PWROG
PWR Owners Group

Program Management Office
4350 Northern Pike
Monroeville, Pennsylvania 15146

WCAP-16530-NP, Rev. 0 (Non-Proprietary)
Project No. 694

April 3, 2007

OG-07-129

U.S. Nuclear Regulatory Commission
Document Control Desk
Washington, DC 20555-0001

Subject: Pressurized Water Reactor Owners Group
Responses to the NRC Second Set of Requests for Additional Information (RAI's) on WCAP-16530, "Evaluation of Chemical Effects in Containment Sump Fluids to Support GSI-191"

References:

1. NRC letter from Sean E. Peters of NRR to Gordon Bischoff of PWROG dated October 4, 2006, "Request for Additional Information RE: Westinghouse Owners Group (WOG) Topical Report WCAP-16530-NP, 'Evaluation of Post Accident Chemical Effects in Containment Sump Fluids to Support GSI-191' (TAC NO. MD1119)."
2. WCAP-16530-NP, "Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191," February 2006.
3. PA-SEE-0275, Revision 1, "Method for Evaluating Post-Accident Chemical Effects in Containment Sump Fluids," June 2006.
4. PWR Owners Group letter, OG-06-387, "Pressurized Water Reactor Owners Group: Responses to the NRC Request for Additional Information (RAI) on WCAP-16530, 'Evaluation of Chemical Effects in Containment Sump Fluids to Support GSI-191'," November 21, 2006.
5. NRC letter from Sean E. Peters of NRR to Gordon Bischoff of PWROG dated March 23, 2007, "Request for Additional Information RE: Pressurized Water Reactor Owners Group Topical Report (TR) WCAP-16530-NP,'Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191' (TAC NO. MD1119)."

The Nuclear Regulatory Commission (NRC) requested additional information via letter dated October 4, 2006 (Reference 1) to support the review of the Westinghouse topical report, WCAP-16530-NP (Reference 2). The topical report was generated to support the Pressurized Water Reactor Owners Group (PWROG) Project Authorization (Reference 3). Responses to the NRC requests for additional information were transmitted in Reference 4.

Following receipt of our responses, the NRC issued a second set of RAIs dated March 23, 2007 (Reference 5). Attachment 1 provides the responses to this new set of RAI's. Enclosures 1-4 supply supporting information to respond to RAI #2 within this new set of RAI's.

D048

If you have any questions concerning this matter, please feel free to call Reginald Dulaney at 412-374-6549.

Sincerely yours,

for

Frederick P. "Ted" Schiffley, II, Chairman
Pressurized Water Reactor Owners Group

FPS:RRD:mjl

Attachment: 1. Responses to 8 additional questions from previous RAI responses

Enclosures:
1. Data Sheets from test laboratories documenting leachable chlorides from epoxy coatings; 21 pages,
2. Letter from PPG/Keeler and Long to John Gisclon date July 16, 2004 documenting exchange with NRC on testing for leachable chlorides,
3. Letter from Analytical Consulting Technology Inc dated July 12, 2004 identifying the interpretation of the leaching test data used in response to RAI #2 is correct.
4. F. Dacquait et.al. "Corrosion Product Transfer in French PWRs During Shutdown," SFEN-Chimie 2002 Conference on Water Chemistry in Nuclear Reactor Systems, Avignon, France (2002).

cc: Systems & Equipment Engineering Subcommittee
Steering Committee
S. Peters - NRC
W. Rinkacs - Westinghouse
A. Lane - Westinghouse

Attachment 1

RAI #1

Your response to RAI #10 appeared to address the multi-part question except for the last part. Please respond to the following questions. Is it plausible for a containment pool at higher pH (e.g., 9 pH) to move a pH unit or more lower due to formation of nitric or hydrochloric acid after an accident? If so, why was no testing performed by adjusting pH from a higher value to a lower value?

RAI #1 Response

It is possible for minor perturbations to occur in the containment pool pH due to acid generation; however, utilities maintain a sufficient quantity of buffer in order to minimize this effect. The intention of the buffer is to maintain the pH of the sump solution. Once the pH of the sump solution has reached 9.0, the solution would be adequately buffered, i.e., sufficient buffer would be present, to account for any acid generation effects on the ultimate pH.

Testing a decrease in the pH would only provide information regarding the solubility of the precipitate. The model conservatively assumes 100% precipitation of the dissolved aluminum. Precipitation of aluminum due to downward shifts in the pH is fully included in the 100% precipitation assumption, so no testing of a downward adjustment in pH is necessary.

RAI #2

The response to RAI#13 indicated that data supporting a conclusion that insignificant chloride leaches from coatings was previously provided to the NRC and a reference was provided to a facsimile transmitted from the NRC staff to a coatings industry representative. The referenced data sheets from Keeler and Long/PPG Industries and Carboline Company, however, do not provide sufficient detail to fully respond to RAI#13. For instance, RAI#13 requested an estimate of chloride in the post-LOCA containment pool from leaching of containment materials (e.g., coatings).

Note: this topic was discussed during the February 8, 2007 public meeting on GSI-191. The PWR Owners Group indicated that they would respond to staff questions about potential interactions between coatings and chemical effects. If a separate response is provided to the NRC that addresses the question above, it will be sufficient to provide a reference to that response instead of repeating the information in the RAI response.

RAI #2 Response

The response to RAI#13 indicated that data supporting a conclusion that insignificant chloride leaches from coatings was previously provided to the NRC and a reference was provided to a facsimile transmitted from the NRC staff to a coatings industry representative. The referenced data sheets from Keeler and Long/PPG Industries and Carboline Company, however, do not provide sufficient detail to fully respond to RAI#13. For instance, RAI#13 requested an estimate of chloride in the post-LOCA containment pool from leaching of containment materials (e.g., coatings).

RESPONSE:

The following items are submitted in response to this RAI related to leachable chlorides in Epoxy coatings:

A summary of the translation of the quantity of leachable chlorides to a concentration in a typical sump volume, and,

Enclosure 1.	Data Sheets from test laboratories documenting leachable chlorides from epoxy coatings; 21 pages,
Enclosure 2.	Letter from PPG/Keeler and Long to John Gisclon date July 16, 2004 documenting exchange with NRC on testing for leachable chlorides,
Enclosure 3.	Letter from Analytical Consulting Technology Inc dated July 12, 2004 identifying the interpretation of the leaching test data used in the response presented below is correct.
Enclosure 4.	F. Dacquait et.al. "Corrosion Product Transfer in French PWRs During Shutdown," SFEN-Chimie 2002 Conference on Water Chemistry in Nuclear Reactor Systems, Avignon, France (2002).

The information in this response and the three enclosures to this letter provide leachable information for epoxy coatings from test data, a calculation of the result of leaching of chlorides from epoxy on resulting chloride concentration in the recirculation sump fluid, and supporting information from both a coatings vendor and a test lab.

Presented below is a summary of the translation of the quantity of leachable chlorides to a concentration in a typical sump volume.

ASSUMPTIONS:

1. 1250 cubic feet of coating inside a large dry containment; typical for a 4–loop PWR (10 mils thickness ~ 1,500,000 sq ft surface area)
2. 1% of all coating inside containment is submerged and subject to leaching (12.5 cubic feet – coatings on containment floor and coatings debris)
3. 80,000 cubic feet of coolant in sump (typical for 3-loop PWR – from the ICET test plan)
4. All leachable material from the submerged coatings is deposited in containment sump inventory.
5. 100 ppm leachable material – from letter from letter from Analytical Consulting Technology Inc dated July 12, 2004

CALCULATING THE VOLUMETRIC CONCENTRATION of LEACHABLE CHLORINE:

Equation used:

$$Volumetric\ Concentration_{Leachable\ Chlorides,\ Coatings} = \frac{Coatings\ Volume \times Leachable\ Fraction}{Volume\ of\ \mathrm{Re}circulation\ Fluid\ Inventory\ in\ Sump}$$

$$Volumetric\ Concentration_{Leachable\ Chlorides,\ Coatings} = \frac{12.5\ ft^3 \times (100\ /\ 1{,}000{,}000)}{80{,}000\ ft^3}$$

$$Volumetric\ Concentration_{Leachable\ Chlorides,\ Coatings} = 15.6/1{,}000{,}000{,}000 = 15.6\ ppb$$

The volumetric concentration value calculated above, 15.6 ppb (parts per billion) is conservative as it maximizes the coating volume (large dry 4-loop PWR) and minimizes the water volume (3-loop PWR).

Even if one assumes all the epoxy coating in the calculation is subject to leaching, and all of the leachable material in the epoxy coatings was deposited in the containment sump inventory, the resulting concentration is only 1.56 ppm (parts per million). This value is very small and is considered insignificant as a chemical reactant.

RAI #3

The reference provided in response to RAI #14, "The Chemistry of Fuel Crud Deposits and Its Effect on AOA (Axial Offset Anomaly) in PWR Plants," provides the basis for the response that 12 to 25 kilograms of crud material represents the upper bound of what could be released during a large-break LOCA. Table 3 in the above reference, under the Polley/Pick Plant Analysis column, indicates a total oxide on stainless steel in the range of 2 to 11 kilograms. Should this value be added to the 12 to 25 kilograms oxide on Inconel to estimate the total amount of corrosion product that could be released from the internal surfaces of the reactor coolant system during a LOCA? Discuss how these oxides may affect the sump strainer. The previous response to RAI #15 indicated that this particulate will be dense and tend to settle. Estimate the percentage of these oxides that may be transported to the strainer and the possible impact on head loss.

RAI #3 Response

It would be reasonable to add the 11 kg of stainless steel oxide to the 25 kg of Inconel oxide mentioned in the reference to produce a bounding oxide mass of 36 kg in the Reactor Coolant System (RCS). This does not alter our conclusion that RCS corrosion product release will have no effect on sump screen performance.

Another reference[1] has been provided, to shed light on the fraction of the oxide that might be released and transported. Over 80 shutdowns were examined, and the amount of material removed from piping surfaces during a shutdown never exceeded 20% of the total. A 20% release was the minimum detection limit for the measurement. Approximately 75 percent of the particles had a particle size greater than 10 microns. Thus, at most 36 x 0.2 = 7.2 kg would be expected to be released. The particle size would be quite large, so much less than this quantity would be transported to the strainers. Based on a density of 3.8 to 6.4 g/cm^3, this equates to a maximum 0.07 ft^3 of oxide, which is only 0.84 ppm for an assumed sump volume of 80,000 ft^3. Due to the small quantity of material which makes it to the strainers, the head loss impact due to oxides would be negligible.

Reference to RAI #3 response:

1. F. Dacquait et.al. "Corrosion Product Transfer in French PWRs During Shutdown," SFEN-Chimie 2002 Conference on Water Chemistry in Nuclear Reactor Systems, Avignon, France (2002).

