EFFECTIVENESS OF SELECTED DISPERSANTS ON MAGNETITE DEPOSITION AT SIMULATED PWR HEAT TRANSFER SURFACES

Paul Burgmayer[†], Rosa Crovetto[†], Carl Turner[‡], Stan Klimas[‡]

ABSTRACT

The effectiveness of three different dispersants - a polyphosphonic acid (PIPPA); a polymethacrylic acid (PMA); and a hydroxyethylidene methacrylic acid (HEME) - at controlling magnetite deposition has been examined under steam generator operating conditions. Tests in a cycling research model boiler showed that the dispersants resulted in corrosion products with a smaller average size and a bimodal size distribution. At a concentration in the boiler of 10 mg/kg, density weight deposit on heated probes was reduced 4-, 3-, and 2-fold for PMA, PIPPA, and HEME, respectively. PIPPA was the most effective at increasing iron transport out of the boiler. In deposition loop tests using a 59-Fe radiotracer, only PIPPA and HEME were effective at reducing the particle deposition rate under flow-boiling conditions. None of the dispersants had any impact on deposition under single-phase forced-convective flow.

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INTRODUCTION

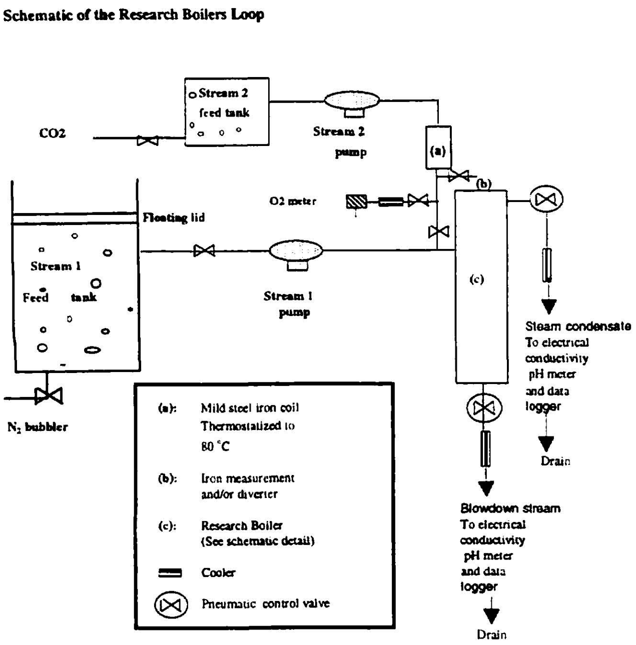
The deposition of iron-based corrosion products and other soluble contaminants in steam-raising plants is a significant problem in both the nuclear and the process industries. Strategies to control the buildup of deposits and minimize corrosion of heat transfer surfaces in the boiler include water treatment to remove soluble contaminants and the addition of an oxygen scavenger along with pH adjustment to reduce corrosion. With gas-fired boilers, where the water boils on the inside of the boiler tube, nonvolatile dispersants are generally added to the boiler feedwater to inhibit scale deposition on the boiler tubes and to reduce the settling rates of corrosion products. Traditionally there has been some reluctance in the nuclear industry to add nonvolatile dispersants to the boiler feedwater because boiling takes place on the shell-side in a nuclear steam generator; however, some utilities are now considering the possibility of adding nonvolatile dispersants to the feedwater to reduce the rate of corrosion product deposition in the steam generators of nuclear power plants.

In this investigation, the effectiveness of selected dispersants to reduce the rate of corrosion product deposition was examined. Both high temperature loop deposition tests, employing an 59-Fe radioisotopic tracer, and model boiler tests were used. The radiotracer tests were performed at Chalk River Laboratories (CRL) under contract to BetzDearborn. They focused on the initial particle deposition rates of spherical particles of magnetite under both single-phase, forced-convective flow and flow-boiling conditions. The model boiler tests were performed in a cycling model research boiler at the BetzDearborn laboratories, and focused on the impact of the dispersants on iron transport, deposit weight density, and particle size of the in-situ formed corrosion product. The dispersants investigated were polyisopropenyl phosphonic acid (PIPPA), an hydroxyethylidenemethacrylic acid (HEME), and a polymethacrylic acid (PMA).

EXPERIMENTAL METHODS

Cycling Model Research Boiler Tests

Test runs were made in Research cycling boilers described elsewhere (1). For this work, four cooled sample ports were added (Figure 1) in different sections of the fluid circulation. Two streams with compositions given in Table 1 were mixed to give the final feedwater to the boiler. The water was cycled up 15 times in the boiler to give a blowdown pH_{25} of 9.5±0.1. Nominal operating conditions for the tests are listed in Table 2.



