (2003)

1.- Description of the dose rate increase in the drywell.

At the beginning of the outage 14 for refuelling at Cofrentes NPP (September 2003) elevated radiation fields were observed in the drywell. A three time increase was measured in contact with the surfaces of the reactor water recirculation system piping, the main source of the drywell general ambient dose rate. This behaviour is shown below in Figure 1.

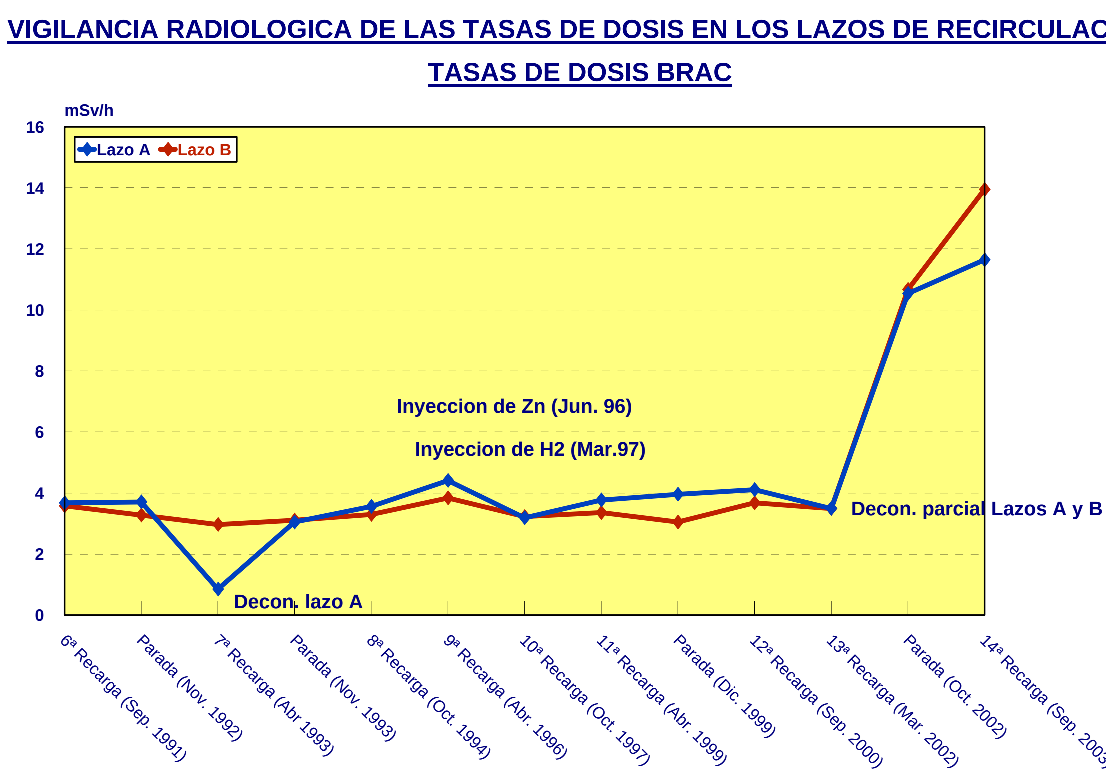

Figura 1. The historical BRAC point behaviour at Cofrentes

This increase in RFO 14 was uniform in nature (no hot spots) and was accompanied by a 2X increase in general area dose rates.

The surface specific activity for the isotopes deposited in the piping has increased significantly, and the isotopic composition (in percentage) over the last three refuel outages (RFO's 12, 13 and 14) is shown in Table 1.1 through Table 1.2 below. The radiation fields are dominated by the contribution of the Co-60 isotope accounting for approximately 85% of the dose in all three RFO measurements. The significant change between Cycles 14 and the previous two cycles is a 3X increase of the curies of Co-60 accompanied by similar increases in the percentage of Co-58 and Zn-65 on the pipes. These isotopes are normally associated with a chemical incorporation from the coolant into the corrosion film of stainless steel, the classic source the drywell shutdown dose rates in BWR's. The total curies of isotopes associated with insoluble crud deposits (Fe-59 and Mn-54) actually decreased at the end of Cycle 14, indicating that the observed increase in radiation levels was due only to the incorporation of soluble species into the structure of the corrosion films on the pipes and NOT due to increased crud deposition.

Note that Cr-51 makes up between 40 and 50% of the total isotopic curie inventory on the surface of the piping, although it contributes little to the dose rate. This isotopic concentration of Cr-51 is very similar to other plants using hydrogen addition and is an indicator that, under reducing conditions, chromium is incorporated to the corrosion film.

