Proceedings of International Conference on Heat Exchanger Fouling and Cleaning - 2013 (Peer-reviewed) June 09 - 14, 2013, Budapest, Hungary Editors: M.R. Malayeri, H. Müller-Steinhagen and A.P. Watkinson

Published online www.heatexchanger-fouling.com

# THE EFFECTS OF CHEMICAL ADDITIVES ON MAGNETITE DEPOSITION IN BOILING HEAT TRANSFER

C. Gasnier<sup>1</sup> and D.H. Lister

<sup>1</sup> Department of Chemical Engineering, University of New Brunswick PO Box 4400, Fredericton, N.B., E3B 5A3, Canada cyprien.gasnier@unb.ca

## ABSTRACT

This paper investigates the effects of three polymeric dispersants – two types of polyacrylic acid (PAA) and sodium polymethacrylate (PMA) – and a commercial film-forming amine (FFA) on the deposition onto heated nickel alloy of particulate magnetite from suspension in water at about 100°C during sub-cooled boiling and bulk boiling.

In bench-top experiments, ribbons of nichrome immersed in a magnetite suspension are heated electrically with and without additives.. Results show that deposits are less numerous in the presence of polymeric additive. The smaller molecular weight PAA is the most effective at preventing magnetite deposition.

Complementary experiments are carried out in a stainless steel recirculating loop with an electrically-heated heat-exchanger tube of Alloy-800. This latter is exposed to flowing water under the chemistry conditions of the bench experiments. A laser micrometer/profilometer is used to measure the thickness of the deposited magnetite at the end of each run. The use of polymeric dispersant is efficient at mitigating magnetite deposition. Again, the smaller molecular weight PAA is the most effective.

Due to its agglomerating effect on magnetite, one can conclude little about the effect of FFA on magnetite deposition.

## **INTRODUCTION**

Typical power-plant heat exchangers, along the feedtrain from the condenser, for example, raise the feed-water temperature in stages to improve the thermal efficiency. Many other water-cooled exchangers operate at relatively low temperatures for systems other than the main steam cycle. The fouling of these units by corrosion products can have serious implications for the operation of the plant, both in terms of the loss of efficiency and the potential for underdeposit corrosion.

Adding a chemical to the boiler feed-water can reduce fouling. By adsorbing on walls and corrosion-product colloids, the molecules affect surface properties and thus modify fouling mechanisms. Three additives of interest are studied: a commercial film-forming amine (FFA) and the two polymers polymethacrylic acid (PMA sodium salt of molecular weight 9500) and polyacrylic acid (two versions – pure PAA of molecular weight 1800 and PAA sodium salt of molecular weight 8000). Ramminger et al. (2012) showed how FFA in the secondary circuit of a nuclear plant reduced the formation of corrosion products and their transport into the steam generator. They reported that FFA protects the metal by creating a hydrophobic film on its surface that acts as a barrier to charge and/or mass transport. Its effect is particularly beneficial during outages, when moisture and oxygen ingress can lead to rapid corrosion.

The polymeric additives PMA and PAA have both reduced magnetite deposition rates under flow-boiling conditions by up to 75% and 80%, respectively, (Balakrishnan et al. 1999, Burgmayer et al. 1998), probably by stabilising magnetite suspensions in the bulk fluid at higher concentrations than in the absence of additive. Balakrishnan (1999) also found that between two types of PAA, the lower molecular weight was the more efficient at reducing deposition. For the present study, low and very low molecular weight PAA (respectively 8000 and 1800) and low molecular weight PMA (9500) are tested.

These additives are studied in three steps: zeta potential analyses on magnetite and Alloy-800 particles and two types of fouling experiment at low pressure and low temperature. In eleven bench-top fouling experiments, ribbons of nichrome immersed in a suspension of magnetite are heated electrically. Deposition is analysed visually and photographically and with scanning electron microscopy (SEM). Seven complementary experiments are carried out in a stainless steel recirculating loop with a vertical glass column as test section. An electrically-heated heatexchanger tube of Alloy-800 is mounted in the top of the column and exposed to flowing water under the chemistry conditions of the bench experiments but under flow-boiling heat transfer. A laser micrometer/profilometer indicates the thickness of the deposited magnetite at the end of the run.

The loop experiments are conducted with the polymeric dispersants only. All the experiments and analyses presented in this paper are carried out with magnetite synthesized by the solid-state method (Mohajery et al., 2012) and characterized with SEM. The magnetite particle size distribution ranges from 300 nm to 600 nm for the dry powder. Its purity was established using X-ray diffraction measurements to verify the species stoichiometry.