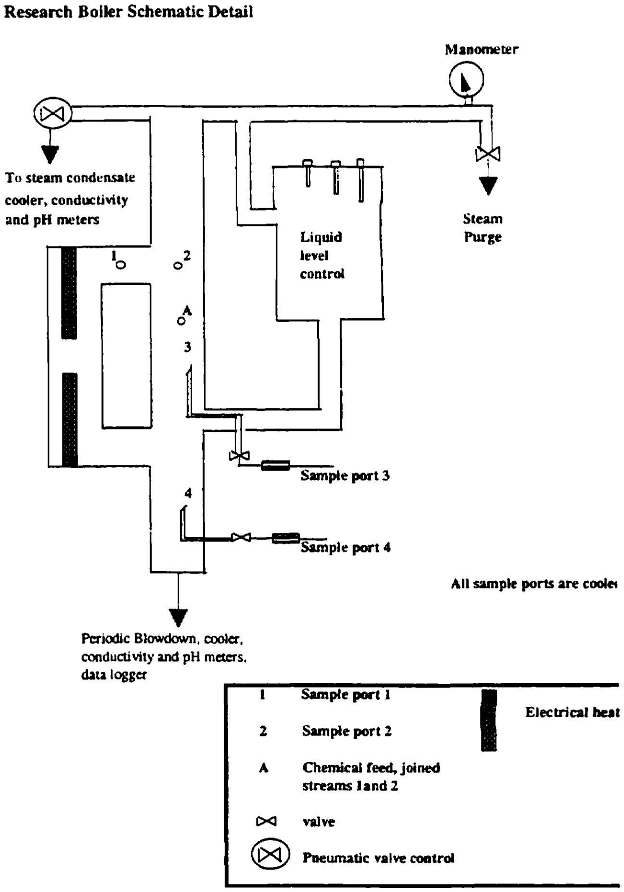


Figure 1(a): Schematic of the cycling research model boiler.

Figure 1(b): Research boiler schematic detail.

Particle size and the total iron concentration of the collected samples were determined. Sampling was performed so as not to disturb the water flow in the boiler. Particle size was measured with a Coultier N4 Plus, which provides particle size measurements from 3 to 3000 nanometers using a light scattering method. Software provided by the manufacturer calculates the diffusion coefficient which is related to the particle size by the Stokes-Einstein equation. The analysis assumes that the particles are spherical. Total iron concentration in the sample was determined by Inductively Coupled Plasma Emission Spectroscopy (ICP).

The boiler water chemistry was adjusted so that only the anions, cations and iron oxides existing in a typical PWR steam generator were present in the boiling liquid phase. Boiler pH was controlled using 3-methoxypropylamine (MOPA). Carbon dioxide dissolved in distilled water was used to produce and introduce soluble iron as iron carbonate from a corroding mild steel coil. Carbon dioxide flashes to the vapour phase in the boiler and leaves the iron behind in the form of precipitates of various iron oxide corrosion products. The corrosion products, thus formed, are cycled up and aged in an amine environment.

Table 1: Composition of streams 1 and 2 used for boiler feedwater.

	Stream #1	Stream #2
Mass Flow (%)	60	40
MOPA (mg/kg)	10	
Hydrazine (mg/kg)	1	
Oxygen (mg/kg)	<0.30 ± 0.10	<0.002
Dispersant (mg/kg)	0-1.33	
pH_{25}	9 .0 - 9.5	5
Iron (mg/kg)	-	soluble = 2 - 3 total = 2.2 - 3.3

At the end of each test, the heated portion of the probes was subjected to a wet chemistry treatment. This treatment consisted of immersing the probes first into a known volume of concentrated HCl solution, then into concentrated HF, and finally scraping them with a plastic spatula to remove insoluble species. The solutions were filtered and the filter paper dried and weighed. The acid solutions were sent for chemical analysis using ICP. The ICP results, weighed insolubles, and the area of the heated portion were used to calculate the deposit weight density (DWD).

The deposit obtained in all cases was 40 to 60% acid soluble. The remaining insoluble residue was sent for X-ray diffraction analysis to determine the phase composition and energy dispersive X-ray analysis (EDX) to ascertain the elements present.

The sample streams were monitored daily for soluble and total iron. Using these data and the total sample flow, the total iron in the cycled up boiler water was calculated. The iron transport is defined as the ratio of the iron removed by blowdown to the total iron injected into the boiler. For the boiler runs with PIPPA, both ortho and total phosphate were also measured in the boiler blowdown samples.

Table 2: Nominal experimental conditions for the model research boiler tests.

