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MASTER

MAGNETITE IN LOFT PRIMARY COOLANT SYSTEM

H. W. Schutz

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H. W. Schutz	52161-900-520	
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LOFT PRIMARY SYSTEM MAGNETITE DEPOSITSI. INTRODUCTION

An ERDA-ID letter of 4-17-76 from R.E. Swanson to L.F. Burdge, then of ANC, stated "Recent samplings of the LOFT primary system water have disclosed significant deposits since conducting Test L1-1. We are not aware of any preplanning which ANC may have performed in anticipation of this problem, but we now believe the consequences of this condition warrant further evaluation for LOFT operation." The letter then listed six questions; these are repeated below and followed by the corresponding answers. A later question by R.E. Tiller in his letter of 6-11-76 to L.F. Burdge is also answered.

II. ANSWERS TO QUESTIONS

Question 1: Was the initial preconditioning properly done?

Answer: Yes, except that temperature cycling may have increased the amount of magnetite produced.

A short description of the chemical mechanism most likely involved in preconditioning (opinions do not totally agree) may help. The typical protective oxide coating found on austenitic (300-series) stainless steel exposed in air is $M_2O_4SiO_2 \cdot nH_2O$ where M is about $7/12Fe + 2/12Ni + 3/12Cr$ and $n \approx 9^{[1,2]}$. However, when this coating is exposed in water and heated, the chromic oxide portion converts to soluble chromate. (The combined silica will also become increasingly soluble.) Opinions differ on the threshold temperature of chromium conversion but agree that once the chromium dissolves, the solid remainder eventually becomes magnetite, Fe_3O_4 , a protective coating as long as it remains in place. Magnetite formed on 300-series stainless is apparently more protective than magnetite formed on carbon steel, for reasons yet unknown. Note that preconditioning really requires a small amount of corrosion in order to form the protective film (plus soluble Cr and Ni corrosion products), and that preconditioning serves primarily to permit nonadherent corrosion products to be produced at a time when removal is simpler.

The temperature fluctuations mentioned earlier can disrupt the freshly formed magnetite coating by creating differential thermal contraction stresses. Calculations indicate that a drop of about 280°F from the temperature of formation will be sufficient to at least crack magnetite. Rate of temperature change is probably of no consequence with such a thin film, but each temperature cycle will produce some loose magnetite. LOFT's total preconditioning time above 350°F before L1-2 was 533.2 hr., equivalent to 22.2 days. However, this comprised seven temperature cycles before L1-1 and three before L1-2, each of which could have caused loss of some magnetite.

The minimum temperature at which chromium in the original oxide coat on 300-series stainless begins to dissolve has been estimated by various parties at from 350°F to > 650°F. LOFT PCS operating temperature is normally 540°F; this is at least as high as, or higher than, any officially recommended preconditioning temperature, regardless of the (uncertain) temperature at which chromic oxide dissolves.

(See Appendix for expanded discussion on magnetite film formation and cracking.)

Question 2: Will these deposits have any adverse effect on instrument operation or calibration as it has been shown to have in steam generators?

Answer: Probably not, since so little is produced. The amount of magnetite trapped on the upper screen of the blowdown ion exchanger (BDIX) during L1-4 was so small that a screen analysis was almost impossible. As to size range, the trapping of particles on 100-mesh screen shows that the largest were > 149 microns (μ); a chemist's visual estimate of the smallest particles was "as small as 5-10 μ ." Much of the trapped material was typical of the construction phase and would not be a recurring load.

No damage is known to occur from the above particle mix in instruments containing no rotating parts. However, purely from the standpoint of particle size, the rotating drag-disc turbine (DDT) flowmeter, which has a shaft-to-bearing clearance of 0.001 in. (25.4 μ) on the diameter, could be damaged or stopped by particles of magnetite (or any other hard material) only slightly smaller than 25.4 μ .

In any case, only three additional practical steps are known for reducing production of loose magnetite: (a) minimize the number of cooldowns, which is impractical from the standpoint of test requirements; (b) add hydrogen and/or hydrazine to the PCS, and these are already being done; and (c) to the extent permitted by experiments, control pH and temperature to minimize solution of magnetite (see Fig. 1).