RAI #4

RAI#15 addressed potential effects from the release of radioactive species during the LOCA and their subsequent affect on the containment pool chemistry. Discuss the possible effects from radiolysis of water within the containment pool and reactor vessel that could modify the reduction potential (i.e., redox potential) of the water depending on the relative amounts of H2, O2 and H2O2 produced. This could potentially alter corrosion rates, chemical speciation and the solubility of compounds. Discuss the basis for not needing to account for radiological effects in the chemical model.

RAI #4 Response

Per the reference provided below, the concentration of H_2O_2 present in the reactor coolant during shutdown achieves a maximum concentration of 1 to 12 ppm about 24 to 48 hours after establishing acid-oxidizing conditions, and is on the order of 2 ppm for the balance of shutdown. This represents a good high estimate for the H_2O_2 concentration under post-LOCA conditions. Consideration of the dilution resulting from flood up to the sump volume from the reactor coolant system volume results in a maximum level of less than 1 ppm.

Hydrogen (H_2) has a similar radiolytic yield to H_2O_2 and thus similar concentrations would be expected. The quantity of hydrogen produced from radiolysis would be negligible when compared to hydrogen production from corrosion of aluminum.

As discussed above, the quantities of hydrogen (H_2) and hydrogen peroxide (H_2O_2) produced from radiolysis of water are low and would not be present in sufficient concentration to measurably influence material release rates. Likewise, the quantity of O_2 produced from breakdown of radiolytically-produced H_2O_2 is low and is negligible when compared to atmospheric oxygen.

Reference to RAI #4 response:

1. EPRI Report 11002884, Rev. 6, *Pressurized Water Reactor Primary Water Chemistry Guidelines, Volume 1, Appendix E*, EPRI, Palo Alto, CA, 2006.

RAI #5

The response to RAI #16 indicated that the dissolution behavior of concrete is expected to be consistent between U.S. PWR sites. The response appeared to address the question except for the following. Please provide the composition and applicable specifications for the concrete tested. Was the concrete tested representative of concrete in the U.S. PWR plants?

RAI #5 Response

The chemical constituents of the sample were determined by SEM-EDS and are available in the WCAP. The base chemical constituents available for dissolution are not significantly affected by different preparations of concrete. The model is concerned with the dissolution of the chemical constituents. In this respect, the dissolution behavior of the concrete sample tested would be representative of concrete in US PWR plants.

From discussions with a representative of the Portland Cement Association, the significant differences in terms of chemical makeup between any concrete mixes rated at differing compressive strengths are (1) the type of Portland cement used, (2) the nature of the coarse aggregate, and (3) the cement-to-water ratio.

It is known that the sample analyzed was 4000-psi concrete that incorporated ASTM C-150 Type II Portland cement and coarse aggregate in compliance to ASTM C-33, and was cured in excess of 28 days. These specifications also apply to typical 6000-psi concrete used in containment. Thus, the sample is representative of concrete used in containment.

The sample itself was prepared such that the coarse aggregate was not pulverized with the remainder of the sample, and only the crushed "matrix" material was used in the dissolution testing. Per the Portland Cement Association, the overwhelming difference in the pulverized matrix material between 4000-psi and 6000-psi concrete mixes is the cement-to-water ratio employed in the original mixture and hence, once cured, pulverized matrix samples from 4000-psi and 6000-psi concrete would be very similar with respect to their chemical makeup. Thus, the sample is representative of concrete used in containment.

Moreover, a comparison of detailed concrete specifications is deemed unnecessary with respect to dissolution testing because testing of the chemical constituents of concrete – with respect to dissolution in the sump fluid - is dependent on the exposed surface area. Applicable specifications dealing with structural characteristics are intended to prevent concrete corrosion by precluding increased surface area (via cracks) for the sump solution to attack the concrete medium. As mentioned in WCAP-15630-NP, the concrete dissolution rate is determined by the exposed surface area of the concrete. By grinding up the concrete sample, high surface areas of the chemical constituents are in contact with the sump solution, accelerating the dissolution rate

relative to in-situ concrete in containment, and the model does not scale the rate of dissolution to the account for the lower surface area actually present in containment.

RAI #6

In the October 4th NRC letter, RAI #23 and RAI #25 were related to WCAP-16530-NP Equation 6-1 and Equation 6-2 aluminum release rates, respectively. In particular, the staff questioned whether there might be a better fit to the aluminum corrosion rate data. In response to RAI #24, a corrected value was provided for the "B" coefficient in Equation 6-1 and it was stated that Equation 6-1 was not used in the chemical model. RAI #24 discussed the corrosion of aluminum during the Integrated Chemical Effect Test 1 (ICET 1), that appeared to occur in stages. The initial ICET 1 corrosion rate (i.e., during the initial 10 days of testing) appears to be approximately 30 mg/m2-min. Following an initial linear rate of aluminum dissolution, the corrosion rate appears to decrease and eventually the dissolved aluminum measurements seem to indicate some type of aluminum coupon passivation. Please provide a table that evaluates the following coefficients (relative to Equation 6-2) for fit to the WCAP data and for the initial 15 days of ICET 1. Discuss whether the coefficients in Equation 6-2 or the coefficients below would be more appropriate for the aluminum release rate in the chemical model.

a = 12.950
b = 0.540
c = -4.467
d = 0.014
e = -1.413

RAI #6 Response

The coefficients as provided by the NRC in RAI #6 for modeling the aluminum corrosion do provide a reasonable fit to the "bench top" data. The table below shows the comparison for the WCAP bench top data. However, the coefficients used in the WCAP were introduced to improve the prediction for a data set that included aluminum release rate measurements from ICET #1 as well as measurements from Oak Ridge (CR-6873) and previous Westinghouse work (WCAP-7153A). The fit to the expanded data set was shown in WCAP-16530-NP.

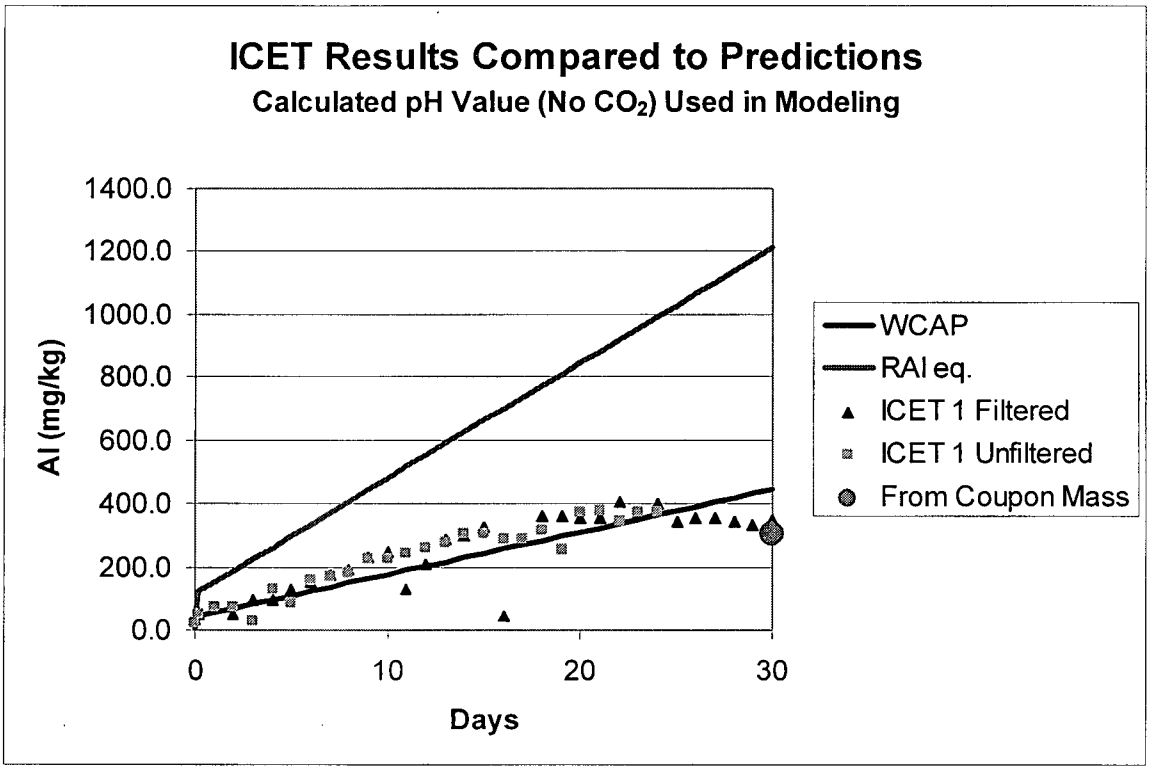
Temp	pHa	Meas. log RR	WCAP Predicted log RR	RAI Predicted log RR
190	4.1	0.968	0.79	0.93
190	8	1.650	1.20	1.71
190	12	3.001	3.03	2.95
265	4.1	1.952	1.92	1.97
265	8	2.597	2.13	2.52
265	12	3.524	3.76	3.52

RR = release rate in mg/m2-min

A more detailed look at the ICET 1 results and the prediction from each model is shown below. A pH of 10 was used for ICET 1 pH. This was the pH of the solution predicted for no CO_2

adsorption from the atmosphere. This pH was used rather that the measured pH values, just the same as for the WCAP-16530-NP bench top testing. This was done to be consistent with post LOCA pH predictions used in the industry, which also do not include predictions from CO_2 adsorption from the containment atmosphere. The predictions in the figure also included the corrosion from the initial spray phase, where the pH of the spray solution was assumed to be 10.

The WCAP-16530-NP prediction is more representative than that made with the coefficients suggested in this RAI.



RAI #7

The response to RAI #47 talks about the one hour settling volume of surrogate precipitates. Please address the final part of RAI #47, i.e., discuss how consistency in surrogate settling data interpretation and settling test technique are maintained between these tests and those that may be performed by strainer vendors. In addition, discuss whether any changes have been made or are planning to be made to the surrogate settlement acceptance criteria considering the recent observations made at a vendor facility that showed aged surrogate met the settlement criteria but apparently underwent physical changes that affected head loss.

RAI #7 Response

The settling rate criteria for the aluminum precipitates provided in the WCAP will be revised to require higher settled volumes during the one hour test to provide added assurance that the surrogates behave in a prototypical manner. Narrowing the band of the settling rate criteria will

eliminate the need for the shelf life criteria and address any concerns regarding appropriate use of the surrogates. The settling rate test guidance in the WCAP is intended to provide consistency between strainer vendors.

RAI #8

The response to several RAI's (e.g., RAI #29, RAI #43) indicate that the surrogate materials were chosen to be representative of the settling and filtration characteristics of precipitates that may form in prototypical plant conditions. Therefore, exact chemical identification of the precipitates that formed during the WCAP-16530-NP testing was not necessary. In the event that future tests are performed to support removing some of the model's conservative assumptions, for example that all dissolved material precipitates, it is important to understand the nature of the precipitate (e.g., boron adsorption affects the structure of amorphous aluminum hydroxide which affects solubility). Therefore, discuss if you have plans to more fully characterize precipitate chemistry to support future model refinements.