Pressure (MPa)	Heat Flux (kW/m^2)	Steaming Rate (kg/h)	Residence Time (h)	Running Time (h)
6.2	790	8.3±0.4	8.3	69

Radiotracer Tests: Initial Particle Deposition Rate

Details of the experimental methods and analyses used to deduce particle deposition rates from radiotracers injected into the loop flow are reported elsewhere (2,3), and are only briefly summarized here. The deposition tests were performed under both single-phase, forced-convective flow and flow-boiling conditions in the H-3 high temperature loop located at CRL. A schematic of the loop is shown in Figure 2 and loop operating conditions are shown in Table 3.

All deposition tests were performed using an Inconel 600 heated test section. The test section was rinsed with hexane and methanol and preconditioned under test conditions for 48 hours prior to the start of each run. Corrosion product was simulated using 0.25 μm particles of magnetite, synthesized by the controlled oxidation of a ferrous hydroxide precipitate (4). Magnetite was irradiated in the NRU reactor at CRL to active 59-Fe and continuously injected into the loop as a suspension at a location approximately 2 meters upstream of the heated test section. Back-washable filters were placed downstream of the test section to prevent the activated corrosion product from being transported around the loop. The pH of the loop water was adjusted to 10 using morpholine. The hydrazine concentration was maintained between 50 and 100 μg/kg and the oxygen concentration was generally less than 10 μg/kg. The suspension of radioactive magnetite was equilibrated with morpholine at pH 10 prior to injection. Dispersant was added to the loop about one hour prior to injecting the magnetite.

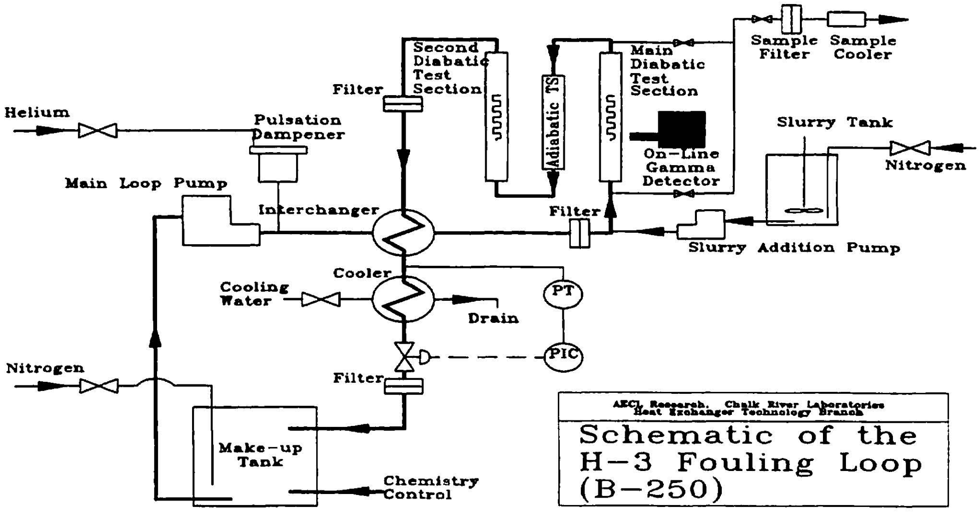


Figure 2: Schematic of the H-3 loop used for the deposition tests.

Loop samples were taken at regular intervals during each test and filtered hot through silver membrane filters with 0.2 μm pore size to determine the particle concentration in the loop. The filtrate was analyzed for dissolved oxygen, hydrazine, and pH. Concentration of PAA and PIPPA dispersants was determined by gel permeation chromatography. No analytical method was available for HEME, so its concentration in the loop water was calculated based on the amount of stock solution that was added to the loop. At the end of the run, the test section was removed from the loop and cut into a number of 30-mm sections. The deposit mass and corresponding deposition rate was calculated from the measured radioactivity of 59-Fe on each section.

A normalized deposition rate, $\rho_{2\phi}K_{2\phi}$, was calculated from the measured deposition rate using:

$$\frac{dm}{dt} = \rho_{2\phi}K_{2\phi}C \qquad (1)$$

The boiling deposition coefficient, a_b was calculated from the deposition rate constant, $K_{2\phi}$ using [5]:

$$a_b = \frac{\rho_{2\phi} H_{f-g} (1-X) K_{2\phi}}{q} \qquad (2)$$

Steam quality was calculated as a function of distance along the test section using:

$$X(l) = \frac{H_{in} + \frac{ql}{FL} - H_{SAT}}{H_{f-g}} \qquad (3)$$

The boiling deposition coefficient is the more fundamental parameter because it factors out the effect of system parameters such as heat flux, mixture density, and steam quality.