(See Appendix for additional data on (1) advantages of hydrogen addition, and (2) probable self-limiting effect in crud deposition.)

Question 3: Can the purification system be used without the ion exchanger becoming clogged and unable to perform its function?

Answer: Yes. During the last four LOCE's, the purification system ion exchanger (CPIX) has performed without clogging. At least part of the performance is due to the following:

(a) Before a blowdown occurs, the purification system is sealed off from the primary coolant and blowdown systems. This protects the CPIX from the worst crud.

(b) During cooldown, purification system flow bypasses the CPIX.

(See Appendix for expanded discussion by others on use of ion exchangers as filters, and for calculations of expected production of magnetite.)

Question 4: Is the remaining magnetite protection on primary surfaces providing adequate protection, or should a re-preconditioning be performed after each blowdown?

Answer: Preconditioning really involves the dissolving (corroding) of the chromium and nickel components out of a surface layer of the 300-series stainless steel in the PCS, and the re-formation of the remaining iron as magnetite^[5,7,11,12,13]. Since this protective magnetite layer is formed at the cost of consuming a small part of the vessel and pipe walls, preconditioning cannot be justified on the grounds that additional protection is being produced compared with normal operating conditions. Preconditioning is more a creator of crud than a preventer of it. The only advantage in additional preconditioning would be to permit generating, then removing, the products of early corrosion before they could collect on the core or become activated by it.

Regardless of the desirability or undesirability of preconditioning immediately before a LOCE, creation of some new magnetite will occur during each heatup, and loss of some of this magnetite from the walls will occur on cooling. Therefore, since production of a large fraction of the magnetite cannot be totally restricted to the prenuclear part of a LOCE, re-preconditioning does not appear worthwhile.

Question 5: Will activation of these particles cause a radiation and/or contamination which would seriously impact the ability to perform maintenance?

Answer: The circulating particles will, of course, activate to an extent as in any reactor. However, the survey by Sawochka, et al^[20] of 13 operating PWRs permits estimation of the rate of increase (about 0.9 mR/hr for each nuclear LOCE). Since the maximum allowable yearly dose per worker varies between 500 mrem and 5000 mrem, depending on the situation, many LOCEs can be performed before worker exposure to the system becomes dangerous.

Hartley of Connecticut Yankee appears to challenge the Sawochka-EPRI survey by showing unexpected local concentrations (in ion exchangers, etc.) in the range 100-1000R. The major portion of the activity was traced to soluble cobalt-58 derived from nickel-58. Hartley et al suspected the Inconel 600 steam generator tubes and the fuel assembly support grids of supplying most of the Co-58. However, Sawochka et al point out that since the beginning of Core II, all Connecticut Yankee fuel rods are clad with stainless, not zircaloy-4. The corrodible surface area of fuel rods is about 30% of that in the corresponding steam generator, and fuel rods are, of course, in a much better position to become activated.

(See Appendix for expanded discussion and calculations of radiation level increase rate.)

Question 6: Can the magnetite be easily removed from the system, or are design changes necessary for easy removal?

Answer: That no PCS design changes will be necessary is argued by the following points:

- (a) References 6 and 20 indicate that the rates of solids production and radiation increase will be small, about 93 gm and 0.91 mR/hr per LOCE.
- (b) The suspended solids load is not as heavy as first envisioned. Table 2 shows crud (suspended solids) in the PCS and BST before and after L1-2, L1-3, and L1-3A. Only one of 18 readings was over the allowable 1 ppm in either, and that condition lasted only 45 minutes.
- (c) Magnetite is somewhat more easily removed from the PCS than from a standard PWR because of LOFT's blowdown system.
- (d) Provision for a backup chemical means of removal exists: Burrill^[24] states that magnetite crystals, even after forming,

may be subject to alternate dissolving and regrowth due to changes in temperature around the circuit, or to changes in pH from one time to another^[21].

Based on anticipated magnetite buildup (see Questions 4 and 5) and reported deposition mechanisms^[21,24], no changes are believed necessary to the PCS design at this time.