#### **EXPERIMENTAL TECHNIQUES**

#### **Zeta Potential Measurements**

The measurements are performed using a 1 mM potassium chloride solution. Magnetite particles are added to the solution to a concentration of 100 mg/kg (ppm) and pH is adjusted with ammonium hydroxide or hydrochloric acid. Additives are introduced as required to the desired concentration. Zeta potential is measured using a zeta meter ZetaPlus (Brookhaven Instruments Corporation®), which determines the particle mobility between two electrodes using a red laser and the Doppler effect. For each pH value, the arithmetic mean of twenty measurements is recorded.

Alloy-800 powder is obtained by grinding Alloy-800 tubing. The result is very coarse and particles can measure up to 100  $\mu$ m; however, some particles are small enough to behave as colloids and zeta potential measurements can be performed the same way as for magnetite except that larger particles have to be allowed to sediment, leaving the smaller particles in suspension. In order to obtain sufficient particles in the samples, an Alloy-800 concentration of 500 ppm is used along with an electrolyte concentration of 10 mM potassium chloride. The concentration of additives is increased accordingly.

#### **Bench-top Experiments**

The effect of an additive on magnetite deposition during pool boiling at atmospheric pressure is estimated quickly via a bench-top experiment that observes fouling on a thin nickel-chromium alloy (nichrome) ribbon (dimensions:  $25 \ \mu m$  by  $1.5 \ mm$  by  $30 \ mm$ ) heated with the Joule effect to create pool-boiling heat transfer. All experiments last 60 minutes and are conducted in a heated 2-L beaker containing the 30 ppm magnetite suspension suitably conditioned with additive.

A beaker is filled with 2 L of deionised water and the pH at 25°C is adjusted to a final value of 9.9 with ethanolamine, a relatively non-volatile base chosen to minimize evaporation losses. The beaker is placed on a heating plate to raise the temperature to ~100°C. The nichrome ribbon is welded at both ends to copper rods acting as supports and electrical connectors. The ribbon assembly and a mechanical stirrer are cleaned with acetone, rinsed with deionised water and mounted in the beaker. The copper rods are connected to a Variac and 5 amperes are passed through the ribbon, generating about 240  $kW/m^2$  on both faces of the ribbon. The start of a run begins with the addition of 60 mg of magnetite, agitated ultrasonically (sonicated) in deionised water, to the beaker. During the run, the stirring is continuous and the bulk temperature is maintained between 99°C and 101°C. Additives are introduced in two batches, the first at 10 minutes before and the second just after, the addition of magnetite. At the end of a run, the pH<sub>25°C</sub> and magnetite concentration in the beaker are measured and the ribbon is detached from the copper rods for further analysis. A sample of the coolant is mixed with HCl and sonicated at 50°C for 60 minutes to digest the magnetite. Following dilution and pH adjustment with 5N NaOH, the iron concentration in the sample is measured colorimetrically with Accuvac ampoules

(HACH®) and a spectrophotometer. The sample concentration is then used to calculate the magnetite concentration in the original coolant.

The ribbon analyses are mainly qualitative, comprising visual observations, SEM examinations and high-speed video recordings.

## **Recirculating Fouling Loop**

Fouling experiments under sub-cooled flow boiling are also conducted in a recirculating loop that has been described in detail before (Basset, 1999; Cossaboom, 2005).

The loop cooling water is contained in a 180-L tank, where it is purged with nitrogen and its temperature maintained at 93°C. It is pumped upwards through the 1.5m long, 10 cm diameter vertical glass column at a flow rate of 10 litres per minute (LPM). For all the runs reported here, the pH<sub>25°C</sub> is maintained between 9.7 and 9.9 using ammonium hydroxide and the magnetite concentration is kept between 8 ppm and 14 ppm. Prior to addition in the loop, the magnetite is sonicated for at least 1h. Before each run, the loop water is purged with nitrogen in the tank for at least 24h. Magnetite concentration is again monitored by sampling and spectrophotometric analysis. The test section is composed of a 59 cm long Alloy-800 tube, 15.6 mm outside diameter and 12.7 mm internal diameter, containing a cartridge heater so as to generate about 110 kW/m<sup>2</sup> at the tube outer surface. Before each run it is cleaned with dilute nitric acid, rinsed with acetone and then mounted centrally in the top of the glass column.

After each run, the Alloy-800 tube from the test section is scanned with a laser profilometer (TLaser 122) that measures diameters with a resolution of 25 nm; it generates a laser sheet across the sample, which is placed between the laser generator and a sensor that measures the projected shadow (see Fig. 1). Here, the sample is the Alloy-800 tube and the projected shadow size corresponds to its diameter. By comparing the diameter of the fouled tube with that of the tube after cleaning, the magnetite deposit thickness can be measured. To obtain consistent measurements, the tube is held in the chuck of a lathe and the profilometer is mounted on a translating platform, as shown in Fig. 1. As the tube rotates typically at 100 rpm its surface is scanned helically as the platform travels at 20.3 mm/minute. The diameter measurement is continuous at a frequency of 400 measurements per second; software calculates the average diameter every 40 measurements and logs the value.