Table 3: Nominal loop operating conditions for the radiotracer deposition tests.

Pressure (MPa)	Heat Flux (kW/m^2)	Mass Flux (kg/m^2s)	Re (X=0)	Velocity (X=0) (m/s)	Outlet Quality
5.6	250	300	30,500	0.34	10%

RESULTS

Cycling Model Research Boiler Tests

Deposit on the heated probes was adherent and of a powdery, semicrystalline nature. The dominant color was black with occasional dark maroon bands. Table 4 lists the results of the X-ray diffraction analyses of the insoluble deposits, and shows that the phase composition varied with chemical treatment. Whereas the dominant crystalline phase was magnetite in runs either without dispersant or with PIPPA, there was a trend toward increasing hematite formation with HEME and PMA dispersants.

Deposit control results for PMA, PIPPA, and HEME are shown in Figure 3. The average DWD for the runs without dispersant served as the reference for the other tests. The concentration scale in Figure 3 is expressed as the molar ratio of the repeating unit in the polymer to the total iron.

Table 4: Phase Composition of deposits for different boiler water chemical treatments.

		Dispersant		
	-	PMA	PIPPA	HEME
Magnetite (%)	97	40±10	95-97	91
Hematite (%)		50±10	-	9

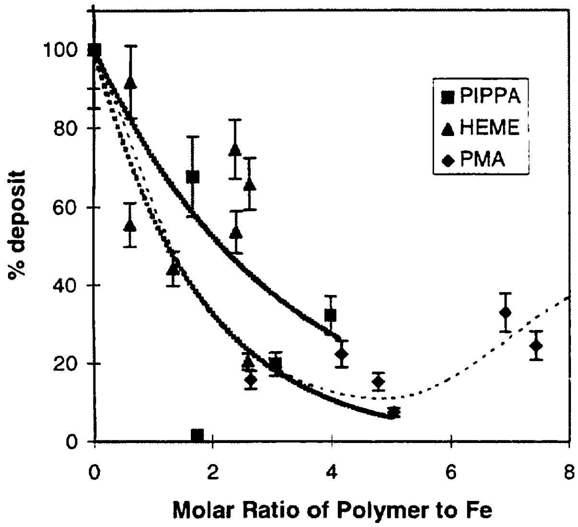
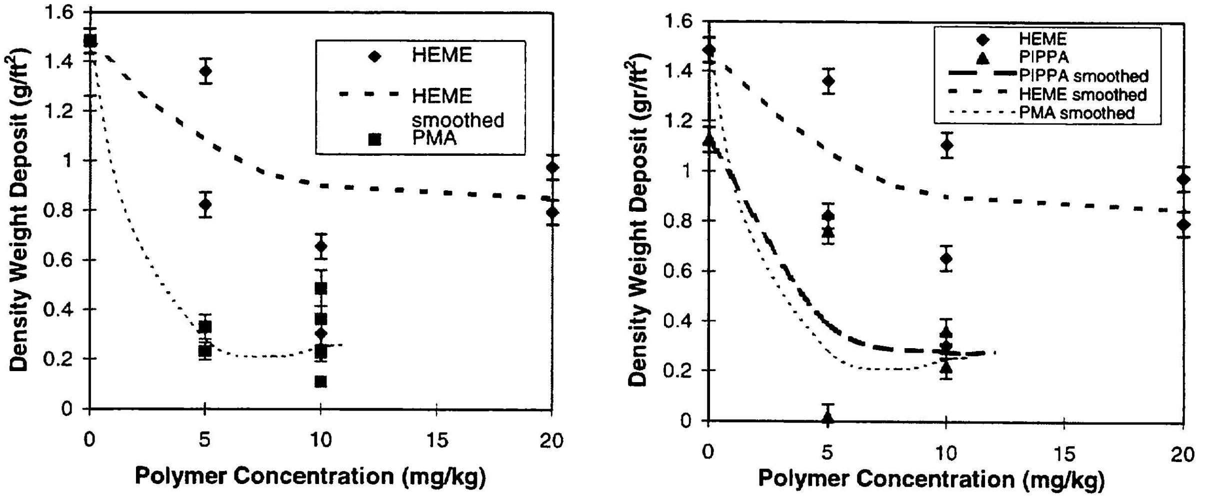


Figure 3: Deposit control results for PMA, PIPPA, and HEME.

Figures 4 (a) and 4 (b) show DWD versus concentration of the dispersant in the boiler for the three dispersants. The results show PMA and PIPPA to be more effective at reducing corrosion product deposition on the heated probe than HEME for the same concentration of polymer. PMA reaches its maximum effectiveness at a concentration of 5 mg/kg, whereas PIPPA continues to reduce corrosion product deposition up to a concentration of 10 mg/kg. HEME is most effective at 10 mg/kg, although not as effective as either PMA or PIPPA.