RAI #8 Response

There are currently no plans to further characterize surrogate materials as part of the effort presented in WCAP-16530-NP. Evaluation of the need for additional characterization of the surrogates to support other work will be performed as part those efforts. For example, additional characterization of the surrogates may be required to support the determination of solubility limits as part of the plant-specific inputs effort under the PWROG program, PA-SEE-0354.

Enclosure 1: Data Sheets from Test Laboratories Documenting Leachable Chlorides from Epoxy Coatings

Dry Film A+B

ANALYTICAL
CONSULTING
TECHNOLOGY, INC.

80 Turnpike Drive, Middlebury, CT 06762 • (203) 598-0040

Certified Laboratory

US EPA CT-021
CT PH-0518
RI A026

PPG Architectural Finishes, Inc
Lynn O'Brien
P.O. Box 460
Watertown,, CT 06795

Report Date: 08/25/1999

ACT Number: 1999080098 - 1 Sample Date: 08/07/1999 Date Received: 08/07/1999
Sample Type: Grab Sample Time: Project number
Collected by: Client Sample Matrix: Material
Location:
Sample ID:KL65487107

Laboratory Test	Result	Units	Method	Analysis Date	Analyst
Total Halogens	129.64	ppm	ASTM D1179	08/22/1999 12:00:00 AM	SD
Water Leachables					
Chloride	126.8	ppm	Ion Chrom.	08/21/1999 11:39:00 AM	JC
Sulfate	34.37	ppm	Ion Chrom.	08/21/1999 11:39:00 AM	JC
Total Organic Halides (TOX)	845	ppb	SW846 9020	08/23/1999 12:00:00 AM	SD

ACT Number: 1999080098 - 2 Sample Date: 08/07/1999 Date Received: 08/07/1999
Sample Type: Grab Sample Time: Project number
Collected by: Client Sample Matrix: Material
Location:
Sample ID:KLE18591

Laboratory Test	Result	Units	Method	Analysis Date	Analyst
Total Halogens	67.42	ppm	ASTM D1179	08/22/1999 12:00:00 AM	SD
Water Leachables					
Chloride	66.65	ppm	Ion Chrom.	08/21/1999 11:52:00 AM	JC
Sulfate	78.77	ppm	Ion Chrom.	08/21/1999 11:52:00 AM	JC
Total Organic Halides (TOX)	772	ppb	SW846 9020	08/22/1999 12:00:00 AM	SD

ACT Number: 1999080098 - 3 Sample Date: 08/07/1999 Date Received: 08/07/1999
Sample Type: Grab Sample Time: Project number
Collected by: Client Sample Matrix: Material
Location:
Sample ID:KLD17938

Laboratory Test	Result	Units	Method	Analysis Date	Analyst

Water Leach performed using ASTM F1277 procedure. Cured coating cut into 1/4-1/2" pieces and leached with 90 ml DI + 10 ml 0.1N NaOH @95 degrees C for 4 hrs.

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Certified Laboratory

US EPA CT-021
CT PH-0518
RI A028

Page 2

PPG Architectural Finishes, Inc
Lynn O'Brien
P.O. Box 460
Watertown, CT 06795

Report Date: 06/25/1999

ACT Number: 1999060098 - 3
Sample Type: Grab
Collected by: Client
Location:
Sample ID: KLD17938

Sample Date: 06/07/1999
Sample Time:

Date Received: 06/07/1999
Project number
Sample Matrix: Material

Laboratory Test	Result	Units	Method	Analysis Date	Analyst
Total Halogens	628.88	ppm	ASTM D1179	06/22/1999 12:00:00 AM	SD
Water Leachables					
Chloride	625.10	ppm	Ion Chrom.	06/21/1999 01:10:00 PM	JC
Sulfate	43.47	ppm	Ion Chrom.	06/21/1999 12:38:00 PM	JC
Total Organic Halides (TOX)	1563	ppb	SW846 9020	06/22/1999 12:00:00 AM	SD

1999060098

For Analytical Consulting Technology, Inc. Laboratory Director

Water Leach performed using ASTM F1277 procedure. Cured coating cut into 1/4-1/2" pieces and leached with 90 ml DI + 10 ml 0.1N NaOH @95 degrees C. Analysis: Environmental Analysis

ANALYTICAL
CONSULTING
TECHNOLOGY, INC.

127 Echo Lake Road, Watertown, CT 06795 • (203) 274-1290

Keeler & Long
James Damery
Box 460, 856 Echo Lake Rd
Watertown CT 06795

Laboratory Report Number: 926589 REPORT DATE: 10/23/92

SAMPLE IDENTIFICATION: Kolor-Poxy Primer #3200
SAMPLE DATE: 09/30/92 DATE RECEIVED: 09/30/92

PARAMETER	METHOD	DATE ANALYZED	RESULT	UNITS	ANALYST	TIM
BROMINE		10/21/92	<10	ppm	BCC	
CADMIUM, TOTAL	SW846-7130	10/15/92	0.13	ppm	S.D	
CHLORINE		10/21/92	720	ppm	BCC	
COPPER, TOTAL	SW846-7210	10/15/92	1.25	ppm	S.D	
FLUORINE		10/21/92	107	ppm	BCC	
IODINE		10/21/92	<10	ppm	BCC	
LEAD, TOTAL	SW846-7421	10/16/92	3.75	ppm	P.C	
MERCURY, TOTAL	SW846-7471	10/08/92	<1.0	ppm	S.D	
PHOSPHORUS, TOTAL	SM4500P-D	10/06/92	50.62	ppm	J.F	
SULFUR		10/21/92	<50	ppm	BCC	
TIN, TOTAL	SW846-7870	10/15/92	<1.25	ppm	S.D	
ZINC, TOTAL	SW846-7950	10/15/92	3.25	ppm	S.D	

For Analytical Consulting Technology, Inc

Certified Laboratory CT PH0518

TESTING DEPARTMENT ABSTRACT REPORT

TESTING PROJECT: 02750 **DATE:** March 19, 1991

REPORT #: One **TIME:** **DATE OF GRADING:** 12/11-20/90

TOTAL DESIGN TEST DURATION: **REQUESTED BY:** Jerry Arnold

TITLE: Carboline 801 Chemical Analysis

REFERENCE: Arkansas Nuclear; Doc. Acc. 08211

PURPOSE: To qualify Carboline 801 from a chemical standpoint for use in containment.

SYSTEMS: Carboline 801 (free films)

EXPOSURE: Chemical Analysis:

1. Toxicity Characteristic Leaching Procedure (TCLP) for Barium.
   Permissible Barium regulatory level is 100 mg/l (per EPA toxicity characteristic rule for hazardous wastes).
2. Leachable chloride
   Permissible level is 100 ppm max. (per Stone & Webster)
3. ASTM D808 total halogens
   Permissible level is 450 ppm max. (per General Electric)
4. ASTM D1179 fluorides
   Permissible level is 300 ppm (per General Electric)
5. ASTM D129 total sulfur
   Permissible level (active and inactive sulfur) is 1,000 ppm max. (per Stone & Webster)
   Chemical analysis was done at SCI Environmental, Inc. Their report is attached.

CONCLUSIONS:

1. Leachable Barium from Carboline 801 (7.6 mg/l) when tested in accordance with TCLP meets regulatory requirements under toxicity characteristic rule (less than 100 mg/l).
2. Carboline 801 meets requirements established by General Electric and Stone & Webster for nuclear industry for leachable chloride, total halogens, fluorides and sulfur.

Carl L. Braun
Carl Braun
Advanced Laboratory Technician
Testing Department

Yuly Korobov
Yuly Korobov
Supervisor
Testing Department

S.L. Steinberg/M.D. Tellor/J.F. Montle/P.S. Litzsinger/ C.S. Benson/
E.W. Skiles/L.S. Salem/S.J. Harrison/Group Leaders

From the Carboline Research & Development Laboratory

The technical data furnished are true and accurate to the best of our knowledge. However, no guarantee of accuracy is given or implied.

carboline
350 HANLEY INDUSTRIAL CT., ST. LOUIS, MO 63144

SCI ENVIRONMENTAL, INC. LABORATORY SERVICES DIVISION

DATA SUMMARY

Client: Carboline Company
350 Hanley Industrial Ct.
St. Louis, Missouri 63144-1599

Project No.: 90-1278-1
Sample Matrix: Paint

Date Sampled: 12/10/90
Date Received: 12/11/90
Date Analyzed: 12/11-20/90

Sampled By: Client
Sample Location: Project #02750
Carboline 801: Part A, Batch #9J9055M
Part B, Batch #0C9427M
Carboline Thinner #4, Batch #9F3625M

SCIE Sample Number: 3935

Sample Identity: Carboline 801

TCLP Barium (ppm as mg/l)*	Leachable Chloride (ppm as mg/kg)**	ASTM D 808 Total Halogens (ppm as mg/kg)**	ASTM D 1179 Fluorides (ppm as mg/kg)**	ASTM D 129 Sulfur (ppm as mg/kg)**
7.6***	< 4.0****	176	24	868

* ppm as mg/l = parts per million as milligrams per liter

** ppm as mg/kg = parts per million as milligrams per kilogram

*** TCLP leachate was 7.6 ppm as mg/l which would correspond to 152 ppm as mg/kg leachable Barium by weight. The solid paint sample was broken to pieces passable through a 9.5 mm sieve to perform TCLP.

**** Approximately 10 grams of sample was leached into 50 mls deionized water at 212 degrees fahrenheit for 1 hour. Less than 4.0 mg of chloride per 1 kg of sample was leachable. The leachate from the analysis was < 1.0 mg/l which corresponds to 4.0 mg/kg leachable chloride by weight.

Submitted By:

1/2/91
Date

Elizabeth M. Cohoon
Elizabeth M. Cohoon
Laboratory Manager

File:12781MIS.dta

INDUSTRIAL TESTING LABORATORIES inc.

CHEMICAL ANALYSIS
MATERIALS TESTING
ENVIRONMENTAL EVALUATION

Report No. 91-08-03326 A

January 10, 1992

Determination of Chloride content on one (1) paint film submitted.

Carboline Company
350 Hanley Industrial Court
St. Louis, MO 63144

P.O.: Lab 22642
Attn: Mr. Yuly Korobov

TEST REPORT

Test Result:	02833
Material:	Carboline 801
Specification:	G.E. Nuclear Energy NEDC-31735P

Leachable Chloride, ppm	
Sized Sample (1/8"-1/16")	100
Solid Sample	44
Total Chloride, ppm	698

Test Method: Symbol "ppm" denotes parts per million

Test Method: ASTM D-808

Respectfully submitted,

INDUSTRIAL TESTING LABORATORIES, INC.

by: William A Rose

LN -208484
LB - 42876
BB/kmm

Invoice # 54499

INDUSTRIAL TESTING LABORATORIES inc.