After a run and laser profiling and before tube cleaning, magnetite is removed at selected positions along the tube using ethanol and a rubber eraser. The ethanol is collected and left for total evaporation, after which the magnetite powder is recovered and dissolved in hydrochloric acid for spectrophotometric analysis. The mass of magnetite deposited on the tube per unit area is then determined.

#### Laser Scan Model

The profilometer results need to be interpreted with care. If the average diameter difference given by the laser is directly converted into a mass of magnetite per unit surface, the result can be two orders of magnitude higher than the actual mass of deposited magnetite. This is because there is not a uniform deposit thickness and the laser measures the average shadow projected on the sensor by a succession of discrete particles. As a consequence, a significant discrepancy from the actual magnetite mass may result, depending on the deposition pattern.

To interpret the profilometer results, a numerical simulation is performed on a simplified deposit model. The objective is to find a disposition of magnetite on the tube that satisfies both the scan results and the measurements of deposit mass. To do so, the model assumes an idealised pattern of deposit and calculates the corresponding diameter increase that would be measured.

Several assumptions are made to construct this model:

- 1. Magnetite particles agglomerate on the tube as spherical clusters of the same radius 'r' (Fig. 2).
- 2. The clusters belong to planes orthogonal to the tube axis, these planes being one cluster diameter apart.
- 3. Clusters belonging to the same plane are separated from each other by the same angle  $\theta^*$  as shown in Fig. 2.
- 4. The laser beam width (0.2 mm) is much larger than a cluster diameter, thus more than one cluster planes project a shadow on the laser sensor.
- 5. The shadow area projected on the sensor is normalized by the laser width, giving the average diameter of the tube over the area illuminated by the laser at any time.
- 6. The scan is performed as if a continuously recording laser were used.

As the deposition pattern is regular along the tube, the model need only consider one cluster plane. The arrangement of a cluster plane with respect to its neighbours does not influence the result, since the average diameter measured by the laser is calculated from the measurements made during several rotations of the tube. Indeed, whether the cluster planes are in phase or not, all the clusters of each plane are taken into account once per rotation. The study can thus focus on only one cluster plane and normalize the projected shadow by the distance between planes. Periodicity by rotation of the tube is exploited in the model. The shadow projected by one cluster as it progressively enters the laser field, reaches the horizon at the top of the tube and recedes below the horizon is the same for all the clusters in a plane. Therefore, only the trajectory of one cluster between the positions  $\theta = \theta^*/2$  to  $\theta = 0$  is considered.

The software Matlab is used to calculate the shadow produced by one magnetite cluster when it is in the interval  $\theta = \theta^*/2$  to  $\theta = 0$ . For each infinitesimal angle within this range, the program calculates the vertical height,  $h(\theta)$ , of the cluster above the tube horizon, see Fig. 2. This height is then use to calculate the extent of the shadow projected on the sensor. All the projections within the interval are averaged and the result is divided by the distance between cluster planes to give the average tube diameter that the laser scan would have measured.

The mass of magnetite per unit surface area that results from a deposition pattern such as that shown in Fig. 2 is obtained from the number and size of clusters disposed on one plane.



Fig. 1 Tube and profilometer installed on a lathe (left); laser beam sheet shadowed by the tube (right)



Fig. 2 Magnetite cluster disposition on the tube (left); cross section of the tube of radius 'R' with clusters of radius 'r' on its surface (right); the laser sheet, in red, is shadowed by the tube and clusters;  $\theta$  is the angular position of the cluster that lies within the field of vision of the laser;  $\theta^*$  is the angle separating clusters belonging to the same plane; the arrow indicates the laser direction

## RESULTS

Error bars from all charts in this paper correspond to standard deviations.

#### **Zeta Potential Measurements**

For the sake of clarity, the standard deviation of the zeta potential measurements is not shown systematically. It always appears for the samples without additive; otherwise, it is shown only if it is greater than 5 mV. Generally, the deviation is lower when PAA, PMA or FFA are used. The zeta potential of the magnetite as a function of pH<sub>25°C</sub> is presented in Fig. 3, which indicates that the PZC without additive is between 7.9 and 8.2. The zeta potential of the Alloy-800 powder as a function of pH<sub>25°C</sub> is presented in Fig. 4, which shows a PZC without additive between 4.4 and 4.6. The zeta potentials of magnetite and Alloy-800 particles are measured in the presence of each of the four additives. The concentrations of the polymers are adjusted to correspond approximately to the same quantity of carboxylic groups per gram of magnetite or Alloy-800. In order to account for losses of FFA due to the coating of the sample cell and the immersed electrode during zeta potential measurements, FFA is added in excess in the samples. The concentration of FFA shown in Figs. 3 and 4 is the concentration measured after the zeta potential has been determined.