Table 1.1 Isotopic source of measured BRAC point radiation (corrected for decay to the first day of the outage).

Isotope	RFO12	RFO13	RFO14	% Change RFO 13 to 14
Cr-51 (microCi/cm^2)	13.8	21.7	56.4	159.9%
Mn-54 (microCi/cm^2)	1.9	1.8	1.5	-16.7%
Fe-59 (microCi/cm2)	1.0	1	0.8	-20.0%
Co-58 (microCi/cm2)	1.6	3	12.9	330.0%
Co-60 (microCi/cm2)	12.5	13.7	51.6	276.6%
Zn-65 (microCi/cm2)	2.6	2.7	8.5	214.8%
Sb-124 (microCi/cm2)	0.3	0.3	n/d	*

Table 1.2 Percentage contribution of the various isotopes to the dose rates at the measured BRAC points (corrected for decay to the first day of the outage).

% OF TOTAL DOSE RATE (CALC)		RFO13	RFO14
Cr-51	0.40	0.6	0.4
Mn-54	3.45	2.9	0.7
Fe-59	2.98	2.8	0.6
Co-58	3.41	5.8	7.0
Co-60	84.26	83.1	88.2
Zn-65	3.88	3.6	3.2
Sb-124	1.63	1.3	0.0
Total	100.0	100.0	100.0

2. Comparison of Cycle 14 with Previous Cycles

From a reactor water chemistry standpoint, there is nothing unusual in the reported chemistry statistics for Fuel Cycle 14 that would indicate any significant change in shut down dose rates during RFO 14.

The reactor water Co-60, both soluble and insoluble, were in their historical range and it was the case of all of the other isotopes. The only significant change is the reduction in copper (and soluble Zn-65) in the reactor water for cycles 13th and 14th, due to the removal of the source of copper and natural Zn, the Admiralty Brass condenser, and it's replacement with a condenser constructed of titanium in the RFO 12 (Sep-2000). Many other BWR's have made similar changes and have seen similar reductions in copper without the observed increase in shut down dose rates.

The summary of the feedwater cycle statistics for Fuel Cycles 12, 13 and 14 is that no parameter is significantly different than the previous 2 cycles except for the reduction in copper values (which is due to the condenser change out). Measurement of final feedwater cobalt levels shows that there was no systematic increase due to the power uprate and/or balance of plant equipment modifications.

3. Analysis of Possible Root Cause Scenarios

A root cause analysis for the dose rate increase has been performed taking into consideration the chemistry, materials and operations. Next is a summary of the main causes analyzed:

New cobalt sources introduced in the previous outage (RFO 13). New components installed in the balance of plant for the power uprate and new components installed in the core (control rod blades), and the increased flow in the balance of plant systems and the core, could have affected the cobalt input in the reactor. However, available data show no increase in elemental cobalt in the feedwater from Cycles 12 and 13 and also no significant increase in reactor water cobalt concentration. This is not the root cause of the phenomenon.

Crud Storm Depositing Fuel Deposits on Out of Core Surfaces. There is no evidence of a crud storm occurring during operation or at either the mid-cycle or end of cycle shut downs. There was no increase in insoluble reactor water activity during operation and only a slight increase during the EOC 14 shutdown. If any thing, the gamma scan information shows a *decrease* in insoluble deposition on the piping compared to the previous Cycle 13. Again, this can be rule out as a cause of the 3X dose increase.

Hydrogen Cycling. It is recommended to minimize feedwater hydrogen cycling to limit shutdown dose rate effects. There was slightly more cycling between low and nominal hydrogen levels in Cycle 14 vs. 13 (8 vs. 6), but there were more trips in Cycle 13 than 14. Trips are usually considered to be more damaging than rate changes. Cofrentes is among the best in the BWR fleet in this topic. Again, this cause can be ruled out.

RFO 13 Piping Decontamination Causing Rapid Co-60 Uptake. A partial decontamination of the recirculation loops was accomplished in RFO 13. Actually, the majority of the recirculation system piping was not decontaminated during RFO 13 due to technical problems and in fact saw no decontamination solvents of any kind. The areas that were decontaminated only recontaminated to 90 to 130% of their pre-decontaminated values, which is the usual behaviour two years after decontamination. Therefore, the decontamination can be ruled out as the root cause on this basis.