CHEMICAL ANALYSIS
MATERIALS TESTING
ENVIRONMENTAL EVALUATION

Report No. 91-08-03326

October 29, 1991

Examination of one (1) coating submitted.

Carboline Company
350 Hanley Industrial Court
St. Louis, MO 63144

P.O.: Lab 22642
Attn: Mr. July Korobov

TEST REPORT

Test Project:	02833
Material:	Carboline 801
Manufacturer:	Carboline Co.
Batch Numbers:	
Part A	1E5302 M
Part B	1F9366 M
Date of Manufacture:	
Part A	May, 1991
Part B	June, 1991
Specification:	G.E. Nuclear Energy NEDC-31735P

Test	Result	Method	Requirements
Nitrate (as N), ppm	0.9	EPA 353.3	820 max.
Nitrite (as N), ppm	0.3	EPA 353.3	1 max.
Total Sulfur, ppm	300	ASTM D-129	630 max.
Active Sulfur, ppm	1.1	EPA Modified Monier-Williams	----
Leachable Chloride, ppm	110		
Total Halogens (as Chloride), ppm	800	ASTM D-808	450 max.

Symbol "ppm" denotes parts per million

Respectfully submitted,

Allan M. Siegel, P.E.
Director

LN - 208484
LB - 40889, 42612
BB/RH/SP/kmm

Invoice # 52874

2350 S. Seventh Street · St. Louis, Missouri 63104-4296 · 314/771-7111 · (FAX) 314-771-9573

INDUSTRIAL TESTING LABORATORIES inc.

Report No. 91-08-03326 A

January 10, 1992

Determination of Chloride content on one (1) paint film submitted.

Carboline Company
350 Hanley Industrial Court
St. Louis, MO 63144

P.O.: Lab 22642
Attn: Mr. Yuly Korobov

TEST REPORT

Test Result:	02833
Material:	Carboline 801
Specification:	G.E. Nuclear Energy NEDC-31735P

Leachable Chloride, ppm	
Sized Sample (1/8"-1/16")	100
Solid Sample	44
Total Chloride, ppm	698

Test Method: Symbol "ppm" denotes parts per million

Test Method: ASTM D-808

Respectfully submitted,

INDUSTRIAL TESTING LABORATORIES, INC.

by: William Blond

LN -208484
LB - 42876
BB/kmm

Invoice # 54499

UNITED STATES GOVERNMENT QA Record 246 86 09 1

Memorandum

TENNESSEE VALLEY AUTHORITY

TO : E. A. Merrick, Supervisor, Codes, Standards, and Materials Section-2, W11 D127 C-K

FROM : W. H. Childres, Supervisor, Singleton Materials Engineering Laboratory, SME-K

DATE : September 11, 1986

8610090S0005 (3)

SUBJECT: WATTS BAR NUCLEAR PLANT - PHENOLINE 305 COATING - LEACHABLE HALIDES AND CORROSION INHIBITORS

As outlined in your test request 8-6-86-1, 95°C leachable halides have been measured on the Phenoline 305 used in Dana wicking tests on this material. Leachable inorganic corrosion inhibitors were also measured on some of the samples. The Dana wicking test results were reported in B46 860801 002.

Leach of dried paint chips (film) was carried out using SME Procedure K501, "Determination of Leachable Halogens in Adhesive Tapes and Sealants." Phenoline 305 coated 3-in. by 6-in. panels were leached as described in an SME report, "Total and Leachable Halides in Coatings" (SME 850107 002). The concentrations of halides, sulfate, sulfite, nitrate, nitrite, and phosphate in leachates was measured by ion chromatography. Chromate, silicate, and sodium were measured by atomic absorption.

Total chloride and fluoride, reported in B46 860801 002, was 880 ppm chloride and 400 ppm fluoride.

Paul V. Bathie Jr.
for W. H. Childres

cc
CAC:BJ
Attachments
cc (Attachments):
RIMS, SL26 C-K

This was prepared principally by Carey A. Chambers, extension 2771.

A36253.1

Buy U.S. Savings Bonds Regularly on the Payroll Savings Plan

Table 1

WATTS BAR NUCLEAR PLANT

PHENOLINE 305 COATING - STRESS CORROSION

95°C LEACHABLE CHLORIDE AND FLUORIDE IN DRIED PHENOLINE 305

Sample	Sample Description	Weight Paint	Leach Volume	Leachable Halide, Weight Basis, ppm		Leachable Halide, Area Basis mg/ft²	
				Cl^-	F^-	Cl^-	F^-
8-15-1	5 mil paint on steel panel	5.92	151	156	<5	3.7	<0.1
8-15-2	5 mil paint on steel panel	6.27	152	166	<5	4.2	<0.1
8-15-3*	10 mil paint on steel panel	10.92	159	113	<5	4.9	<0.2
8-15-4*	10 mil paint on steel panel	10.37	150	112	<5	4.6	<0.2
8-8-1	dried phenoline chips	13.65	250	154	<5	na	na
8-8-2	dried phenoline chips	12.28	250	245	<5	na	na
8-8-3	dried phenoline chips	25.09	250	277	<5	na	na
8-8-4	dried phenoline chips	25.12	250	289	<5	na	na

*Paint partially peeled from panel during leach.

A36253.2

Table 2

WATTS BAR NUCLEAR PLANT

PHENOLINE 305 COATING - STRESS CORROSION

95°C LEACHABLE INORGANIC INHIBITORS IN DRIED PHENOLINE 305

Sample	Sample Description	Leachable Inhibitor, ppm									Leachate pH
		Na^+	$SiO_3^=$	$CrO_4^=$	NO_3^-	NO_2^-	$SO_4^=$	$SO_3^=$	$PO_4^{\equiv}$	I^-	
8-15-1	5 mil paint on steel panel	1.0	<70	9	na	na	na	na	na	na	7.0
8-15-2	5 mil paint on steel panel	0.7	<70	7	na	na	na	na	na	na	7.0
8-15-3	10 mil paint on steel panel	0.8	<40	4	<3	<1	2.5	<1	<10	<10	7.2
8-15-4	10 mil paint on steel panel	1.2	<40	4	<3	<1	2.5	<1	<10	na	7.1
8-8-1	dried phenoline chips	1.3	<50	3	na	na	na	na	na	na	6.1
8-8-2	dried phenoline chips	1.2	<50	4	na	na	na	na	na	n.	7.4
8-8-3	dried phenoline chips	1.1	<30	4	2	1	6.1	<1	<5	<15	7.9
8-8-4	dried phenoline chips	1.1	<30	3	2	1	6.3	<1	<5	na	8.1

A36253.3

U 5081

Professional Service Industries, Inc.

TESTED FOR:	Carboline 350 Hanley Industrial Court St. Louis, MO 63144	PROJECT:	831-43212-2 *Corrected Report
Attention:	Bob Rehg	DATE RECEIVED:	April 18, 1994
PA CERTIFIED ID NO.: 02-349		Date Corrected: REPORT DATE:	April 26, 1994 April 22, 1994

REMARKS: PO #MLAB26657 LABORATORY NO.: INO40628

Sample Description	:	One (1) Sample of Product
Submitted By	:	Client
Method of Test	:	ASTM D512, D808, D3987*
Acceptance Criteria	:	FPL PTNP-91-2254 Rev. 4 Attachment 'A' to 021-49410-0

Sample Identification
Project #03087; Product Batch Number's Part A-B7869L; Part B-3M0078M
Carboline 890*

Determination, ppm	Results	Specification
Total Chloride	211	*
Leachable Chloride	4	-

*Note: No specification fot Total Chloride. Chloride plus Fluoride = 1000 ppm Max.

Respectfully Submitted,
PROFESSIONAL SERVICE IND., INC.

Chris Mendoza, Level II
Chemistry Department Manager

1-Client
plh

Enclosure 2: Letter from PPG/Keeler and Long to John Gisclon, Dated July 16, 2004, Documenting Exchange with NRC on Testing for Leachable Chlorides

Keeler&Long

PPG High Performance Coatings

856 Echo Lake Road P. O. Box 460 Watertown, CT 06795 Tel: 860-274-6701 Fax: 860-274-5857

July 16, 2004

Mr. John Gisclon
Electric Power Research Institute
P. O. Box 1256
Ashland, OR 97520

References:

1. "Test Plan: Characterization of Chemical and Corrosion Effects Potentially Occurring During a PWR LOCA," Revision 10.a, May 11, 2004

Dear Mr. Gisclon:

A test plan has been developed to determine and characterize the chemical reaction products that may develop in a representative post-LOCA containment sump environment for PWRs (Reference 1). Based on testing of epoxy coatings performed using ANSI N5.9-1967 and ANSI N5.12-1974, and the favorable results obtained from that testing, the test plan does not include epoxy-based protective coatings. After reviewing the test plan, Mr. Martin Murphy, US NRC, questioned if there was sufficient leachable material in epoxy protective coatings that they should be included in the test plan.

Leach testing of Keeler & Long PPG (K&L PPG) epoxy coatings designed for use inside containments of nuclear power plants was conducted by Analytical Consulting Technology, Inc. Data sheets summarizing the results from leaching tests of the K&L PPG coatings were provided to T. S. Andreychek of Westinghouse Electric Co. for subsequent release to NRC to address the questions raised by Mr. Murphy. Upon reviewing the data sheets, Mr. Murphy requested additional information regarding the manner in which the leach testing was performed.

On Friday, July 9, 2004, a conference call was held with Mr. Murphy of the NRC, Mr. Bert Geiser of Analytical Consulting Technology, Inc., Mr. Tim Andreychek of Westinghouse, and me. Mr. Geiser described the testing and explained how the test data was evaluated and presented for the K&L PPG epoxy coating of interest. He stated that the results report laechable material in terms of mass of the coatings tested.

A letter summarizing the conversation, including a summary of how the data was reduced and presented on the data sheets previously provided to Mr. Andreychek is attached. Please transmit this letter and its attachment to the appropriate personnel

within NRC.

I trust this information satisfies your needs at this time. If you have any questions, or require additional information, please feel free to call me at 800-876-8035 Ext. 138.

Sincerely,

John F. De Barba
Technical Service Manager

cc: Timothy S. Andreychek
Westinghouse Electric Co., LLC
P. O. Box 355
Pittsburgh, PA 15230

d/letters/EPRI_JG

Enclosure 3: Letter from Analytical Consulting Technology Inc., Dated July 12, 2004, Identifying the Interpretation of the Leaching Test Data used in the Response to RAI # 2 is Correct

ANALYTICAL
CONSULTING
TECHNOLOGY, INC

168 Railroad Hill St., Waterbury, CT 06708 • (203) 757-3960 • Fax (203) 759-2155
www.actlabs.biz

PPG Industrial Finishes
John Debarba
856 Echo Lake Road
PO Box 460
Watertown, CT 06795.