Figure 5 shows the % iron transport as a function of polymer concentration in the boiler. PIPPA is clearly the most effective dispersant, with over 25% of the injected iron transported out at a dispersant concentration of 10 mg/kg. PMA is less effective, with just over 10% of the injected iron transported out of the boiler at a dispersant concentration of 10 mg/kg; HEME appears to be the least effective with less than 10% transport at this concentration.



(a)

(b)

Figure 4: Density weight deposit (DWD) versus polymer concentration for PMA, PIPPA and HEME.

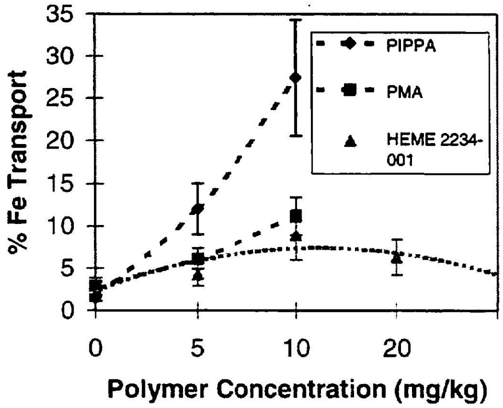


Figure 5: % iron transport versus polymer concentration for PMA, PIPPA and HEME.

The dispersants also had an effect on the particle size distribution of the corrosion products formed in the boiler, as shown in Table 5. In each case, the particle size distribution in the presence of dispersant was bimodal, with some fraction of the particles being formed at an average size that was 6 to 30 times smaller than in the absence of dispersant.

Table 5: Effect of dispersant on particle size of corrosion products formed in the boiler.

	Average Size (μm)	%>2 μm	Bimodal
Blank	0.6±0.2	4-30	No
PMA	0.70±0.10(50%) 0.08±0.01(50%)	0-4	Yes
PIPPA	0.20±0.10(98%) 0.02±0.01(2%)	0	Yes
HEME	0.60±0.20(60%) 0.10±0.02(30%)	0-6	Yes

Radiotracer Tests: Initial Particle Deposition Rate

Figure 6 shows magnetite deposition data for a test with 10 mg/kg of PMA dissolved in the test loop. The radiotracer data from the on-line γ-ray detector is shown in Figure 6 (a). Injection of the active suspension of magnetite started at t = 0. Thereafter, the radioactivity of the heated test section increased steadily over the next 10 hours, signifying a constant rate of particle deposition. Deposition stopped at t = 10 h when the injection pump was switched off and the deposit mass remained constant with continued loop operation over the next 18 h, signifying a negligible rate of particle removal.

Figure 6(b) shows both the normalized particle deposition rate and wall superheat temperature versus mixture quality for the test with 10 mg/kg PMA. This is an example where the addition of dispersant had a negligible effect on the particle deposition rate. The normalized deposition rate was relatively low for mixture qualities less than -0.2, where the heat transfer mode is single-phase, forced-convection. With the onset of subcooled nucleate boiling at X = -0.2, the deposition rate started to increase dramatically with increasing mixture qualify and reached a plateau for X = -0.1 to 0. With the attainment of saturated nucleate boiling at X = 0, the normalized deposition rate started to decrease gradually with increasing mixture quality. A second set of measurements on adjacent 3-mm lengths of the test section showed that the trend with X was real.

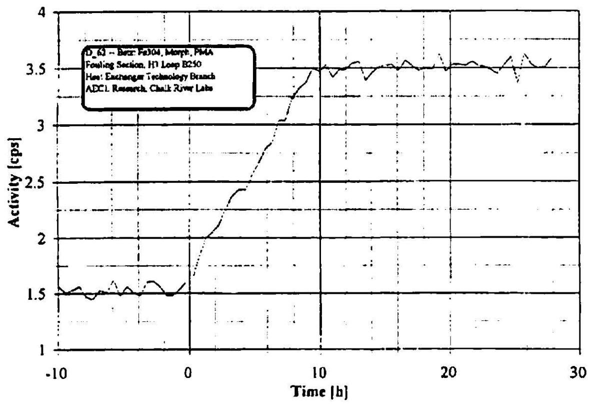


Figure 6(a): On-line radiotracing data for magnetite deposition with 10 mg/kg PMA.