Low-zinc HWC Effect. Plants that have implemented moderate HWC that were not injecting zinc have seen large increases in dose rates at the next refuelling outage. The phenomenon occurs because the low ECP's are established on the surface of the recirculation piping and cause a restructuring of the stainless steel corrosion film oxide from a hematite structure to a spinel structure stable at the low ECP's of HWC. The spinel structure has a much higher capacity for cobalt (and Co-60) in its lattice than does hematite, thus there is a significant jump in Co-60 concentration in the film and a resulting increase in shut down dose rates. When there is sufficient zinc in the water, zinc will preferentially exclude the cobalt (and Co-60) from the favored sites and the net result is no change in shut down dose rates. Experience has shown that a value of 5 to 10 ppb is sufficient to mitigate the HWC dose rate effect, and since Cofrentes has been at 5 ppb zinc in reactor water since mid 1996, it can be rule out low reactor water zinc as a root cause of the 3X dose increase. Nevertheless, it is probable that the ECP on the piping at Cofrentes decreased significantly during Cycle 14 and may have reached the range of restructuring.

Cooper effect in the ECP. The current hypothesis is that the root cause for the Cofrentes dose rate 3X increase might be the effect that Cu has played in the ECP changes and the subsequent restructuring of corrosion films under hydrogen water chemistry. At Cofrentes plant, since the initial operation under HWC (Feb-97) the ECP at the piping has been controlled by the presence of Cu species in the oxide layer. At 1 ppm H2 injection in FFW, the recirculation piping ECP was about +50 mV(SHE) in spite of a reducing environment in the bulk water .

During the cycle 13^{th} (first without the Admiralty Condenser) the piping ECP was reduced very slowly showing a value of -100 mV(SHE) after 18 months operation.
On cycle 14^{th} the ECP is assumed to have decreased more due to Cu depletion in the film. As the ECP is established at some value more positive than the normal HWC potential of –450 mV(SHE), the oxide on the stainless steel restructures. The resulting oxide is thicker than that formed at lower potentials and thus incorporates more Co-60, Co-59 and Zn-65 into it's lattice. A factor of X thicker means that the resulting shut down dose rate is X times higher. The cause of the thicker oxide is debatable. It may be that the spinel oxide formed at the higher ECP is thicker or it may be that the copper impurity promotes a defect structure that results in a thicker film. In any event, the thicker corrosion film with its higher incorporated Co-60 content is the most likely the root cause of the higher dose rates in copper contaminated BWR's.
Another possibility is that the film is no thicker but the copper presence induces a defect structure that allows the incorporation of X more interstitials than a "normal" film of the same thickness. In both cases, the factor of "X" is due to the effect of copper on film properties

4.- Summary

During the RFO 14 in September 2003, an unexpected dose rate increase in the Drywell was experienced. This phenomenon caused that the initial estimate of the collective dose for the outage was changed from 1,8 Sv-p to 2,8 Sv-p. The final collective dose of the RFO 14 was 2,6 Sv-p. The dose rate increase was 3X in contact with the recirculation loops and in general areas was a 2X increase, from the historical values.

The current hypothesis is that the elevated shut down dose rate observed in the Drywell during the RFO 14 were due to corrosion film restructuring process in the piping. This process has occurred in other BWR's after the implementation of moderate HWC and the attainment of ECP values below –230 mV(SHE). At Cofrentes, the effect occurred early in Cycle 14 when the ECP values finally dropped as copper concentration decreased to low levels. The resulting restructured corrosion films are believed to have grown to a higher thickness than normal because of the effect of copper compounds deposited on and in the legacy oxide. The resulting thicker films incorporated a proportional increased amount of Co-60, Zn-65, Mn-54, and Cr-51 resulting in significantly higher dose rates.

Plant chemistry control during Cycle 14 was excellent and no change in the operation of the plant during Cycle 14 could have prevented the observed phenomenon from occurring.

UNEXPECTED DOSE RATE INCREASE AT COFRENTES NPP, SPAIN (BWR-1100MWe) IN THE DRYWELL DURING REFUELLING OUTAGE 14 (2003)

The Problem Observed During RFO 14:

- **Increase in average BRAC contact dose rates of ~3X**
- **Increase in drywell general dose rates of ~2X in lower areas**
- **Uniform increases…no hot spots**
- **Final outage collective dose 2,6 Sv-p. Previous estimate 1,8 Sv-p**

