


To: Lynn, for your files.

JAN 12 1981

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December 12, 1980

Walt Pasedag
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Dear Walt:

This letter is in reference to our telephone conversations of November 26 and December 2, 1980, concerning the potential drop of a steam generator and the subsequent release of radioactive material. Your assumption that 20% of the total activity in the steam generator (as calculated prior to decontamination) would be released is, in our view, highly conservative (i.e., it is an overestimate of what would actually be released). It is, however, the assumption used by PNL in the assessment for moving a Surry steam generator to Hanford.

We believe that the amount of activity released due to such an occurrence would be on the order of a few percent, certainly less than 10%, of the amount on the tubes. It is likely that some material might be removed from the tubesheet by abrasion during the fall, but the radioactive deposits would likely remain attached to the abraded metal. Our conclusions are based primarily on the fact that PWR corrosion films are compact (or tightly adherent) and would not shake or break free during the postulated drop. It is unlikely that the radioactive deposits would be easily released.

I am enclosing an article on deposits in primary systems. For further information on decontamination, you may also wish to refer to NUREG/CR-0968, The Impact of Decontamination on LWR Radioactive Waste Treatment Systems and to Appendix A of NUREG/CR-1595 (now in publication), Radiological Assessment of Steam Generator Removal and Replacement: Update and Revision.

If you have further questions or need additional information, please call L. G. Faust (444-3613), L. D. Perrigo (444-9024) or me (444-3754).

Sincerely,



G. R. Hoenes
Associate Section Manager
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Enclosure

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54. Nature of deposits on BWR and PWR primary system surfaces—relation to decontamination

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BWR and PWR crud/oxide layers on out-of-core surfaces differ in composition and morphology. They also differ in response to decontamination reagents.

INTRODUCTION

1. Investigations are underway in several countries to improve decontamination methods for nuclear reactor coolant systems. An important aspect of those investigations is to better understand the compositions and morphologies of the radioactive deposits which must be removed from reactor coolant system surfaces during the decontamination.

2. Studies have been sponsored by the Electric Power Research Institute (EPRI) at Battelle-Northwest to investigate decontamination methods for boiling water (BWR) and pressurized water (PWR) reactors. The work has included detailed examination of radioactive films on specimens from components exposed in BWR and PWR reactor coolant systems. This paper summarizes observations regarding characteristics of the radioactive films. Details of reagent studies are given elsewhere (ref. 1-4,9).

Formation of radioactive deposits on reactor coolant system surfaces

3. The need for decontamination of reactor coolant systems arises because radioactive deposits develop on out-of-core surfaces. Numerous materials, including iron-base, nickel-base, cobalt-base and copper-base alloys, release a fraction of their corrosion product to the reactor coolant. The species are carried to the reactor core, undergo neutron activation and are re-dispersed to out-of-core locations. The radioactive coolant-borne species are transported in both dissolved (ionic) and particulate forms.

4. Thus radioactive films on reactor coolant system surfaces arise from two sources:

- oxide growth on the metallic surfaces; radioactive ions carried in the reactor coolant are incorporated into the growing oxide;
- deposition of radioactive particulates on the outer surface of the oxide.

5. In summary, the radioactive film is a composite of the deposited crud layer and the growing oxide on the metal substrate.

6. The two factors which most strongly influence the types of films which form are: the system materials; and the coolant system environment.

7. The BWR and PWR reactor coolant systems differ markedly in both materials and environments. The system characteristics are summarized in the BWR and PWR sections, respectively.

INVESTIGATION OF BWR DEPOSITS

BWR reactor coolant system materials and environment

8. The principal materials in the BWR reactor coolant system are: Zircaloy fuel cladding, stainless steel piping and reactor vessel cladding, and cobalt-base alloy (Stellite) hard-facing alloys. Other deposit sources are: corrosion products from the feedwater system (carbon steel and stainless steel); and species which leak through the condensate demineralizers. For example, if the condenser is Admiralty brass, some zinc and copper carried into the BWR reactor vessel will be incorporated into deposits on reactor coolant system surfaces.(5)

9. The BWR reactor coolant operates at 290°C, near neutral pH (normal range: 5.5 to 7.5). Radiolysis generates dissolved oxygen concentrations of 0.1 to 0.5 ppm (liquid phase). Thus, deposits on BWR system surfaces form under conditions which are substantially oxidizing.