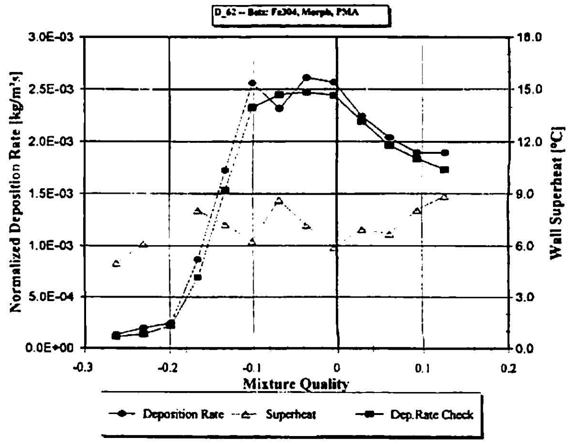


Figure 6(b): Normalized deposition rate and wall superheat versus mixture quality with 10 mg/kg PMA.

Figure 7 shows an example where the addition of dispersant, in this case 10 mg/kg of PIPPA, had a significant effect on the particle deposition rate. The on-line radiotracing data are shown in Figure 7(a). Again, the level of radioactivity on the test section increased linearly with time once injection of the active magnetite suspension was started at t = 0. There was a slight increase in the activity on the test section after the injection pump was switched off, suggesting some movement of active corrosion product from one part of the loop to another. The normalized deposition rate and wall superheat are shown in Figure 7(b). There was no increase in the particle deposition rate with the onset of subcooled nucleate boiling at X = -0.2, and, apart from a "spike" near X = -0.1, the normalized deposition rate remained low throughout the saturated nucleate boiling regime up to a mixture quality of X = 0.1. Repeat measurements on adjacent 3-mm lengths of the test section showed that the "spike" near X = -0.1 was quite localized, with adjacent pieces of tubing having significantly different levels of radioactivity. This suggests that the spike may be the result of some local contamination after the test was completed.

The results of all the tests are shown in Table 6. Included in the table for comparison are normalized deposition rates and wall superheat temperatures for two runs under similar operating conditions but without the addition of a dispersant. The presence of dispersant had no significant effect on the magnitude of the normalized deposition rate under single-phase, forced-convective flow. In one case (HEME 10 mg/kg), the rate was actually higher in this regime. Under flow-boiling conditions, however, PIPPA at 10 mg/kg and HEME at 20 mg/kg reduced the particle deposition rate by factors of 10 and 20 respectively. PMA was not effective under flow-boiling conditions at concentrations of either 10 or 20 mg/kg.

Also shown in Table 6 for each of the tests is the boiling deposition coefficient , a_b, which is equivalent to the fraction of magnetite deposit per kg of liquid evaporated at the heat transfer surface. In the reference cases, i.e., pH 10 adjusted with morpholine, about 1% of the particles that are transported by convection to the heat transfer surface actually deposited when the liquid was vaporized. The presence of PIPPA at 10 mg/kg reduced this to approximately 0. 1%, and HEME at 20 mg/kg reduced the fraction further to approximately 0.05%. Table 6 also shows that all of the dispersants reduced the wall superheat for bubble nucleation, regardless of whether they had any effect on the particle deposition rate.

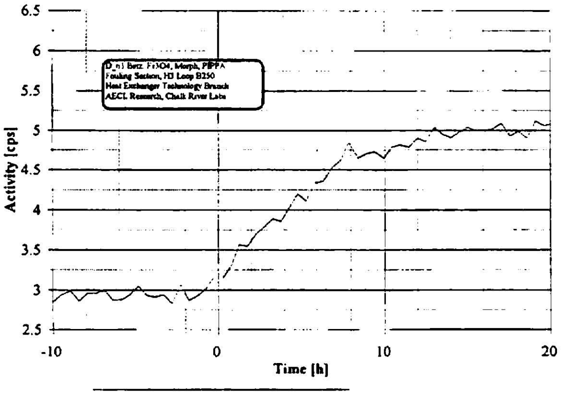


Figure 7(a): On-line radiotracing data for magnetite deposition with 10 mg/kg PIPPA.

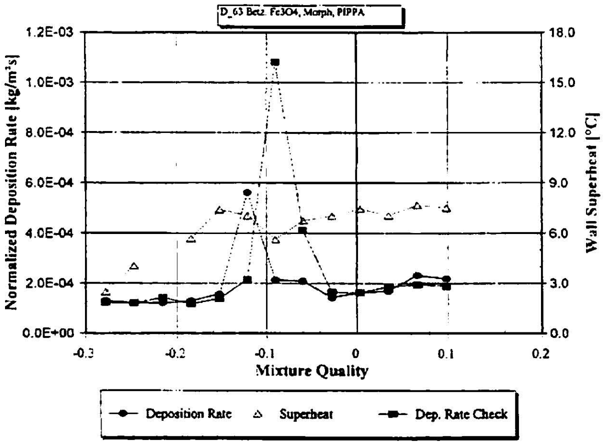


Figure 7(b): Normalized deposition rate and wall superheat for 10 mg/kg PIPPA.