Question 7: An additional question, raised in ERDA letter R.E. Tiller to L.F. Burdge, June 11, 1976, is whether to precondition after core load.

Answer: As previously described, the primary objective of preconditioning is to permit the high-rate corrosion to occur before actual operation, so that soluble and nonadherent insoluble corrosion products can be removed before they can radioactivate or deposit on the core. Since after core load, however, there will be no convenient chance to flush such products until an actual LOCE, there is no real point in preconditioning after core load. The secondary objective of preconditioning, conversion of all the adherent iron corrosion product to magnetite, will occur during operation just as during preconditioning, so that preconditioning cannot be justified on this ground.

In a normal LOFT heatup, the PCS will require from 16 to 168 hours to heat from 212°F or 350°F (the minimum temperature of magnetite formation depending on the authority cited) to 540°F. When one recalls that reactor makers' preconditioning times fall in the range 72-240 hours, and when Figure 2 shows that the bulk of the corrosion occurs in the first 120 hours, it can be seen that most of the corrosion aspect of preconditioning will occur in LOFT whether it is desired or not.

No need to precondition the zircaloy-4 cladding is seen. Sawochka et al^[21] quote Fletcher's estimate^[22] of corrosion products formed in PWRs: "Negligible corrosion product contribution from the 5,600 m² of zircaloy-4 cladding was estimated."

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TABLE II

UNDISSOLVED SOLIDS MEASUREMENTS DURING LOFT BLOWDOWNS

<u>LOCE DATE</u>	<u>LOCE NO.</u>	<u>PRIMARY COOLANT SYSTEM</u>		<u>BLOWDOWN SUPPRESSION TANK</u>	
		<u>U.S. Before</u>	<u>U.S. After</u>	<u>U.S. Before</u>	<u>U.S. After</u>
5/10/76	L1-2	0.1 ppm (5/10)	0.175 ppm (5/14 1670) 0.1 1820 <0.1 2000	0.1 ppm (5/10)	0.5 ppm (5/11 0430) 0.43 0530 0.1 1130 0.01 1330 0.01 1730
6/28/76	L1-3	0.5 ppm (6/28)	<0.1 ppm (7/8) no cleanup required	<0.5 ppm (6/28)	0.5 ppm (6/28 2330) <0.5 <0.1 (6/29 0400)
7/15/76	L1-3A	0.1 ppm (7/15)	<0.1 ppm (7/21)	0.1 ppm (7/15)	1.6 ppm (7/16 0600) 0.25 0645 0.18 0745 0.25 0815 <0.1 0845

- Source of Data: Notebook of D. E. Smoot, Plant Chemist

Fig. 1 Solubility of Fe_3O_4 in Solutions Saturated with H_2 at 1 atm. at 25°C.

SOURCE:

- ORNL-TM-1667

- pH'S FROM COMF-700314

Figure 2. Corrosion Rate of AISI Type 347 Stainless Steel at 600F. [26]

APPENDIX A

EXPANDED DISCUSSION

Question 1 - Expanded Discussion

Combustion Engineering Co. (CE) in its report Recommendation for LOFT Primary System Chemistry Control recommended (in 1971) preconditioning at or above 350°F before boric acid addition, but gave no time requirement. This was questioned by the writer, not because it was thought wrong but because insufficient, vague, or no basis for the recommendations was given.

The 350°F minimum preconditioning temperature was questioned because of a 1976 telecon with John Griess of ORNL^[3], in which he stated that above 250°C (482°F), the Cr_2O_3 in the protective oxide coating on 300-series stainless oxidized to chromate and dissolved in the water. D. D. Whyte^[4] of Westinghouse, when asked to comment on Griess' statement, said, "The statement is probably true only in the presence of dissolved oxygen (concentration not stated - HWS). In the absence of dissolved oxygen, stainless will resist breakdown to at least 650°F." Whyte's statement is now believed overoptimistic, as Reference 5 shows magnetite forming from stainless as low as 572°F and Reference 6 at 500°F, the lowest temperatures investigated in each case. Furthermore, data from Reference 7 indicate that (a) corrosion rates on 304 SS typical of 300-series stainless, increase rather uniformly, at least between 200°F and 400°F; and (b) 200 ppb dissolved oxygen is actually protective to 304 SS compared with 3 ppb oxygen, as shown:

TABLE IEFFECT OF TEMPERATURE AND DISSOLVED OXYGEN ON CORROSION OF 304 SS

<u>Temp.</u>	<u>Corrosion Rate</u> (mg/dm ² mo)		<u>Corrosion Product Release Rate</u>	
	<u>3 ppb O₂</u>	<u>200 ppb O₂</u>	<u>3 ppb O₂</u>	<u>200 ppb O₂</u>
100°F	--	<0.1	--	<0.1
150°F	0.8	<0.1	0.8	<0.1
200°F	0.7	<0.1	0.7	<0.1
250°F	1.0	0.6	1.0	<0.1
300°F	2.1	1.2	2.0	<0.1
350°F	3.5	1.4	3.4	<0.1
400°F	7.5	1.5	7.3	0.1

Reference 6 tends to confirm the Table I data; it states, "Degassed water seemed to be somewhat more corrosive than water containing about 2 ml oxygen per liter of water" (2.8 ppm).

Westinghouse prefers to precondition at regular PCS operating conditions of 540°F and 2200 psig but without boric acid,^[4] probably so that undesired dissolved materials can be drained without loss of boric acid. Inquiry of CE as to why it chose 350°F elicited the answer, based on References 8, 9, and 10, that iron corrosion products formed below 350°F would not convert to magnetite until 350°F was exceeded. There is apparently some basis^[5,11,12,13] for that answer. On the other hand, Burrill's statement^[14,15] that "ferrous hydroxide converts to magnetite at 212°F" suggests a lower conversion temperature. Only Brush & Pearl's work (Table I) indicates that the protective spinel-type oxide coating on austenitic stainless begins to fail in pure water as low as 150°F.

CE recommends preconditioning 7-10 days above 350°F. It claims that this treatment will result in (a) a full coat of magnetite on the stainless, and (b) the maximum corrosion rates on the stainless having occurred before core load, thus minimizing the potential crud load on the core^[4].

A slightly different order of events (but with the same net consequences) is proposed by Burrill, a Canadian investigator: "Corrosion adds dissolved metals to the loop continuously. Therefore, at least one of these metals must precipitate at some temperature and location in the circuit. The metal, probably iron, crystallizes (as Fe_3O_4 -HWS) on the heated or cooled surfaces and may control the movement of minor elements, such as nickel, chromium, and cobalt. These elements are grown into the iron oxide crystals as they form and are released when the crystals dissolve^[24].....The water chemistry was varied by changing the pH additive (LiOH , NH_4OH), the pH, the dissolved hydrogen concentration....Heavy deposits (up to 40 g Fe/m^2) were formed by crystal growth. In the absence of crystal growth only light deposits (<0.1 g Fe/m^2) were formed by particle deposition and indicate release by dissolution^[25]....Repeated batch additions of small amounts of magnetite slurry had no effect on the suspended particle concentration^[25].... Water velocity had no large effect on the deposit weight of iron on fuel sheaths exposed to neutral boiling water."^[25] D. H. Charlesworth, also of AECL, observes,

"Our observations show that iron oxide deposits on fuel elements very quickly reach a steady state under steady conditions and do not continue to increase with time." [27]

Magnetite formed at operating temperature (540°F for LOFT) is relatively free of stresses imposed on it by the stainless on which it forms, but cooling produces stresses due to differential contraction. Thermal expansion coefficients for pertinent materials in the pertinent temperature range are:

<u>Material</u>	<u>Expansion Coefficient μ</u>		<u>Ratio $\mu\text{Fe}_3\text{O}_4/\mu\text{ metal}$</u>
Magnetite, Fe_3O_4	5.9×10^{-6} (ave. 68°-572°F)	7.5×10^{-6} ~572°F [16]	--
300-Series SS	9.6×10^{-6} (ave. 68°-572°F)	10.3×10^{-6} ~572°F [17]	1.37 near 572°F
carbon steel	6.5×10^{-6} (ave. 68°-572°F)	8.2×10^{-6} ~572°F [18]	1.26 near 572°F