10. The principal out-of-core material in BWR reactor coolant systems is 304 stainless steel.* The principal source of BWR specimens for this study was 304 stainless steel recirculation bypass pipe sections from the Vermont Yankee reactor. Specimens from Millstone 1 and Quad Cities 1 reactors were examined for comparison.

*71% Fe, 18% Cr, 8% Ni, 2% Mn, 1% Si.

11. Selected examinations and analyses were conducted on the following types of specimens:

- *in situ* SEM/EDX inspection of the outer film surfaces, before and after reagent treatments;
- inspection of film cross-sections, before and after reagent treatments;
- inspection of particles separated from the film during or after reagent treatments (particles deposited on filters or removed from the surface on tape);
- inspection of the as-received film, separated from the substrate by a methanol-bromine treatment;
- inspection of particles removed by mechanical scraping.

12. The scope of the paper permits no more than an overview of the results.

Morphologies and Compositions of BWR films

13. Vermont Yankee films. A prominent feature of the inner (coolant-side) Vermont Yankee pipe surface is a shallow attack at metal grain boundaries. A similar attack is evident on archive specimens, suggesting that it was caused by post-fabrication pickling.

14. The Vermont Yankee crud/oxide layer has four features, summarized in Table 1 and in

Figure 1. The Vermont Yankee film morphology was more complex than films from the other two reactors. In fact, the dual film structure on Millstone and Quad Cities pipes appears to be characteristic of films from several BWRs. (5-8) The Vermont Yankee and Millstone 1 films differed markedly in composition and morphology, but the decontamination rates were very similar, (4) for example, in an HEDTA/oxalic acid/citric acid reagent at 180°C. In both cases, the compact inner film dissolved, while outer layers remained, detached but undissolved. Approximately 80 to 90% of the radioactivity was removed, appearing to correspond to dissolution of the compact inner layer.

15. Activity removal from Quad Cities pipe specimens was less effective than for specimens from the other two reactors. The Quad Cities surface film was superimposed on a rough metal surface, having fissures up to 0.01 in. (250µm) deep. (4,6) As with the shallower (up to ~20µm) fissures on other pipe surfaces, the fissures appear to be a consequence of pre-service pickling. The hypothesis that radioactive species are trapped in the fissures is consistent with effects of ultrasonic vibration on pipe surfaces after decontamination. About 28% of the residual activity was removed from the Quad Cities specimen, while the corresponding fractions for Millstone and Vermont Yankee were only 4% and 10%, respectively.

Table 1 Summary of BWR Film Characteristics on 304 SS pipe

Feature	Composition ^{a)}					Response to Reagents ^{b)}
	Fe	Cr	Ni	Cu	Zn	
A - Vermont Yankee Film						
Superficial Particles ~1 to 10µm	85-93	3-7	1-2	1	2-4	Undissolved
Shroud ~0.1µm thick	Unknown					Dissolved or Washed Away
Faceted Crystals ^{c)} 0.1 to 1µm	52	18	7	1	22	Undissolved - Detached Washed Away by Turbulence
Compact Oxide Layer up to 2µm thick	63-76	12-16	5-8	1	9-19	Dissolved Principal source of activity
B - Millstone 1 Film(7)						
Outer Layer	86	7	6	t	1	Undissolved
Inner Layer	61	11	25	t	3	Dissolved Principal Source of activity
C - Quad Cities 1 Film(6)						
Outer Layer	90	5	5	NR	NR	Undissolved
Inner Layer	68	18	14	NR	NR	Dissolved (Efficiency for radio- activity removal reduced by rough metal surface)

t = trace

NR = not reported

EDX = Energy Dispersive X-ray

a)Based on EDX analysis - Not fully calibrated; percent metallic species normalized to 100%.

b)Based on exposure to EDTA, NTA, HEDTA, etc.

c)Based on analysis of particles detached by reagent treatments.