Table 6: The effect of selected dispersants on the normalized deposition rate and wall superheat temperature.

Dispersant	Normalized Deposition Rate, pK (kg/m^{2}s)		a_b (average)	Superheat (°C)
	average for X<-0.2 single-phase	average for 0<X<0.12 saturated nucleate boiling	0<X<0.12	
	#1.6x10^{-4}	1.9x10^{-3}	1.1x10^{-2}	7.5
	#1.6x10^{-4}	1.7x10^{-3}	0.99x10^{-2}	8.5
PMA 10 mg/kg	1.6x10^{-4}	2.0x10^{-3}	1.1x10^{-2}	7.2
PMA 20 mg/kg	0.79x10^{-4}	1.2x10^{-3}	0.72x10^{-2}	6.1
PIPPA 10 mg/kg	1.2x10^{-4}	2.0x10^{-4}	0.12x10^{-2}	6.9
PIPPA 10 mg/kg	0.95x10^{-4}	1.6x10^{-4}	0.090x10^{-2}	6.1
HEME 10 mg/kg	7.4x10^{-4}	1.7x10^{-3}	0.94x10^{-2}	6.8
HEME 20 mg/kg	1.0x10^{-4}	8.3x10^{-5}	0.049x10^{-2}	5.5

DISCUSSION

We have used two independent, complementary methods to assess the effectiveness of dispersants in preventing tube deposition under boiler operating conditions. In the research model boiler cycling tests, the corrosion products were formed in-situ in the presence of dispersant, thus capturing the effect of the dispersant on the particle size. The effectiveness of the dispersant in preventing tube deposition was assessed on the basis of both the percentage of iron that was removed from the boiler by "blowdown" and by the deposit weight density (DWD) in tests lasting up to 69 hours. For the radiotracing tests in the H-3 loop, preformed corrosion product was injected into the loop. The particle deposition rate was then measured under both single-phase, forced-convective flow and flow-boiling conditions on a heated test section immediately downstream from the point of injection. This latter method measured the effect of the dispersant on the early stage of particle deposition in 10 hour tests before much deposit had formed on the heated surface. It also provided useful information about the rate of particle removal, or re-entrainment, from the heat transfer surface.

All three dispersants had an effect on the particle size of the corrosion products formed in the boiler, producing a bimodal particle size distribution with one size fraction 6 to 10 times smaller than the other. In addition, PIPPA shifted the size of the larger particles from 0.7 to 0.2 µm, whereas with PMA and HEME the larger particles were about the same size as those formed without dispersant. A reduction in particle size will reduce the rate of gravitational settling in the boiler, which may have contributed to the increased iron transport in tests with dispersant. The three dispersants also reduced the extent of fouling on the heated probe in the model boiler tests and increased the rate of iron transport out of the boiler. Both PMA and PIPPA reduced the DWD between 3 and 4-fold at a dispersant concentration of 10 mg/kg, while HEME reduced it about 2-fold. Thus, PMA and PIPPA proved to be more effective at preventing deposition on the heated probe than HEME. The iron transport data showed a significantly higher iron transport rate out of the boiler with PIPPA than with either HEME or PMA, whereas one would have expected PMA and PIPPA to show comparable iron transport rates based on the DWD results. However, it should be noted that corrosion product that does not deposit on the heated probe will either settle out somewhere in the boiler or be removed by "blowdown." The particles formed in the presence of PIPPA tended to be smaller than those obtained with the other dispersants. Smaller particles have a lower settling velocity than larger ones, which will favour their removal by "blowdown" as opposed to settling out in low flow regions of the boiler.

The radiotracer tests in the H-3 loop gave complementary information which provides insights into the mechanism by which dispersants may control particle deposition. In the H-3 tests, PMA did not reduce the particle deposition rate under flow-boiling conditions, whereas both PIPPA and HEME did. In addition, PIPPA and HEME reduced the deposition rates significantly more in the H-3 tests than might have been expected from the model boiler runs. Finally, the radiotracer deposition tests in H-3 loop testing showed clearly that dispersants which reduced the deposition rate under flow-boiling conditions still had no effect on the deposition rate in single-phase, forced-convection.