July 12, 2004

Dear Mr. Debarba:

Per your request, I have compiled a synopsis of the procedure used to test "Water Leachable " compound concentration extracted from cured coatings (our reports dated June 25,1999).

The leachate test was based on ASTM F1277. Cured Coatings were tared, cut into ¼ to ½ inch squares and subjected to a leaching solution (10% 0.1N NaOH) @ 95*C.

The resultant leaching solution was analyzed to determine the concentration of analyte in the leachate solution (post extraction) by ion chromatography or amperometric titration (for TOX).

Based upon the resultant concentration in the leachate and the original weight of cured coating subjected to extraction, a concentration of leachable analyte was calculatated in ppm (or mg/Kg).

Example:

The weight of cured coating subjected to 100ml of leachate solution was 6.63g .

The concentration in the resultant leachate was 8.544 mg/L

Therefore there was 0.8544mg of chloride in the 100ml of extract.

When this is compared to the original coating weight it can be derived that 0.8554 mg of leachable chloride was contained in 6.63 g of coating; and the report value of 128.8mg/Kg (ppm) of leachable chloride.

Respectfully.

Donald J. Carew, Lab Director

Enclosure 4: F. Dacquait et.al. "Corrosion Product Transfer in French PWRs During Shutdown," SFEN-Chimie 2002 Conference on Water Chemistry in Nuclear Reactor Systems, Avignon, France (2002).

CORROSION PRODUCT TRANSFER IN FRENCH PWRs DURING SHUTDOWN

F. DACQUAIT, COMMISSARIAT A L'ENERGIE ATOMIQUE, CEA / DEN, FRANCE
C. ANDRIEU & M. BERGER, ELECTRICITE DE FRANCE, EDF / SEPTEN, FRANCE
J-L BRETELLE, ELECTRICITE DE FRANCE, EDF / GDL, FRANCE
A. ROCHER, ELECTRICITE DE FRANCE, EDF / GPR, FRANCE

ABSTRACT

Physicochemical conditions significantly vary during cold shutdown in French PWRs: power and temperature decrease, chemical conditions are modified (pH decrease and change from reducing to oxidizing conditions). These changes involve corrosion product releases in the primary water (dissolving and crud bursts) which can be seen by a considerable corrosion product increase, from 2 to 3 orders of magnitude, in the activity concentrations (about a hundred GBq/t of ^{58}Co, about one GBq/t of ^{60}Co...) and in the chemical species quantity (several kilograms of nickel, several hundred grams of chromium...).

The ^{58}Co peak activities which are lower than the French PWR average are generally due to delayed or incomplete oxygenations or unscheduled shutdowns with oxygenation during operating cycles. An unscheduled shutdown with oxygenation in the last six months of an operating cycle must reduce the ^{58}Co activity peak during refueling shutdown, more especially as the unscheduled shutdown occurs near the end of the cycle. Thus, when the shutdown happens in the three months prior to the end of the cycle, it is very likely that the ^{58}Co peak during the refueling shutdown will be two times lower than the expected peak.

The large quantity of corrosion products released during shutdown mainly come from the dissolution of the in-core deposits due to primary system oxygenation, in particular the dissolution of nickel metal or nickel oxide, leading to the dissolution of the ^{58}Co derived from the nickel sites in the crud. Thus, the total ^{58}Co activity released during oxygenation is equal to, or even higher than, the out-of-core total surface activity. Therefore, the cold shutdown procedure must prevent the transfer of this considerable activity from the in-core to the out-of-core surfaces. Deposited activity measurements carried out in French PWR primary circuits have never shown any visible contamination reduction during cold shutdown. On the contrary, recontamination can occur because of a temperature plateau or an oxygenation at a temperature over 80°C.

That is the reason why:

- Primary circuit oxygenation at 80°C,
- Rapid temperature decrease and
- Improvements on primary fluid purification,

during cold shutdowns, have, up to this day, been the main points in the EDF strategy to reach the required dosimetric goals (ALARA), all the while optimizing unit outage schedules (availability).

This paper thus proposes a description of corrosion product behaviour during French PWR shutdowns in order to optimise cold shutdown procedures.

INTRODUCTION

Physicochemical conditions significantly vary during cold shutdown in French PWRs: power and temperature drops, chemical condition changes of the primary coolant. These changes lead to corrosion product releases in the primary coolant (dissolving and crud bursts), which can be seen by considerable corrosion product increase in the radiochemical and chemical species.

This is why the cold shutdown procedure must meet the following objectives:

- Minimize corrosion product release when this does not constitute an out-of-core contamination decrease,
- Lower primary coolant activity as quickly as possible,
- Avoid contaminating the primary circuit,
- Facilitate fuel-handling operations while maintaining reactor cavity water transparency and reducing the surface dose rate during core unloading.

To meet these objectives, studies have been carried out in France to optimise the shutdown procedure for many years. These studies are founded on the chemical and radiochemical analysis of primary coolant samplings and on the measurements of the activities deposited on the circuits during cold shutdowns.

COLD SHUTDOWN DESCRIPTION

The physicochemical parameter variations during a cold shutdown on a French 1300 MWe PWR (Reactor A) are described in Figure 1.

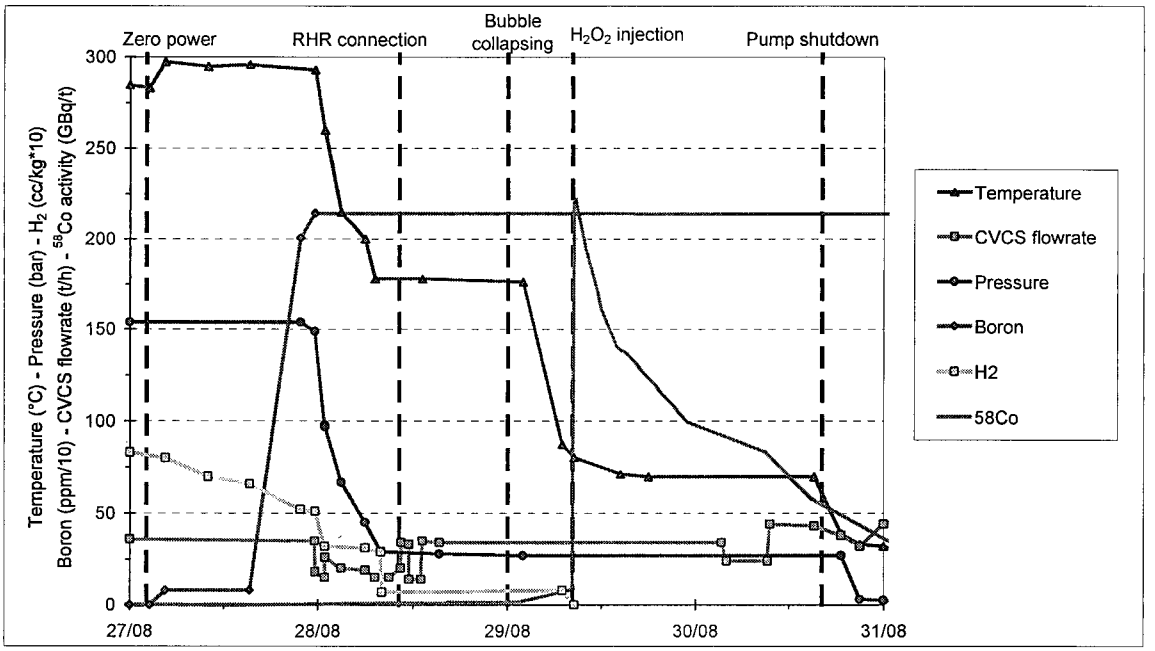

Figure 1 : Cold shutdown – Parameter variation

After an H_2 decrease to a content lower than 3 cc/kg STP, in order to oxygenate the primary circuit, 15 litres (900 MWe PWR) or 23 litres (1300 MWe PWR) of hydrogen peroxide (30%) are injected and the vapor space of the CVCS volume control tank is scavenged. The hydrogen peroxide injection is carried out when the primary coolant temperature is at 80°C, if possible with all the primary coolant pumps in operation.

Because of the oxygenation, corrosion product activity concentrations significantly increase in the primary circuit, especially the ^{58}Co volume activity.

ACTIVITY AND CHEMICAL ELEMENT CONCENTRATIONS

To assess corrosion product behaviour, primary coolant samplings are made during PWR cold shutdown. During the reactor A shutdown described in the previous paragraph, 250 to 1000 ml samplings were filtered through 0.45 µm millipore filters and ion exchange papers. The volume activities of the corrosion products in solution and suspension were measured by gamma spectrometry (☞ Figure 2 and Figure 3), the chemical concentrations by X-ray fluorescence (☞ Figure 4). Thanks to these measurements, the total released nickel mass, the ^{58}Co total released activity and the ^{58}Co specific activity during the shutdown can be evaluated (☞ Figure 5).