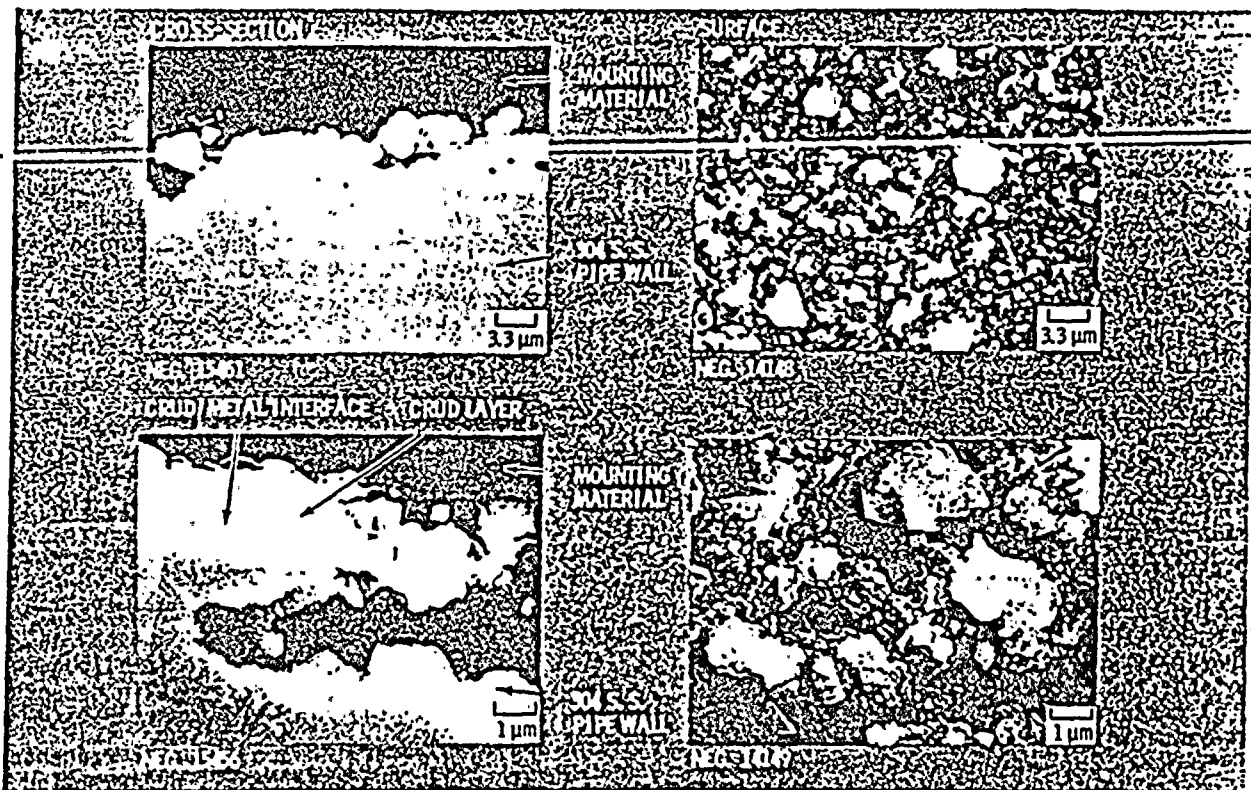


Fig. 1 Cross Section and Surface Views (SEM) - Vermont Yankee BWR Recirculation Bypass Pipe Specimens.