FFA increases the zeta potential of magnetite and maintains it at positive values for all pH values tested. Nothing can be concluded about the PZC of magnetite in the presence of FFA except that it is outside the range pH  $\sim$ 2 to pH  $\sim$ 10.

The effects of PAA and PMA on the zeta potential of magnetite are very similar. These two polymers reduce significantly the PZC of magnetite from pH 8 to about pH 3. It should be noted, however, that their effect levels off as the pH increases and reaches pH 9. It may be assumed from the present results that the difference of zeta potential with and without polymer is no more than 20 mV for the values pH 9.5-10, the pH range of interest for the rest of the study. In the case of the PZC of Alloy-800, the effects of all four additives are similar to the ones observed for magnetite; PZC values fall between pH 2.5 and pH 3 for all three polymers, and zeta potential values at the pH of interest (9.8) are about +40 mV in the case of FFA and -70 mV in the case of polymers. The curves obtained with PAA(1800) and PMA(9500) suggest that the zeta potential values in the case of PAA(8000) at the pH of interest can be obtained by extrapolation.

To illustrate the influence of polymer loading on the magnetite surface, Fig. 5 presents the zeta potential of magnetite in the presence of PAA(8000) at three different concentrations, 2 ppm, 20 ppm and 100 ppm. The negative charge density on magnetite surfaces is increased by increasing the PAA concentration, especially at high pH, although more measurements would be necessary to see any effect on the PZC. From the previous results and due to the similar behavior of the different polymers on magnetite particles, it is reasonable to suggest that the loading effect of PAA(8000) on magnetite could also apply to PAA(1800) and PMA(9500). Similar polymer loading effects probably occur on Alloy-800 surfaces, too.

### **Bench-top Experiments**

Beaker experiments under the various chemistry conditions lead to observations summarized in Figs. 6 and 7. At the end of all runs, the coolant pH is in the interval 9.6-9.9 and magnetite concentration is higher than 25 ppm except when FFA is used, in which case the final magnetite concentration drops to 5 ppm (the particles severely agglomerate at the liquid-vapour interface and stick to the beaker wall). For each condition, two runs provide two ribbons for analysis (although the run with FFA is not repeated due to the difficulties maintaining the magnetite concentration in the bulk). Accordingly, the results obtained with FFA and presented below are for information only. Any comparison with other runs is to be done carefully.

A high-speed camera is used to record the bubble nucleation frequency and departure diameter during the runs. Note, however, that the variation of these two quantities between nucleation sites on the same ribbon and the few nucleation sites studied per ribbon add uncertainty to the data collected. The use of additive has little effect on the bubble nucleation frequency, which generally ranges from 40 to 70 bubbles/second, except when FFA is used, in which case the frequency can reach 80 bubbles/second. Also, a high concentration (300 ppm) of PAA(8000) decreases the nucleation frequency to about 30 bubbles/second. The bubble departure diameter ranges from 2 to 3.5 mm for most runs, but when PAA(8000) is used at a concentration of 300 ppm it ranges from 3.2 to 4.2 mm.



Fig. 3 Effect of additives on the zeta potential of magnetite



Fig. 4 Effect of additives on the zeta potential of Alloy-800



Fig 5 Zeta potential of PAA-loaded magnetite



Fig. 6 Average number of deposition sites per ribbon in grey; average magnetite deposit diameter in black



Fig. 7 Effect of additive on magnetite coverage fraction on ribbons (result for FFA not comparative)

At the end of the run, the number of deposition sites that can be detected visually (corresponding to bubble nucleation sites) is recorded and SEM pictures of the ribbon are used to measure the average diameter of deposition sites. Although uncertainty is high, Fig. 6 shows a trend in the magnetite deposit diameter. Higher molecular weight polymers, PAA(8000) and PMA(9500), seem to produce larger deposition sites (up to 2.5 times larger) than when no additive is used. Runs with PAA(1800) and FFA show similar site diameters to those seen in runs without additive. Additives also have a clear effect on the number of deposition sites on the ribbon, reducing them by about 50% when PAA(8000) or PMA(9500) are used and by about 75% when PAA(8000) is used at the high concentration of 300 ppm or PAA(1800) or FFA are used.

Because attempts to measure iron deposits on ribbons via acid dissolution and spectrophotometry produce uncertain results (traces of iron in the reagents and in the nichrome give excessive blank corrections), SEM pictures are also used to estimate magnetite coverage, producing average fractions as in Fig. 7, which shows that each deposition site is 10% to 55% denser when low molecular weight polymers PAA(8000) and PMA(9500) are used than when there is no additive. On each ribbon, a dense magnetite deposit is selected and its SEM picture is analyzed using the software ImageJ. This digitizes the SEM photograph into a binary black and white picture showing magnetite particles in black and the ribbon surface in white (see a typical example in Fig. 8). The total area occupied by black magnetite particles is then computed and normalized to the total area of the analyzed ribbon portion to give the 'Magnetite coverage fraction' of Fig. 7. The increases in density of deposition sites are probably underestimated as the image analysis method accounts for only the surface coverage and not the deposit thickness. In general, very low molecular weight PAA reduces by about an order of magnitude the amount of deposit at each site. FFA also reduces significantly the magnetite coverage of the ribbon, but the reduction will be at least partly due to the lowered magnetite concentration during the FFA run.