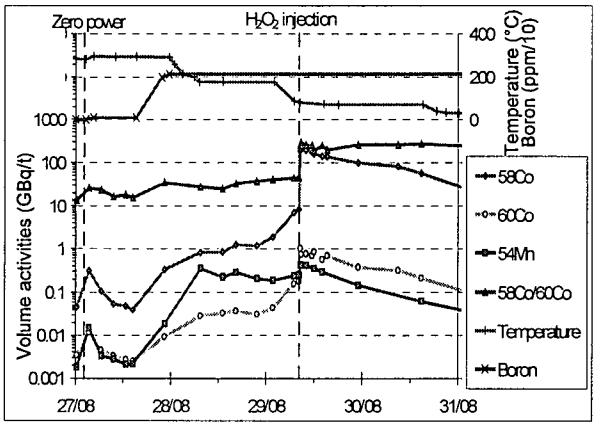

Figure 2 : Volume activities

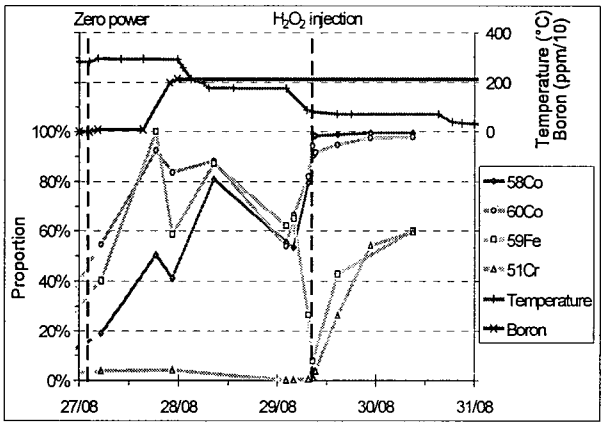

Figure 3 : Dissolved radionuclide proportion

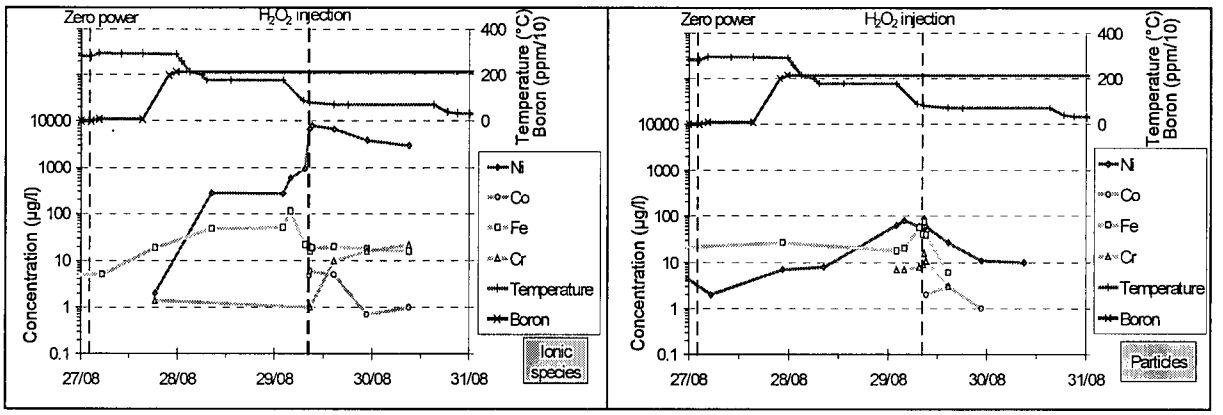

Figure 4 : Chemical element concentration

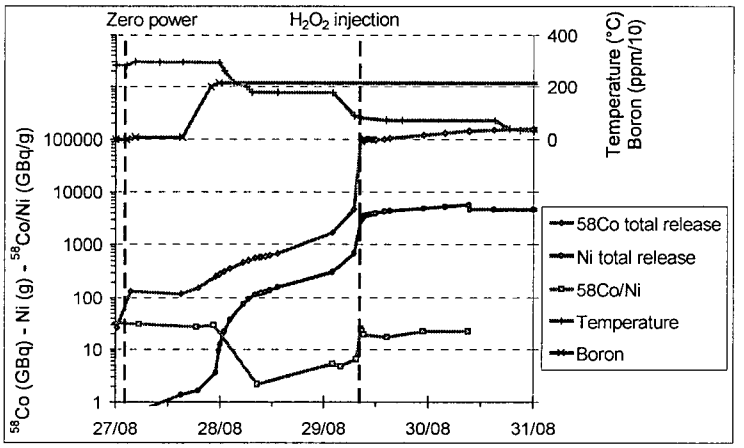

Figure 5 : ^{58}Co total release and specific activity

Moreover, during another 1300 MWe PWR (Reactor B) shutdown, particle size analyses were determined by 1 litre samplings through a succession of millipore filters with decreasing meshes: 10 µm, 5 µm, 1.2 µm and 0.45 µm (□ Figure 6).

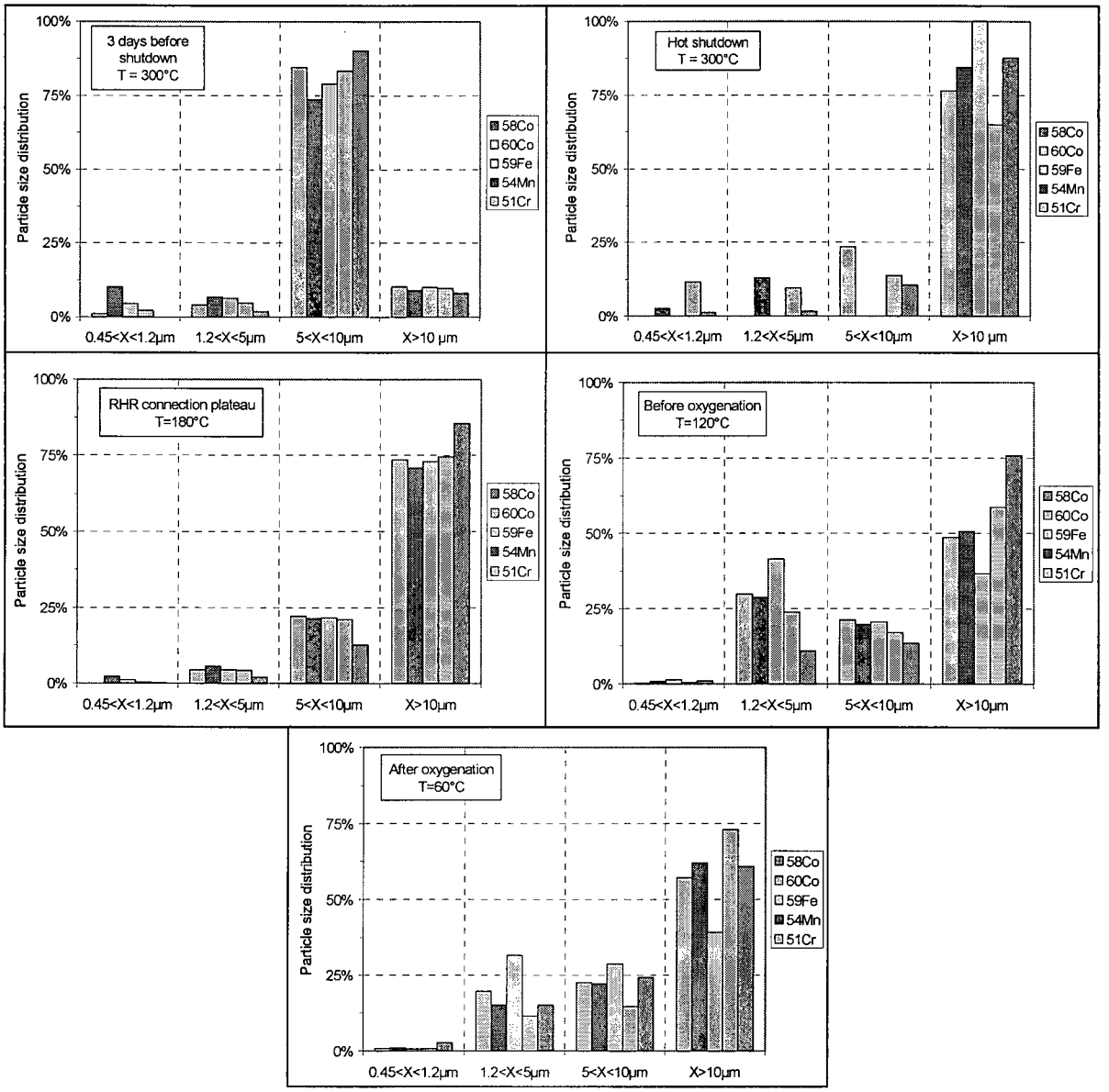

Figure 6 : Radionuclide particle size distribution before and during shutdown

Three main phases lead to corrosion product transfers [1, 2]:

- Power reduction,
- Primary coolant boration and cooling,
- Primary circuit oxygenation.

Power reduction is characterized by a rapid increase in volume activity. However, this increase is slight, about 100 GBq of ^{58}Co, versus the total activity released during shutdown. This activity mainly consists of particles, part of which deposits very rapidly. The radionuclide particle size is between 5 and 10 µm for reactor B before shutdown, while it is mostly greater than 10 µm during hot shutdown.

The $^{58}Co/^{60}Co$ activity ratio, about 20 (this varies between 2 and 6 for out-of-core deposits), and the ^{58}Co specific activity, about 30 GBq/g (this is about 45 GBq/g at in-core equilibrium), show that these particles originate from an in-core deposit detachment, due to thermal and mechanical stress variations during control rod insertion.

The primary coolant boration and temperature decrease (from 290 to 180°C and then from 180 to 80°C) result in a fast increase in the activity and chemical concentration mainly by dissolution. This corrosion product dissolution is related to the solubility increase due to temperature and pH decreases.
The $^{58}Co/^{60}Co$ ratio, about 20, and the ^{58}Co specific activity, less than 10 GBq/g, indicate that this dissolution affects in-core and out-of-core deposits. The activities and masses released in the primary coolant come from deposit decomposition (nickel ferrite). During the temperature plateau at 180°C, the similar variation of the nickel and iron concentrations and the low ^{58}Co specific activity (less than 5) show that this nickel ferrite decomposition especially takes place on out-of-core surfaces.
As the soluble radionuclide ratio decreases after the dissolution due to the falling temperature or pH, part of these radionuclides must precipitate. For reactor B during the temperature plateau, approximately 25% of the particulate activity is in the 5-10 µm range and about 75% greater than 10 µm. During the temperature decrease from 180 to 80°C, half of the particulate activity is equally distributed between the 1.2-5 µm and 5-10 µm ranges, the other half being greater than 10 µm.
The ^{58}Co activity concerned during this phase is about several thousands of GBq, a low activity compared to the total activity released during shutdown.

Primary circuit oxygenation causes a large dissolving of nickel (a concentration of about 8 ppm), and, to a lesser extent, of cobalt. On the other hand, iron precipitates to form particles (Fe^{2+} oxidized to Fe^{3+}), the ^{59}Fe activity being mainly in particulate form. Chromium, in particulate form under reducing conditions, dissolves in oxidizing conditions. The particle size distribution is not greatly modified by oxygenation.
The high $^{58}Co/^{60}Co$ ratio (> 200) and the ^{58}Co specific activity (approximately 25 GBq/g) show that an in-core nickel deposit dissolves. It is an in-core nickel metal or nickel oxide deposit that is stable in reducing conditions at high temperature and that dissolves in oxidizing conditions at low temperature. This is confirmed by an experiment in the SOZIE loop [3]. The nickel dissolution involves the dissolution of ^{58}Co, derived from the nickel sites in the crud (^{58}Ni (n,p) ^{58}Co). A ^{58}Co activity peak then appears within the half-hour following hydrogen peroxide injection. The total ^{58}Co activity released during oxygenation is considerable, about 150000 GBq for reactor A. The total nickel mass released during this shutdown is about 5.7 kg, including 5 kg during oxygenation.

Oxygenation thus creates high activity peaks. The available statistical data on ^{58}Co and ^{60}Co peak values in French PWRs are gathered in Table 1.

		^{58}Co (GBq/t)		^{60}Co (GBq/t)
PWR	Data	Average peak	Standard deviation	Average peak
900 MWe	All available data	110	55	
	Year 2000	103	47	0.7
1300 MWe	All available data	180	80	
	Year 2000	165	64	1.0

Table 1 : Peaks during refueling shutdown

The high ^{58}Co peak values in 900 MWe PWRs are generally due to Steam Generator Replacements (SGR) that cause a ^{58}Co released activity increase which lasts during several shutdowns after the SGR cycle [4].
For the 1300 MWe PWRs, the higher peaks occurred during the first cycles, probably because of a larger release of Steam Generator (SG) tubing at the beginning of life.
Note that the SG tubing material in the French PWRs is alloy 600 for the oldest or alloy 690 for the most recent.