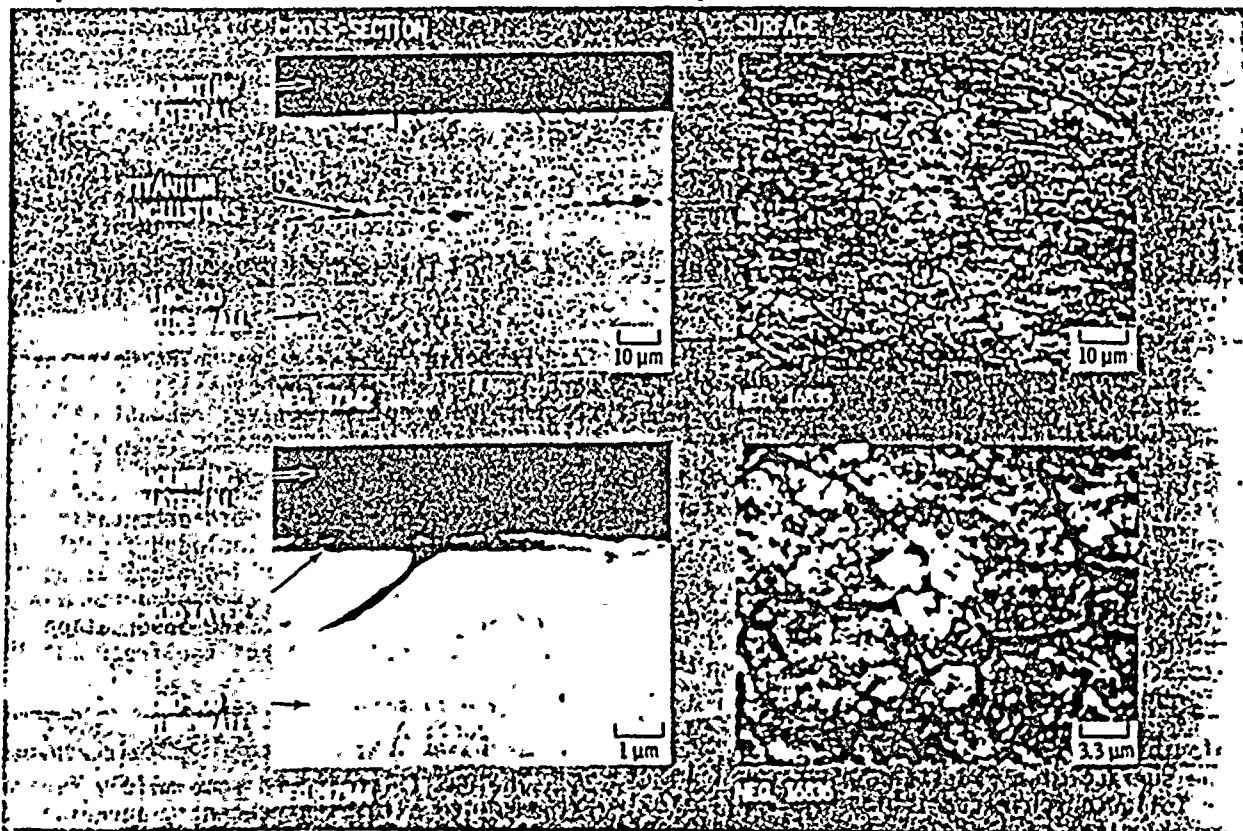


Fig. 2 Cross Section and Surface Views (SEM) - Indian Point 2 PWR Steam Generator Tube Specimens.

16. Crystallographic analyses by X-ray diffraction suggested that the principal species on the BWR pipe surfaces are Fe_2O_3 and spinels of the type: $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$, with radioactive species substituted at cation positions. The Fe_2O_3 remains after the decontamination, and some spinel species also were undissolved. Studies by General Electric Co. (5-7) suggest that the species which dissolve are nickel ferrites (spinel). The outer layer, which is higher in iron, remains undissolved. Our experience suggests that the faceted crystals which do not dissolve are somewhat higher in Cr than the layer which does dissolve, but only mildly so (Table 1). It is possible that the species higher in Cr are interspersed with a lower Cr species which dissolves. If so, the EDX analyses may not properly resolve the lower Cr species.