The above figures shown that during each cooldown from operating or preconditioning temperature, the magnetite formed at that temperature will be under considerable internal tensile stress, tending to crack it and shear at least some of it off its 300-series stainless base. The modulus of elasticity of magnetite is 16.6×10^6 psi [16]. Unfortunately, its ultimate strength is unavailable, but if we assume it to be 13,000 psi (the strength of its crystallographic mate, spinel, MgAl_2O_4), calculation shows that a temperature drop of 280°F would produce the stress necessary to crack the adhering magnetite and probably dislodge it from the spot where it was formed.

The effect of boric acid is limited mainly to its mild effect on pH, which influences the solubility of magnetite. [Fig. 1; Refs. 21,24]

Question 2 - Expanded Discussion

Wohlberg [6] states: "Hydrogen concentrations greater than 50 ml H_2 per liter of water had a very definite effect in reducing the corrosion rates of the 300-series stainless steels to very low values. The corrosion rates were about $1 \text{ mg/dm}^2\text{mo}$ ($0.01 \text{ mg/cm}^2\text{mo-HWS}$) after 1500-2000 hr. The largest gain in weight, $3 \text{ mg/dm}^2\text{mo}$ ($0.03 \text{ mg/cm}^2\text{mo-HWS}$), was noted after 250 and 500 hr test; thereafter, no changes occurred." (The higher corrosion rates earlier in the test are typical, not unusual; rates usually begin high and taper off [Fig. 2] except in rare cases involving rather catastrophic degradation.)

An experimental reactor such as LOFT with its frequent temperature cycling is bound to create more loose crud per operating hour than a power reactor operating at more nearly constant temperature.

Question 3 - Expanded Discussion

Ion exchangers act as filters and are expected to act so. Wohlberg^[6] stated in 1953: "The effectiveness of ion exchangers has sometimes been overshadowed by the fact that they were also acting as filters. They contribute to reducing the deposition problem in the following ways: (a) reducing soluble impurities which might become radioactive and create a radiation hazard, (b) removing impurities which might retard the recombination of oxygen and hydrogen, (c) minimizing corrosion by maintaining proper water conductivity, and (d) retaining charged particles by electrostatic forces on ion exchange resins."

Cohen^[19] states, "Filtration at low temperatures is not widely utilized in nuclear power plant primary systems because the ion exchangers included in the purification system are reasonably effective filters....Although the issue is not yet settled, it appears that the use of ion exchange bed filters is being widely adopted in conventional power plant practice."

Two estimates of the crud load generated exist:

- A. Wohlberg and Kleimola, dealing with an all-stainless system, state:^[6]
 "With a corrosion rate of 0.05 mg/cm²mo for AISI Type 347 stainless steel, there will be produced in 6 months of steady-state operation of the Mark I system (area about 6000 sq. ft or 5.6x10⁶ cm²) about 1700 gm of magnetite." Converting the foregoing to an annual basis, the rate of magnetite production becomes:

$$\frac{1700}{(1/2)(5.6 \times 10^6)(10^{-4})} = 6.1 \text{ gm/m}^2 \text{ yr (from Type 347 SS surface)}$$

- B. Sawochka et al,^[20] quoting Fletcher's^[22] calculations on a Westinghouse PWR-type reactor, state, "In a PWR system, the major corrosion product input to the primary coolant occurs from the Inconel 600 or stainless steel steam

generator tubing. Fletcher has estimated that 114 kg/yr of corrosion products will be produced with the Westinghouse reference chemistry with LiOH and boric acid and a pH of 6.4 to 7.7 @ 300°C (572°F) from a system with 18,600 m² of exposed Inconel 600 and 470 m² of stainless steel. Negligible corrosion product from 5,600 m² of zircaloy-4 cladding was indicated."

Reducing Fletcher's calculations to an annual basis, we have:

$$\frac{1.14 \times 10^5}{(1.86 + 0.047)10^4} = 6 \text{ gm/m}^2 \text{ yr}$$

In spite of Fletcher's Table 4 showing corrosion rates for Inconel 600 of 2 to 6 times those for Type 304 SS @ 315°C depending on pH, the resulting crud production estimate is surprisingly close to that of Wohlberg and Kleimola for Type 347 SS at ~500°F.