The low peak values are generally due to delayed, incomplete oxygenations or unscheduled shutdowns with oxygenation in the course of cycle. The unscheduled shutdowns allow nickel and ^{58}Co deposited on fuel to be solubilized and purified. These deposits do not have time to reform before the refueling shutdown.

Figure 7 shows the ratio between peaks during refueling shutdowns after an unscheduled shutdown with oxygenation and the expected peaks if there had not been any unscheduled shutdown, versus operating time after an unscheduled shutdown with oxygenation.

It appears that an unscheduled shutdown with oxygenation of about 6 months before the refueling shutdown allows the ^{58}Co volume activity released during the refueling shutdown at the end of the cycle to be reduced, particularly as this unscheduled shutdown occurs near the end of the cycle. Thus, when the shutdown occurs three months before the end of the cycle, it is extremely likely that the peak during the refueling shutdown will be reduced by at least half compared to the expected peak.

However, before the increase in the primary circuit temperature during an unscheduled shutdown, the corrosion product volume activities must be sufficiently low (EDF criteria: $^{58}Co < 7$ GBq/t and $\gamma_{total} < 14$ GBq/t) to prevent their precipitation, due to temperature and pH increase, from causing their deposition on out-of-core surfaces. This risk of primary circuit recontamination would lead to a dose rate increase during the refueling shutdown at the end of the cycle.

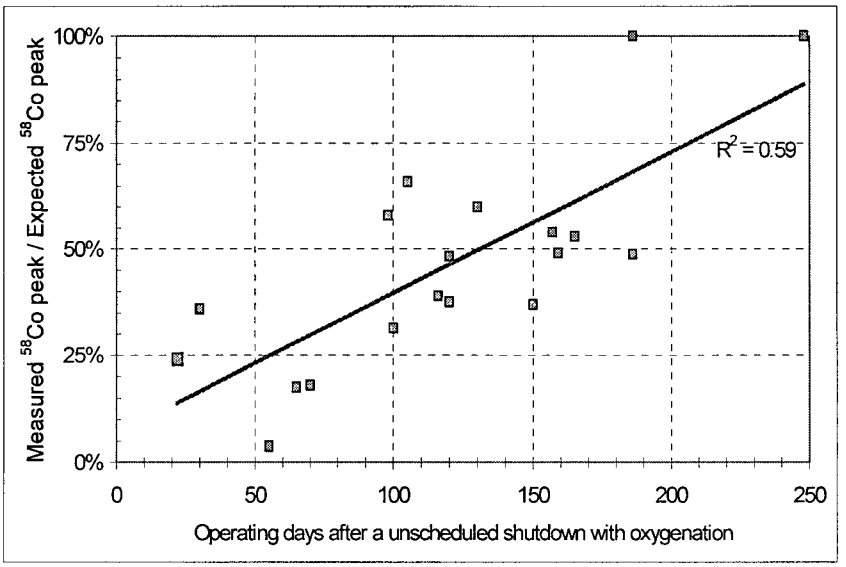

Figure 7 : Impact of unscheduled shutdowns with oxygenation

PRIMARY COOLANT PURIFICATION

The previous paragraph showed that, during a cold shutdown, a great quantity of corrosion products was transported by primary coolant. This huge quantity of corrosion products is trapped in the filters and demineralizers of CVCS as shown in Figure 8. The CVCS Decontamination Factor (DF = upstream filtration activity / downstream filtration activity), given during a 1300 MWe PWR shutdown, shows that purification efficiency is high for radioactive corrosion products: from 100 to 10^6. It would seem that the higher the decontamination factor, the more significant the upstream filtration activity. But this is perhaps also due to the particular behaviour of the ion exchange resins with respect to radioelement retention.

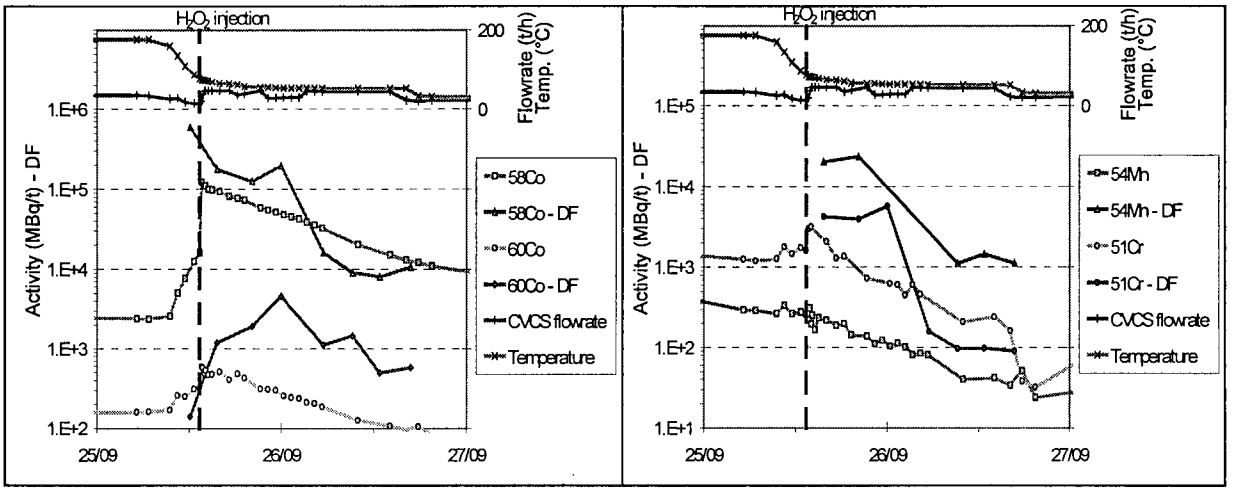

Figure 8 : Purification efficiency

Thus, the activities and the masses of the "traditional" corrosion products are trapped by the prefilter and by the ion exchange resins of the CVCS. On the other hand, other undesirable radioelements such as ^{122}Sb and ^{124}Sb, as well as ^{110m}Ag, are not systematically properly trapped by filters and demineralizers and these can significantly add to dosimetry [5].

The activity criteria currently specified for corrosion products at EDF during cold shutdowns in French PWRs are defined in Table 2.

Hold points	Activity criteria relating to corrosion products during purification by CVCS
Primary pump shutdown	^{58}Co < 50 GBq/t and γ_{total} < 100 GBq/t
Reactor cavity filling	^{58}Co < 2 GBq/t and γ_{total} < 4 GBq/t

Table 2 : Activity criteria

In order to quickly meet these goals by means of purification, while taking into account specific problems (presence of ^{122}Sb ^{124}Sb and ^{110m}Ag), two complementary research projects are under development and design engineering at EDF: increase the purification flow rate and optimise the purification supports [6].

Volume activity A_t (at moment t) in the primary circuit is :

$$A_t = A_0 \cdot \exp^{[-\frac{Q \cdot t}{M}(1-\frac{1}{DF})]}$$

with

- A_0 : initial volume activity
- Q : CVCS letdown flow rate
- M : total water mass to be purified (including CVCS volume)

The decontamination factors being higher than 100, this expression is simplified in:

$$A_t = A_0 \cdot \exp^{[-\frac{Q \cdot t}{M}]}$$

Thus, the purification flow rate increase allows an increase in the CVCS purification constant to be obtained (Q/M). One can discount a significant savings of time in obtaining the primary pump shutdown criteria (availability) or, for the same scheduled purification time, in obtaining the prescribed activity criteria (ALARA) below. Moreover, the increase in the CVCS purification flow rate helps meet the reactor cavity filling criteria more quickly.

Consequently, the increased CVCS letdown flow rates retained by EDF are:

Standardized plants		Letdown flow rate *Q* (t/h)
CPY	900 MWe	40 (in two prototype units)
P4 and P'4	1300 MWe	47
N4	1450 MWe	50 (studies in progress to increase to 70 t/h)

SURFACE ACTIVITIES

In order to evaluate the cold shutdown impact on contamination, the activities deposited in the PWR primary circuit have been measured for many years by means of the EMECC gamma spectrometry system [7]. These measurements are carried out before and after oxygenation, mainly on hot legs and SG tube bundles.
Figure 9 shows the variation in the ^{58}Co and ^{60}Co activities deposited in the hot legs and SG tubing, measured before and after oxygenation. Those variations of less than 20% are not significant because of the measurement uncertainty.

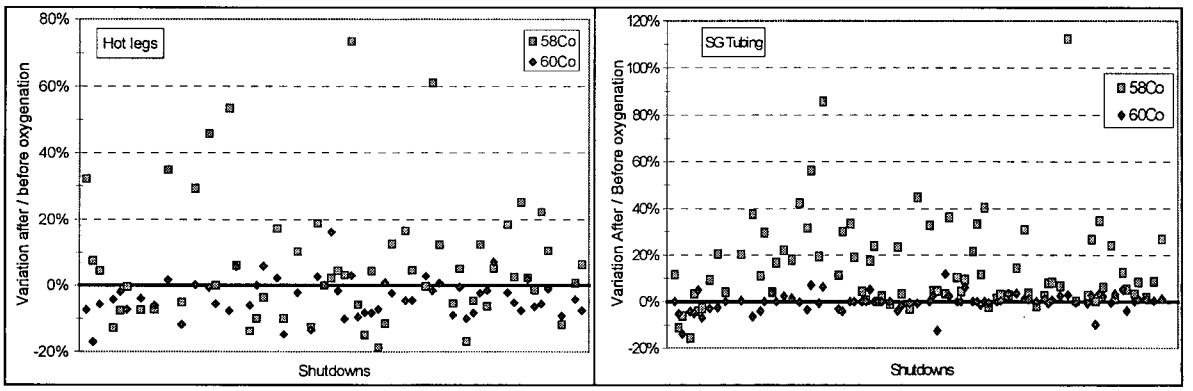

Figure 9 : Surface activity variation during oxygenation

On approximately 80 analysed shutdowns, a visible reduction in the ^{58}Co and ^{60}Co activities deposited on the primary circuit during oxygenation has never been observed. However, a strong increase in ^{58}Co deposited activity can occur on out-of-core surfaces if the effective oxygenation temperature of the primary circuit is higher than 80°C (□ Figure 10) [1]. Recontamination then occurs very rapidly (less than one hour) and at the time of the activity peak. On the contrary, the oxygenation temperature does not seem to have an impact on ^{60}Co contamination (□ Figure 9). This is due to the fact that the ^{60}Co released quantity, suitable to be deposited on the out-of-flux surfaces, is probably not significant enough to be measured. Let us note that at identical oxygenation temperatures, ^{58}Co SG recontamination, when significant, is roughly the same as in the procedures using hydrogen peroxide or CVCS venting (□ Figure 10).