17. In summary, the BWR films respond favorably to common decontamination reagents (e.g., EDTA, HEDTA, NTA), most effectively when they are reducing. The most important aspect of the decontamination appears to be dissolution of the compact layer adjacent to the metal surface. This layer appears to incorporate a large fraction of the radioactivity (e.g., $^{60}\text{Co}^{+2}$), probably as metal cations which substitute into the spinel oxide lattice.

18. A relatively small fraction of the radioactivity is associated with species not dissolved by the decontamination (Fe_2O_3 and certain spinels, probably relatively high in substituted Cr). However, these detached particles (0.1 to 10 μm) must be dealt with in a decontamination, by filtration and by assuring flow conditions which will not deposit the particles at unwanted locations.

INVESTIGATION OF PWR DEPOSITS

PWR Primary System Materials and Environment

19. The principal materials in the PWR primary circuit are: Zircaloy fuel cladding, Inconel-600 steam generator tubing and stainless steel piping, reactor vessel cladding; cobalt-base alloy hard-facing materials.

20. The PWR primary coolant has additions of boric acid (~ 2000 ppm B) and lithium hydroxide (0.2 to 2.0 ppm Li). Hydrogen is added to control oxygen at <0.01 ppm during operation. While metals continue to oxidize, the system is substantially reducing. The system temperature is 320-340°C.

21. The principal out-of-core material in most PWR primary systems is Inconel-600 steam generator tubing. Tubing filmed in two PWR steam generators has been examined, by methods indicated for BWR films.

Morphologies and Compositions of PWR Films

22. The surface of a PWR steam generator film had the following characteristics (Fig. 2): a sparse population of large superficial particles; a layer of fine platlets; a network of dark grain boundaries.

Table 2 summarizes compositions of two PWR films.

23. Fig. 2 also shows a cross section of a crud/oxide layer. The layer thickness is $\sim 0.5 \mu\text{m}$. Thin filaments of the layer protrude into the metal along what we shall see are grain boundaries.

24. Confirmation that the film is keying along grain boundaries developed from treatments which separated the film from the base metal. Figure 3 shows separated film flakes. Location A is a flake oriented to show the side adjacent to the metal. The filaments embedded in the metal are now evident around the grain boundary contours. Location B shows a flake oriented to show the coolant side.

25. Responses of the PWR films to reagent treatments are still being investigated. To date, the following responses have been observed:

- Decontamination occurs slowly in the common reagents (EDTA, HEDTA, NTA)(4)
- Addition of H_2O_2 to EDTA caused only temporary increases in decontamination rate(4)
- Addition of reducing metal ions (e.g., Cr^{+2}) caused rapid increases in decontamination rate(4)
- Certain oxidizing and reducing reagents dissolved the base metal, undercutting the film, removing it almost completely as flake-like particles.

DISCUSSION

26. Our studies have clearly demonstrated that BWR and PWR films respond differently to common reagents such as EDTA, HEDTA and NTA. The BWR films are easier to decontaminate. Early in the studies we began to examine the questions:

- Do BWR films, formed under oxidizing conditions, respond most effectively to reducing decontamination reagents?
- Do PWR films, formed under "reducing" conditions, respond most effectively to oxidizing reagents?

27. Responses of BWR films to decontamination were in line with the hypothesis: oxidizing reagents were not effective; reagent effectiveness increased with increasing reducing character.

28. Beaker studies also suggested that reduction processes promoted rapid decontamination. BWR pipe specimens which included freshly-cut metal surfaces had higher decontamination rates than specimens where the exposed metal was coated with silicone.(9) The observation suggested that corrosion of the fresh metal produced electrons (e.g., $\text{Fe}^0 \rightarrow \text{Fe}^{+2} + 2\text{e}$) which were available for reduction of species in the radioactive film.