All the bench-top experiments without FFA show a superheated layer of water at the bottom of the beaker, which is in contact with the heater, but no sign of bubble nucleation sites. The run with FFA, however, resulted in the generation of bulk boiling at the beaker bottom, as shown in Fig. 9. It is believed that vapour bubbles trap magnetite particles as they rise to the surface. Coated with FFA, magnetite becomes hydrophobic and particles agglomerate at the water-air interface where they are "trapped". The vortex created by the stirring eventually brings agglomerates to the beaker wall where they deposit. The intense boiling at the beaker bottom, as well as the hydrophobic properties of surfaces are probably responsible for the dramatic decrease of magnetite concentration in the bulk.



Fig. 8 Original and digitised SEM pictures (respectively above and below) of typical bubble nucleation sites



Fig. 9 Pictures of the beaker bottom without (left) and with (right) FFA; heat flux is the same

Table 1 Run conditions in the recirculating loop

Run #	Tube #	Duration	Chemistry
1	Tube 1	50h	No additive
2	Tube 2	25h	No additive
3	Tube 3	15h	No additive
4	Tube 1	50h	No additive
5	Tube 1	50h	PAA(1800) 20ppm
6	Tube 3	50h	PMA(9500) 30ppm
7	Tube 3	50h	No additive



Fig. 10 Magnetite deposit mass per unit surface area after Runs 1, 2 and 3 along with data from a previous study



Fig. 11 Magnetite deposit mass from Runs 4 to 7; results for Runs 4 and 7 are averaged into 'No additive'

#### **Recirculating Fouling Loop**

Run conditions in the recirculating loop are summarized in Table 1. The first experiments are used to study the evolution of magnetite deposit with time in ammoniated coolant and no surface-active additive. Three runs of different duration provide the magnetite deposit mass results shown in Fig. 10. They conform to results from previous experiments under similar conditions (McCrea, 2001). Those previous experiments, mostly done in ammoniated water but with some under neutral conditions, also showed a proportionality between magnetite deposition under sub-cooled boiling and deposition under bulk boiling in the early stages of fouling in neutral water. This proportionality is applied to convert data from bulk boiling conditions to sub-cooled boiling conditions with ammonia.

For the rest of the fouling tests, run duration is maintained at 50h. For each of the two runs with additive, PAA(1800) and PMA(9500), a blank run is performed without additive but with the same Alloy-800 tube and cartridge heater assembly. The polymers are added to the loop once the magnetite concentration has reached the target value. The PAA(1800) is used at a concentration of 20 ppm (a carboxylic group density of 2.8 moles per gram of magnetite) and the PMA(9500) is used at a concentration of 30 ppm to reach the same carboxylic group density. Just after polymer addition and frequently during the run, the coolant pH is measured and adjusted if necessary. Magnetite concentration in the coolant decreases continuously and needs to be adjusted once or twice a day. When magnetite is added, equivalent amounts of PAA and PMA are added to maintain the carboxylic group density per mass of magnetite. After each run, portions of the magnetite deposited on the tube are collected at four different locations and weighed. The average mass per square meter is presented in Fig. 11.

The mass of deposited magnetite in Runs 5 and 6 is reduced below the amounts deposited in runs without additive by about 80% in the presence of PAA(1800) and 55% in the presence of PMA(9500). These results are in agreement with visual observations made on the Alloy-800 tubes at the end of Runs 4, 5, 6 and 7. Figure 12 shows the magnetite deposit site density on the Alloy-800. Pictures a) and b) are of the same position on Tube #3. Similarly, pictures c) and d) are of the same position on Tube #1. The tube exposed in the presence of PAA(1800), which carries the lowest deposit mass, has the lowest site density and lowest deposition site diameter. The tube used in the presence of PMA(9500) shows intermediate values of deposition mass and site density, between those of the PAA run and those of the runs without additive. Mature deposition sites seem to have the same diameter as those observed without additive. Besides the deposition sites observed on Fig. 12, a very thin but apparently uniform layer of magnetite deposits on the tube between nucleation sites. This layer, which is not visible on the pictures, has a density that increases with the deposition site density.