- C. The close agreement between the Wohlberg and the Fletcher corrosion rates suggests that a close estimate can be made of the magnetite production per LOCE for LOFT. This was done as follows:

LOFT PCS surface area, calculated by

T. Samuels & J. Lusher: 2559 ft²

LOFT steam generator area, calculated

by T.S., J.L., & D.H. Stevenson: 3272

Total LOFT PCS area, including

steam generator 5831 ft² or 542 m²; 542 x 6 =

3250 gm, expected magnetite production in LOFT for one full operating year. However, each LOCE should involve only about 200 EFPH of operation plus 50 hours of nonnuclear exposure near 540°F; 250/8760 = 0.0285 year. Multiplying 3250 x 0.0285 = 93 gm, expected magnetite production per LOFT LOCE if operation were steady state and long enough to attain low corrosion rates (see Fig. 2). However, since operation is shorter and more irregular, an estimate of twice the 93 or about 185 gm appears more realistic.

Question 5 - Expanded Discussion

The aforementioned EPRI report^[20] permits estimating system radiation build-up from actual experience (10 BWRs and 13 PWRs). Sawochka et al state:

"Shutdown radiation levels on out-of-core surfaces at current generation design BWRs have increased linearly for the first four effective full power years (EFPY) of operation at a rate of ~150 mR/h-EFPY. Levels are expected to increase by a factor of 2 to 3 above those encountered at 4 EFPY after an additional 10 EFPY of operation. Average contact levels on recirculating piping are expected to approach 1 to 2 R/h.

"Trends in shutdown radiation levels on out-of-core surfaces of current generation design PWRs are not as clearly defined as for BWRs. After 4 EFPY, levels on primary coolant piping appear to be 25% to 50% of those at BWRs and to be increasing at a rate of 20 to 50 mR/h-EFPY. After 15 EFPY, radiation levels on primary coolant piping are expected to be between 200 and 600 mR/h.

"Activated corrosion products, particularly Co-58 and Co-60, are the major nuclides leading to observed out-of-core radiation levels in the absence of gross fuel failures."

The applicability of the foregoing to LOFT appears to be as follows. The design equivalent core energy expenditure for each LOFT LOCE is 200 effective full power hours (EFPH) or $200/8760 = 0.0228$ EFPY. Dividing the EPRI high 15-year radiation estimate of 600 mR/h by 15 yields 40 mR/h as the maximum radiation increase per EFPY, barring fuel rod failure. Multiplying 0.0228×40 yields 0.91 mR/h, the expected increase in radiation per nuclear LOCE.

Since no radiation transmittable through the PCS or Blowdown Suppression System (BSS) has a relative biological efficiency (RBE) other than 1, 1 rad in the foregoing calculations can be considered equivalent radiobiologically to 1 rem.

The permissible annual radiation dose per worker without special management permission is 500 mrem; with justified permission the amount may be up to 5 rem.^[23] This means that maintenance workers would be permitted roughly $500/0.91$ or 550 hr annually after L2-1, $500/2(0.91)$ or 275 hr annually after L2-2, $500/3(0.91)$ or 183 hr annually after L2-3, etc.

The question has been asked, "If the entire corrosion product producing the 0.91 mR/h (when uniformly distributed) should become concentrated in the blowdown ion exchanger (BDIX) by circulation within the BDSS (a reasonable possibility), would the resulting radiation constitute a real hazard?" The problem was approached as follows:

Total original PCS corroding area: 5831 ft²
Internal area of BDIX: 28 ft²

The radiation inside the BDIX becomes $0.91 \times \frac{5831}{28} = 190$ mR/hr. However, the BDIX is protected by 4" of lead. According to L. K. ²⁸Poppe, EG&G Safety Standards, the fraction of the original radiation traversing the 4" of lead is only 0.004. Multiplying $190 \times 0.004 = 0.76$ mR/hr, about the same as when the corrosion product was uniformly distributed.