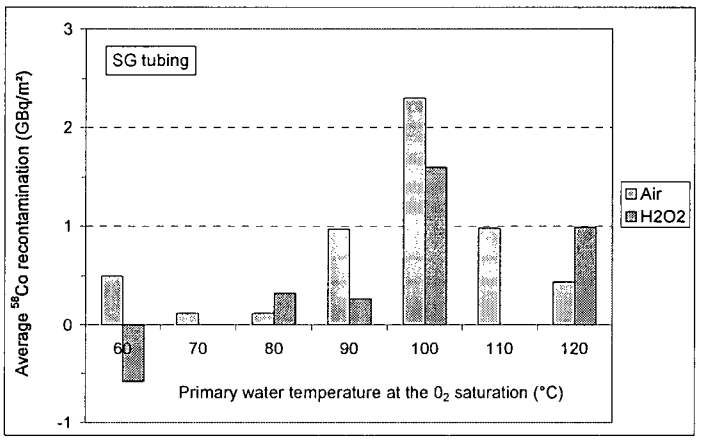

Figure 10 : Impact of the effective oxygenation temperature

The increases in the ^{58}Co activities deposited on the hot legs and the SG tubes during oxygenation presented in Figure 9 are due to an effective oxygenation temperature higher than 80°C, in particular for the most significant variation rates. However, these increases can also be due to prolonged temperature plateaux.

Thus Figure 11 shows the evolution of the ^{58}Co activity deposited on a SG tube bundle during a cold shutdown characterized by a temperature plateau at 120°C during 5 days. Although the volume activity during this plateau is not very significant (between 15 and 20 GBq/t), the SG ^{58}Co contamination increases appreciably during the plateau at 120°C. Note that since part of the ^{58}Co activity is released during the temperature plateau, the activity peak due to oxygenation at 80°C is not very high (33 GBq/t). However, the total released activity is equivalent to what it would have been without a temperature plateau, but with a more significant peak at the time of oxygenation. Finally, let us note that the H_2O_2 injection temperature being 80°C, oxygenation did not lead to primary circuit recontamination.

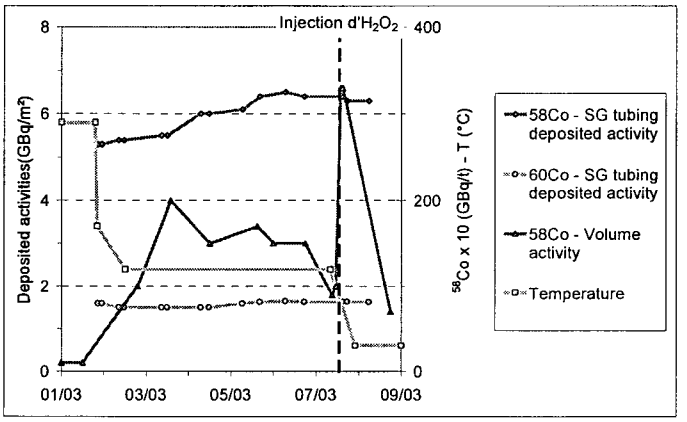

Figure 11 : Impact of a temperature plateau

DISCUSSION

During a cold shutdown in an EDF PWR, a significant transfer of corrosion products mainly occurs at the time of primary circuit oxygenation. A nickel peak (several ppm) and a ^{58}Co peak (a hundred GBq/t) then appear half an hour after the H_2O_2 injection.

During reactor A shutdown (□ § Cold shutdown description), about 95% of the total ^{58}Co released is due to oxygenation. This activity is equal to, or even higher than, the total activity deposited on the out-of-core primary surfaces. Indeed, the ^{58}Co total activity released during the shutdown is about 150000 GBq, whereas the ^{58}Co out-of-core total surface activity is about 75000 GBq before and after oxygenation, that is to say two times less. This confirms that the activity released during oxygenation comes from in-core deposits and not out-of-core deposits. This activity is due to the dissolution of nickel oxide or metal nickel in-core deposits in an oxidizing medium, leading to the dissolution of the ^{58}Co derived from the nickel sites in the crud. Although the released activity is primarily in soluble form, crud bursts occur during cold shutdown, and these particle sizes can be relatively significant: larger than 10 µm.

Gamma spectrometry measurements carried out by the CEA have never shown a visible reduction in the ^{58}Co and ^{60}Co contamination on the out-of-core primary surfaces. On the other hand, a significant ^{58}Co recontamination of the primary circuit can occur if the effective temperature of the primary circuit oxygenation is higher than 80°C. Moreover, ^{58}Co recontamination is probably accompanied by a cobalt and nickel re-deposition. These elements are redistributed during the following cycle and can be activated in core, thus creating an additional source of radioactive corrosion products.

In the paragraph "Activity and chemical element concentrations", it was stated that the nickel ferrite deposits were to decompose during the temperature plateau at 180°C. But this dissolution of the out-of-core deposits is negligible, since it represents less than 1% of the out-of-core total surface activity. Moreover, the measurements of the activities deposited on the primary circuit have never shown a reduction in the ^{58}Co and ^{60}Co contamination of the out-of-core surfaces during this phase.
However, as nickel ferrites are decomposed by dissolved hydrogen, the hydrogen concentration is perhaps not high enough during French PWR shutdowns to be able to observe a reduction of the out-of-core surface

activities ([H_2] < 3 cc/kg). According to [8], the dissolved hydrogen content should be higher than 10 cc/kg and the temperature should range between 120 and 150°C during at least 16 hours, in order to decompose nickel ferrites. However, the reaction kinetics is not known and a temperature plateau can lead to out-of-core surface recontamination (☞ Figure 11). The hypothetical benefit is thus likely to be masked, all the more so as the acid-reducing conditions can also decompose the in-core nickel ferrites and thus recontaminate out-of-flux surfaces. In order to evaluate its impact, an acid-reducing chemistry will be applied and monitored during a French PWR shutdown this year.

In France, the current procedure for the cold shutdown prescribed by EDF does not aim at decontaminating the out-of-core surfaces, but, at, as soon as possible, reaching the criteria of the reactor cavity filling by avoiding recontaminating the primary circuit out-of-core surfaces. That is why:

- The primary coolant temperature is reduced as quickly as possible,
- The oxygenation temperature of the primary circuit is 80°C,
- The high flow rate purification is being evaluated so as to be applied to EDF PWRs. The corrosion products are effectively trapped on the CVCS filters and demineralizers, except for specific pollutions (antimony and silver) for which studies on the optimisation of the purification media are in progress.

Although penalizing, among other things, to availability, an unscheduled shutdown with oxygenation can have a beneficial effect on the refueling shutdown at the end of the cycle. Indeed, an unscheduled shutdown with oxygenation in the last six months of a cycle allows the ^{58}Co activity peak to be decreased during the refueling shutdown. As for purification, an unscheduled shutdown makes it possible to more quickly reach the criteria of reactor cavity filling or, for the same purification duration, to obtain activity values below the criteria.
This is why EDF recommends oxygenating the primary circuit if the unscheduled shutdown lasts more than 3 days. Moreover, it allows the reduction of out-of-core contamination, since part of the in-core corrosion product deposits is removed and trapped by CVCS filtration. Let us recall that it is advisable to purify the primary circuit sufficiently to avoid recontaminating the out-of-flux surfaces, because of the temperature and pH increase at the end of the unscheduled shutdown (EDF criteria: ^{58}Co < 7 GBq/t and γ_{total} < 14 GBq/t). These criteria are to be respected all the more so as, since the unscheduled shutdown occurs near the end of the cycle, the radionuclides have less time to decrease.

CONCLUSION

Cold shutdown in French PWRs leads to considerable corrosion product increase in the primary coolant (2 to 3 orders of magnitude). This is highlighted by high activity peaks (about a hundred GBq/t of ^{58}Co, about one GBq/t of ^{60}Co) and high chemical concentrations (several ppm of nickel...). This abrupt increase is due to the changes in the thermal and chemical conditions of the primary circuit: temperature and pH decrease, change from oxidizing to reducing conditions.

This significant quantity of corrosion products primarily comes from the dissolution of in-core deposits during primary circuit oxygenation, in particular, the dissolution of metal nickel or nickel oxide, involving the ^{58}Co formed from nickel. Thus, the total ^{58}Co activity released during oxygenation is equal to, or even higher than, the total activity deposited out-of-core. It is thus advisable that the cold shutdown procedure be adapted to avoid transferring this considerable activity from in-core surfaces to out-of-flux surfaces, particularly as the measurements of primary circuit surface activities in French PWRs have never shown a visible reduction in contamination during cold shutdown. On the contrary, recontamination can occur during temperature plateaux or oxygenations at a temperature higher than 80°C.

That is why:

- Primary circuit oxygenation at 80°C,
- Rapid temperature decrease and
- Improvements on primary fluid purification,

during cold shutdowns, have, up to this day, been the main points in the EDF strategy to reach the required dosimetric goals (ALARA), all the while optimizing unit outage schedules (availability).

REFERENCES

[1] S. Anthoni, P. Ridoux, C. Caramel – *Behaviour of the corrosion products during PWR shutdowns*, Chemistry in Water Reactors: operating experience & new developments, Nice (France), 1994

[2] S. Anthoni, P. Ridoux, C. Chevalier – *Evaluation of corrosion products in a pressurised water reactor during shutdown*, Water Chemistry of Nuclear Reactor systems 5, BNES, London (GB), 1989

[3] D. You, E. Blanchard, D. Féron, C. Masson – *Corrosion product transfer in PWR primary circuits during cold shutdowns*, this conference

[4] F. Dacquait, S. Anthoni, P. Ridoux, C. Brun, N. Engler – *Impact of Steam Generator Replacement on PWR primary circuit contamination by radioactive corrosion products*, BNES, Bournemouth (UK), 2000

[5] J.L. Bretelle, A. Rocher, M. Berger, F. Dacquait, R. Rosset – *Study of various chemical species behaviour for contamination risk*, this conference

[6] M. Berger, J. Cohen, A. Rocher - *Policy and Good Practices in Electricité de France PWRs, for Primary Coolant Purification during Refuelling Cold Shutdown*, WANO Workshop: Low Level Waste and Liquid Separation Technology in Nuclear Applications, Varbergs (S), 2001.

[7] R. Eimecke, S. Anthoni – *Ensemble de Mesure et d'Etude de la Contamination des Circuits (EMECC)*, 7th Int. Conf. On Radiation Shielding, Bournemouth (UK), 1988

[8] PWR *Primary Water Chemistry Guidelines: Volume 2, Revision 4,* EPRI, Palo Alto, CA:1999. TR-105714-V2R4