Fig. 12 Alloy-800 tubes with magnetite deposition



Fig. 13 Tube scans from Runs 1, 4 and 5



Fig. 14 Tube scans from Runs 6 and 7

Table 2 Average measured deposit thickness and corresponding magnetite deposit mass for Runs 4 to 7

Run #	Thickness (µm)	Mass (mg/m <sup>2</sup> )
Run 4 (No additive)	3	340
Run 5 (PAA 20 ppm)	0.5	75
Run 6 (PMA 30 ppm)	6	160
Run 7 (No additive)	5	340

Table 3 Deposition patterns fitted to experimental data

Run #	Cluster radius(µm)	$\theta^*$ (rad)	Closest neighbor (µm)
Run 4	1.70	0.0035	4.8
Run 5	0.28	0.0003	0.8
Run 6	4.50	0.041	12.7
Run 7	3.05	0.019	8.6

Tubes are scanned before and after cleaning off the magnetite deposit at the end of each run. Scans of the clean bare metal after Runs 1, 4 and 5 are superimposed on the fouling results in Fig. 13 under the label 'Bare metal'. Scans of fouled tubes from Runs 1 and 4 are labelled 'no additive'. The scan of the fouled tube from Run 5 is labelled 'PAA(1800) 20 ppm'. The difference between the diameter scan obtained before tube cleaning ('no additive' or 'PAA(1800) 20 ppm') and the scan obtained after tube cleaning provides the contribution of the deposit to the measured diameter. The apparent thickness on the tube is thus half of this contribution. From Fig. 13, the fouling experiments without additive give an apparent average magnetite thickness of 2.5 to 3.5 µm. The run with 20 ppm of PAA(1800) shows an apparent thickness of 0.5 to 0.75 µm. Globally, the reduction of the magnetite layer by PAA ranges from 50% to 80%, which is in agreement with the magnetite deposit mass reduction shown in Fig. 11. Likewise, Fig. 14 shows the four scans performed after Runs 6 and 7, the two scans done on the clean tube being lumped together. The scan of the run with 30 ppm of PMA(9500) shows an apparent average magnetite thickness of 6 to 6.5 µm. The run without additive results in an apparent average thickness of 3.5 to 5  $\mu$ m. The fact that the magnetite seems thicker in the presence of PMA contradicts the magnetite deposit mass results (Fig. 11) that show a decrease of about 55% of the mass of magnetite collected on the tube when PMA is used.

## Laser Scan Model

Magnetite removal from the tubes, during the recirculating loop experiments, is performed separately on regions with circular deposition sites and regions only covered by a thin layer of magnetite, as mentioned earlier.



Fig. 15 SEM picture of a typical magnetite deposit between nucleation sites; this magnetite "layer" looks uniform from a macroscopic point of view

The mass collected per surface area from the latter regions is only 10% to 40% lower than from regions covered with circular deposition sites. Therefore, neglecting the presence of deposition sites in the model should give results that remain reasonably close to reality. Besides, the assumption made during the model construction stating that magnetite deposits on the tube under the form of spherical clusters, can be confirmed to some extent with Fig. 15. This picture, which has been taken from an Alloy-800 surface exposed to sub-cooled boiling in a magnetite suspension, shows that magnetite deposition is reasonably approximated by an ideal pattern of spherical clusters regularly spaced.

Three parameters are changed independently to reconcile the apparent diameter difference and the deposit mass per unit surface pertinent to the experiments, see Table 2. They are the cluster radius, the angle  $\theta^*$  separating clusters and the cluster packing factor (porosity).

Above a packing factor of 0.45 (i.e., below a porosity of 0.55), the experimental values from Run 6 with PMA cannot be reached with the idealized deposition pattern described earlier; a high diameter increase due to magnetite and low deposit mass per unit surface area are incompatible at higher packing factors. The packing factor value of 0.45 is then used for all the simulations. For each run, the two remaining parameters, cluster radius and angular spacing, are varied and their values recorded when both the magnetite deposit mass and tube diameter increase correspond to experimental values. Table 3 summarizes the parameter values that fit with the target values shown in Table 2. For the magnetite cluster arrangement on the tube shown in Fig. 2, the distance between a cluster's centre and the centre of its nearest neighbour is calculated and specified in Table 3. The cluster plane configuration on the tube is assumed to be the one shown on Fig. 2 where the angular position of planes is gradually shifted. From this configuration, the closest neighbour is the distance between one cluster and the cluster placed on the adjacent plane. The shifting that gives the more distant closest neighbour is selected and the distance is presented in Table 3. The closest neighbour value is given as an indication only as there are certainly other more complex plane configurations that give a higher closest neighbour value. The patterns on a macro scale would appear as uniform deposits.

According to this model, experimental results can thus be reached in the case of PAA(1800), used during Run 5, providing that the magnetite clusters are about the size of a magnetite particle and that the cluster density is very high on the tube surface. The latter configuration gives a very low tube diameter difference and magnetite deposit mass. In the case of PMA(9500), the large diameter difference requires very large clusters in the model; however, the magnetite deposit mass being moderate, these large clusters have to be spaced widely. The runs conducted without additive, Runs 4 and 7, show intermediate values of cluster size as well as cluster spacing. The variation of results for these two runs conducted under the same operating conditions may be due to the fact that two different tubes were used. For the same mass of deposited magnetite, the tube used in Run 7 may have a topography that makes the diameter difference more important than that in Run 4.