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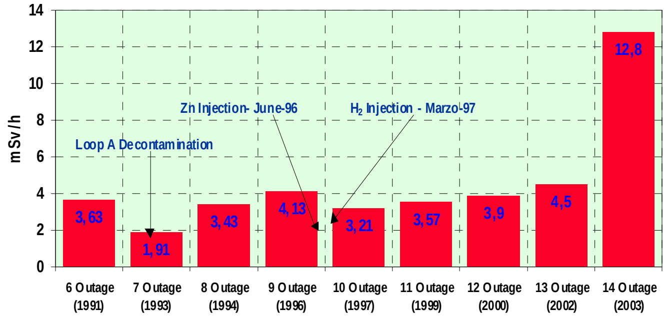
Historical Evolution of the BRAC Dose Rate in the Drywell



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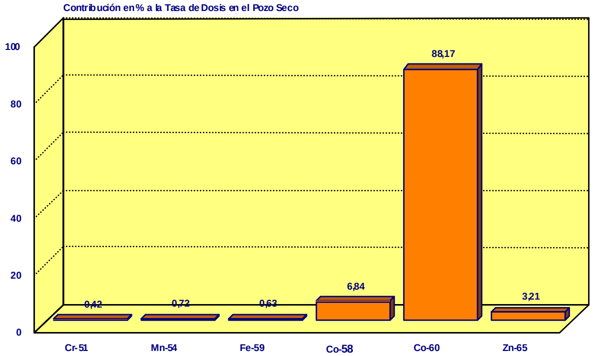
Isotopic Contribution to the Drywell Dose Rate



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Summary of Chemistry Data

- Reactor water cobalt-60 constant over past 3 cycles
  Higher than average for the fleet
- Measured feedwater cobalt also constant
- Soluble cobalt-60 incorporation in corrosion film increased in cycle 14, also Zn-65 and Mn-54
- Reactor water copper decreased Cycle 12 to Cycle 14
- Conductivity constant and typical of fleet apart from transient in Cycle 13
- Good control of hydrogen (with less shutdowns and more turn downs in Cycle 14)
- Reactor water zinc slightly lower than fleet average
- ECP decreased slightly Cycle 12 to 13 but no data for Cycle 14

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Root Cause Scenarios That Can Be Ruled Out (I)

- **New Sources of Cobalt**
  No increase in either soluble or insoluble Co-60 or Co-58
- **BOP Modifications during RFO 13**
  No significant change in composition of the final feedwater including elemental cobalt…except for Cu reduction
- **Power Uprate (from 104% to 110%)**
  No increase in either soluble or insoluble Co-60 or Co-59
  Decrease in RW insoluble Fe and Mn…so no flow erosion of deposits
- **Crud Storm Moves Fuel Deposits to Out of Core Surfaces**
  Isotopic composition of dose source unchanged except for *decrease* in curd
- **Hydrogen Cycling**
  No real significant change form Cycle 13 to 14…operation equal to best in BWR Fleet

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Root Cause Scenarios That Can Be Ruled Out (II)

- **Impurity Transient (s)**
  Lube oil impurity transient in Cycle 13 (> 10 µS/cm) , nothing > 0.27 µS/cm in Cycle 14
- **Chronic Impurity Ingress**
  Cycle median conductivity of 0.0997 µS /cm and identification of all small conductivity spikes eliminates this concern
- **RFO 13 Piping Decon Caused Rapid Co-60 Uptake**
  Only small portion of system decontaminated and that area recontaminated to values of only 80 to 90% of EOC13 values

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BEST ESTIMATE ROOT CAUSE SCENARIO

- The ECP of stainless steel surfaces dropped to lower values early in Cycle 14 when coolant copper concentrations reached a very low level
- Restructuring of the stainless steel corrosion films occurred at this lower potential
- The new corrosion film incorporated more Co-60 as the film restructured and resulted in a significant increase (~3X) of the curie content of Co-60, Co-58 and Zn-65.

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CONCLUSIONS

- The elevated shut down dose rates seen during the 14th outage were due to corrosion film restructuring process
- The effect occurred suddenly when ECP dropped as copper concentration decreased to a low level.
- The copper concentration decreased due to the previous change of the main condenser from copper to titanium.
- **No change in the operation of the plant could have prevented the phenomenon from occurring**

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ACTION PLAN

To Control Rate of Radiation Buildup during Cycle 15
Minimize hydrogen turn-downs
Increase reactor water zinc to 6-7ppb
Operate with maximum RWCU capacity

To Reduce Radiation Fields at next Refueling Outage
Chemical decontamination of the recirculation loops and reactor clean-up system

Longer Term Action
Cobalt reduction campaign to reduce fields over a 10 year period
Enhance dry well shielding

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