For the H-3 tests, the dispersant was added only to the loop makeup tank (see Figure 2) and not to the slurry tank which contained the radioactive suspension of magnetite particles. This was done deliberately to minimize the time available for the dispersant to adsorb onto the surfaces of the particles. In this way, we could test the hypothesis that dispersants affected particle deposition through some aspect of the boiling process rather than through adsorption onto the surface of the particle. That dispersants which reduced the particle deposition rate under flow-boiling conditions had no impact under single-phase, forced-convection flow supports this hypothesis. This might not be the case for PMA, however, which reduced corrosion product deposition in the model boiler but not in the H-3 loop tests. The lack of a clear correlation between wall superheat temperature and deposition rate also suggests that the relationship between boiling and deposition is not very simple.

All three dispersants reduced deposition in the model boiler tests, whereas only PIPPA and HEME (at 20 mg/kg) reduced the deposition rate in the H-3 loop tests. The model boiler tests were designed to replicate the field conditions as closely as possible. Thus, the effect of dispersants on the nucleation and growth of the corrosion products was captured in the model boiler tests. Also, there was sufficient residence time in the boiler for the dispersant to influence deposition through both adsorption and modification of the surface tension of the liquid/vapour interface of the growing steam bubbles. Although model boiler tests provide a good simulation of how dispersants will perform in a field application, they do not necessarily provide a determination of the mechanism controlling deposition. In the H-3 loop tests, preformed corrosion product is injected into the loop and the deposition rate measured at a location immediately downstream of the injection point. Although these tests do not replicate the field conditions exactly, they enable one to examine the importance of specific mechanisms on the deposition process. Both tests identified PIPPA as an effective deposit control agent; the results from the H-3 tests suggest that the mechanism for deposit control is related to the effect of PIPPA on surface tension. PMA performed well in the model boiler tests, but was ineffective in the H-3 tests. Thus, surface adsorption may be a more important factor in determining the effectiveness of PMA as a deposit control reagent than surface tension. Identification of the mechanism responsible for deposit control is important, and can ultimately be used to help optimize specific properties of the dispersant molecule for effective use in the field.

In addition to reducing tube bundle deposition and increasing iron transport through the boiler via "blowdown," dispersants may also alleviate (to some degree) the negative impact of thermal performance degradation in nuclear power plants by reducing the wall superheat temperature for bubble nucleation in a steam generator (See table 6). The average wall superheat in the H-3 tests was 1.6°C lower in the tests with dispersant. In a PHWR CANDU plant that operates at constant boiler pressure, this would result in a 1.6°C reduction in the primary coolant temperature. In a PWR plant operating at constant primary coolant temperature, this reduction in wall superheat temperature would increase the boiler pressure by approximately 0.24 MPa (~34 psig). In both cases, this corresponds to a significant fraction of the "fouling margin" allocated to the steam generator at the design stage to take account of all factors that will contribute to a loss in thermal performance throughout the plant life.

ACKNOWLEDGMENTS

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NOMENCLATURE

a_b = boiling deposition coefficient
l = distance along test section (m)
m = deposit mass (kg/m^2)
q = applied power (kW)
q = heat flux (kW/m^2)
t = time (s)

C = concentration (kg/kg)
F = flow rate (kg/s)
H = enthalpy (kJ/kg)
K = deposition rate constant (m/s)

L = test section length (m)
X = mixture quality -

ρ = density (kg/m^3)

Subscripts

2ϕ = two-phase
f-g = vaporization
in = inlet
sat = saturation

REFERENCES

(1) J.J. Schuck, I.T. Godlewski, "Development of Boiler Water-side Deposit Control Agents: from Laboratory through Industrial Application," 40th International Water Conference, Pittsburgh, PA, USA, Oct. 30 - Nov. 1 (1979).

(2) Turner, C.W. and M. Godin, "Mechanisms of Magnetite Deposition in Pressurized Boiling and Non-Boiling Water," Second International Steam Generator and Heat Exchanger Conference, Toronto, Canada, June 13-15 1994. AECL- 11046, COG-94-66 (1994).

(3) Turner, C.W., S.J. Klimas, and M.G. Brideau, "The Effect of Alternative Amines on the Rate of Boiler Tube Fouling," C.W. Turner, S.J. Klimas, and M.G. Brideau. Atomic Energy of Canada Ltd. Report - 11848 / Electric Power Research Institute Report EPRI TR 108004 (1997).

(4) T. Sugimoto and E. Matijevic, "Formation of Uniform Magnetite Particles by Crystallization from Ferrous Hydroxide Gels," J. Colloid and Interface Sci. 74 227 (1980).

(5) Asakura, Y., M. Kikuchi, S. Uchida, and H. Yusa, (1978), "Deposition of Iron Oxide on Heated Surfaces in Boiling Water," Nuclear Sci. and Eng., 67, (1978) 1.