## DISCUSSION

Hajdù et al. (2008) studied magnetite nanoparticle dispersion and suggested that surfactants adsorb on magnetite via the surface -FeOH sites. Also, for fatty acids such as PAA and PMA, these sites could create chemical bonds with the carboxylic groups along the polymer chains. The same study showed that the addition of citric acid to a magnetite suspension shifts its PZC to more acidic values because of the presence of carboxylate anions at the magnetite surface. The citric acid counteracts particle agglomeration at favourable values of pH, i.e., when the pH is close to the PZC. This stabilizes a narrow particle size distribution over a wide pH range. Particle size distribution was not measured in the present study but, like citric acid, PAA and PMA provide anionic groups and should behave similarly. Burgmayer et al. (1999) found consistent results when they showed that PMA added to a boiler led to smaller corrosion product particles. Those effects of citric acid on the zeta potential are consistent with our results, which show an increase in the negative charge density on both magnetite and Alloy-800 particles when PAA or PMA are present. These polymers coat surfaces with carboxylate groups, giving an effect measurable at a group concentration per mass of particle as low as 0.22 mmol/mg. Polymer adsorption on both the Alloy-800 and the magnetite could thus be responsible for an increased electrostatic repulsive force between the heating surface and the particles. Moreover, such a force seems to be effective over a wider pH range in the presence of polymers than in their absence. Thus, these polymers could help to mitigate agglomeration and/or adhesion where the local pH differs from that in the bulk water, such as in crevices or under deposits. Similarly, FFA also could provide an electrostatic repulsive force over a large range of pH, since both the Alloy-800 surface and the magnetite particles are positively charged in its presence. The FFA molecule contains primary and secondary amine groups, so its protonation should lead to positively-charged species; one of the amine groups is probably the anchor point of the molecule to the Alloy-800 or magnetite surface. If FFA is used in a high-pH coolant circuit, the main concern is that, contrary to polymers that provide extra negative charges on surfaces that are already negatively charged at high pH, FFA will shift completely the surface charges to positives values. This could lead to unexpected effects that need to be investigated.

Video footage of boiling on the nichrome ribbons suggests that PAA(8000) or PMA(9500) reduce the number of bubble nucleation sites; the SEM pictures of exposed ribbons indicate that the number of major deposition sites of magnetite is correspondingly reduced, although the deposits are larger and thicker and surrounding surfaces are cleaner. When the concentration of PAA(8000) is increased the effect of polymer is amplified – the deposition sites are less numerous but each apparently carries more magnetite. In terms of overall reduction of deposition, PAA(1800) is the most efficient, decreasing significantly both the deposition site density and the deposition rate at each site. This is consistent with the study conducted by Balakrishnan et al. (1999), which compared the effectiveness of PAA of two molecular weights and showed that, under flow boiling conditions, a lower molecular weight polymer (Mw 3500 to 5000) is more efficient at stabilizing magnetite concentration in the bulk water. Therefore, it can be concluded that the molecular weight of the dispersant has a major influence on magnetite deposition. Dense deposition sites could then be the result of a longer polymer chain that promotes inter-particle bonding. Thus, PAA(8000), which has a theoretical maximum extended length of about 21 nm, could be long enough to link two magnetite particles together while PAA(1800), with its 6 nm theoretical maximum extended length, would be too short. The fact that bench-top experiments show similar results when PAA(8000) and PMA(9500) are used supports the idea that molecular weight governs polymer efficiency. It must be noted however, that the agglomerating effect of PMA(9500) at ribbon nucleation sites cannot be observed visually on the tube nucleation sites.

The recirculating loop experiments also show a clear reduction in magnetite deposition when PAA or PMA are present. These two dispersants reduce the deposition site density on the tube as well as the magnetite deposition mass. In this case, however, PAA(1800) proves more effective than PMA(9500) in reducing both the number of deposition sites on the tube and the magnetite deposition rate at a site. Although the tube diameter increase at the end of Run 4 (without additive) and Run 5 (with PAA(1800)) shows a good correlation with the magnetite deposit mass, it is not yet understood why the laser scan for Run 6 (PMA(9500)) shows a high diameter difference for a moderate magnetite deposit mass. It was observed, at the end of the run, that the tube colour was slightly different from that in other runs. It had a faint orange-red tone, possibly due to polymer deposition; however, it is unlikely that a polymer coating could be 1 µm or more thick, as indicated by the profilometer. Another reason for the tube coloration could be the formation of haematite due to an oxygen ingress during the run. The difference in magnetite thickness measured by the laser between Runs 4 and 7, which correspond to the same operating conditions, is also questionable and seems to be due to the fact that two different tubes are used for these two runs.