29. The PWR films showed some mildly favorable responses to oxidizing reagents, agreeing with the hypothesis proposed above. However, the response was not dramatic. In fact, the PWR films also have shown favorable responses to reducing conditions. (4)



3000X

Fig. 3A Crud/Oxide Flake Separated From Inconel-600 Steam Generator Tube IP2-3-7 During Decontamination Treatment at 180°C



2000X

Fig. 3B Crud/Oxide Flake from IP2-3-7; Oriented to Show Side Exposed to Reactor Coolant

Table 2 - Summary of PWR Film Characteristics on Inconel-600 Steam Generator Tubing:

Table 2 - Summary of PWR Film Characteristics on Inconel 600 Steam Generator Tubes						
Feature	Composition ^{a)}					Remarks
	Fe	Cr	Ni	Si	Zn	
A - Tube IP2						
Superficial Particles 2 to 9µm	40-86	4-15	7-40	2-5	t	See Fig. 2, right-hand views
Compact Layer <i>in situ</i>	11	23	63	1	2	Analysis of cross section, near film outer edge; base metal shine probable
Compact Layer detached	14	55	18	10	3	Separated from base metal by HEDTA/OXALIC acid reagent, 120-150°C ^{b)}
Compact Layer detached	9	40	19	17	t	Separated from base metal by HEDTA acid reagent, 180°C ^{b)}
B - Tube I-4-30HL						
Superficial Particles 2µm	18-31	18-26	40-60	2-4	0-2	--
Compact Layer <i>in situ</i>	31	26	40	2	2	Film up to 3µm thick; minimal base metal shine
Compact Layer detached	35	29	31	4	2	Film flakes separated from base metal by EDTA/H ₂ O ₂ reagent at 180°C ^{b)}
Compact Layer detached	24	46	28	3	-	Film flakes separated from base metal in methanol-Bromine at 25°C
Film Removed by Scraping	29-34	25-27	36-38	3-7	1-2	Some base metal possible--appears minimal

a) Determined by Energy Dispersive X-ray (EDX); not fully calibrated; percent metallic species, normalized to 100%.

b) Reagents also include boric acid and lithium hydroxide, characteristic of PWR system chemistries.

30. On the hypothesis that the radioactive species are largely present at substitutional positions in the compact oxide, removal of the radioactivity appears to require partial or complete dissolution of the oxide, depending on the degree of activity reduction required. On this hypothesis, it does not appear possible to remove the radioactive species (e.g., ^{60}Co) by selective dissolution even though higher ratios of ^{60}Co to removed film were observed. This conclusion also was reached by other investigators. (4)

31. It is important to minimize post-decontamination activity buildup associated with corrosion of the decontaminated surfaces. Our studies on oxidized laboratory specimens suggest that the post-reagent film growth at reactor temperatures was proportional to the amount of oxide dissolved during the reagent treatment. (9) This suggests that modest DFs* may leave some protective oxide, minimizing subsequent corrosion. This supposition has not been confirmed on reactor specimens in our studies.

32. The BWR films comprise Fe_2O_3 and a range of spinels, some soluble in common reagents; some insoluble. The particulate species which remain undissolved after reagent treatments include Fe_2O_3 and certain spinels, apparently those with relatively high Cr contents (~18%). However, the major fraction of the radioactivity is soluble and therefore may be removed by ion exchange, while particulates can be removed on filters. This technology has been demonstrated in dilute reagent decontamination performed in Canadian reactors. (11)

33. The PWR films comprise a variety of spinels and oxides. (12) Our analyses indicate that the sparse population of superficial particles tend to be high in Fe, but have a wide range of compositions (Table 2). The radioactive oxide layer is sometimes less than one micron thick. The relative insolubility in common reagents probably relates to the high Cr content (30 - 55%, Table 2). However, we have been able to achieve relatively effective decontaminations by metal ion reduction, (4) or by both oxidizing and reducing reagents which undercut the film, resulting in a large fraction of the activity being removed as particulates.

* $\text{DF} = \frac{\text{Radiation Level Before Decontamination}}{\text{Radiation Level After Decontamination}}$

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ACKNOWLEDGMENTS

The following have made significant contributions to this study: R.L. Dillon, J.L. Daniel, J.E. Coleman, D.B. Mackey, and R.L. McDowell. We are grateful to the Electric Power Research Institute (EPRI) for permission to publish the results of this study.