The laser-scan model based on the idealised fouling pattern indicated that the loop experimental results for PMA(9500) could be explained providing that the uniform magnetite deposit between bubble nucleation sites was in the form of larger and more spaced-out clusters on the tube than were invoked to explain deposits without additive or with PAA. This contradicts the dispersant properties of PMA mentioned earlier, although it could be linked to the fact that bench-top experiments show thicker magnetite deposits at nucleation sites when this polymer is used.

## CONCLUSIONS

1. Helical scans with a laser profilometer of Alloy-800 tubes show very good repeatability and resolution at the micrometer scale for measuring diameter increases due to fouling. The interpretation of the scan results in terms of deposit mass and dispersion is complex, however, and requires further development, especially when local deposition is increased by bubble nucleation.

- 2. Screening experiments conducted in a beaker with heated nichrome ribbons are useful for indicating qualitatively the influence of chemical additives on magnetite deposition under low-pressure and low-temperature conditions.
- 3. A film-forming amine (FFA) significantly improves boiling heat transfer in beaker experiments but also agglomerates magnetite particles from suspension at high concentration – notably at the vapour-liquid interface; agglomerates then stick to most surfaces.
- 4. The addition of polyacrylic acid PAA(1800), PAA(8000) or polymethacrylic acid PMA(9500) to water with pH adjusted with ethanolamine reduces the magnetite deposition site density on nichrome ribbons under pool-boiling conditions.
- 5. Similar results are obtained with heated Alloy-800 tubes sustaining flow-boiling conditions in ammoniated water in a recirculating loop. During a 50 h exposure of an Alloy-800 tube in the loop, the addition of PAA(1800) and PMA(9500) reduces the magnetite mass deposited on the surface by about 80% and 55% respectively.
- 6. The molecular weight of a polymer has a major impact on its ability to mitigate magnetite fouling. A polymer of low molecular weight has the greater effect.
- 7. The polymers PMA(9500) and PAA(8000) have similar effects on deposition during beaker experiments, possibly because they have carbon chains of about the same length and thus carry about the same number of functional carboxylic groups.
- 8. Zeta potential measurements indicate that PAA and PMA impose negative charges on magnetite and Alloy-800, reducing the pH of zero charge (PZC) and probably increasing the repulsive force between particles and tube surfaces. FFA imposes a positive charge on magnetite and Alloy-800 surfaces over a wide range of pH, pushing the PZC outside the range 2 10.5.

## ACKNOWLEDGEMENTS

The authors are grateful to Atomic Energy of Canada Limited for helpful discussions, the Natural Sciences and Engineering Research Council of Canada and the CANDU Owners Group for funding, and BK Giulini for providing a commercial FFA product.

#### REFERENCES

Balakrishnan, P. V., Klimas, S. J., Lépine, L., and Turner, C. W., 1999, Polymeric dispersants for control of steam generator fouling, *AECL*, Ref. COG-99-165-I.

Basset, M., McInerney, J., Arbeau, N., and Lister, D. H. 2000, The fouling of Alloy-800 heat exchanger surfaces by magnetite particles, *The Canadian Journal of Chemical Engineering*, Vol. 78, pp. 40-52.

Burgmayer, P., Crovetto, R., Turner, C. W., and Klimas, L., 1998, Effectiveness of selected dispersants on magnetite deposition at simulated PWR heat-transfer surfaces, *Proc. 3rd Int. Steam Generator and Heat Exchanger Conference 1998*, Toronto, Canada.

Cossaboom, J. L., and Lister, D. H., 2005, The fouling of Alloy-800 heat exchanger tubes by nickel ferrite under bulk boiling conditions, ECI Symposium Series, *Proc. 6th Int. Conference on Heat Exchanger Fouling and Cleaning* 2005, Kloster Irsee, Germany, Vol. RP2, pp. 109-118.

Hajdù, A., Tombàcz, E., Illés, E.,Bica, D., Vékàs, L., 2008, Magnetite nanoparticles stabilized under physiological conditions for biomedical application, *Progr. Colloid Polym. Sci.*, Vol. 135, pp. 29-37.

McCrea, L., 2001, Deposition of corrosion product particles onto heat exchange surfaces, *M.Sc.Thesis. University of New Brunswick*, pp. 57-63

Mohajery, K., Deydier de Pierrefeu, L., and Lister, D. H., 2012, The dissolution rate constant of magnetite in water at different temperatures and pH conditions, *Proc. Nuclear Plant Chemistry Conference 2012*, Paris, France, Ref. 14-015.

Ramminger, U., Fandrich, J., and Drexler, A., 2012, An innovative strategy for secondary side system lay-up using film-forming amines, *Proc. 7th CNS Int. Steam Generators to Controls Conference 2012*, Toronto, Canada.