KINETICS OF GROWTH OF IRON OXIDE PARTICLES AT HEATED METAL SURFACES*

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ABSTRACT

A kinetic method is described for the study of iron oxide growth at heated metal surfaces. Iron oxide particles nucleate preferentially at gas-liquid interfaces provided by steam bubbles escaping from the heated surface, and subsequently grow by a surface controlled process. The influence of iron dispersing agents on the rate of iron oxide growth has also been investigated.

1. INTRODUCTION

Iron oxide particles returned to the boiler as corrosion products from the condensate and preboiler system can deposit on the internal boiler surface, preferentially at the high heat transfer areas. This phenomenon can cause tube overheating and can lead eventually to tube failures. Water soluble polymers are commonly used to control this problem by dispersing the iron oxide particles and minimizing their agglomeration. Previous studies /1-3/ have indicated that maintaining iron oxide particles finely dispersed in the boiler water reduces deposition problems and enhances its removal from the boiler via continuous blowdown.

Deposition of iron oxide particles at heated metal surfaces has been the subject of extensive studies. Asakura /4,5/ reported that iron oxide deposition is a function of heat flux, bulk iron concentration, boiling water flow rate and pressure. Rabah /6,7/ conducted similar experiments and concluded that chemical impurities (calcium and aluminum ions) and organic colloids (gelatin and tannic acid) increase the deposition of iron oxide particles on heat transfer areas. Iwahori /8/ studied the effect of water pH and reported that minimum iron oxide deposition at heated metal surfaces occurs at the point of zero charge of hematite. Kawaguchi /9/ confirmed these results and showed that iron oxide growth is also a function of the iron oxide particle size in solution.

However, all the studies reported above were done by measuring the amount of iron oxide deposited at the heat transfer area, and no attempt was made to evaluate the order of the reaction process. The objective of this paper was to determine the kinetics of growth of iron oxide particles at heated metal surfaces and to investigate how physical (heat flux, specific surface area, surface roughness) and chemical (iron dispersing agents) parameters influence such growth.

2. EXPERIMENTAL PROCEDURE

The apparatus used in this work consisted of a four neck glass flask and a condenser (Figure 1). All the experiments were conducted at boiling water conditions and atmospheric pressure. The heat source was provided by a stainless steel heater immersed in the flask. The heater was able to operate up to a heat flux of 600,000 W/m^2. In some experiments, in order to evaluate the effect of surface roughness, the heater surface was polished with different grades of emery paper. To evaluate the effect of surface metal composition, a carbon steel sleeve, able to tightly cover the stainless steel heater, was used.

All the experiments were conducted under nitrogen atmosphere in order to eliminate any oxygen from the system. Iron hydroxide solutions were freshly prepared prior to each experiment, and the precipitated iron hydroxide was of consistently very small particle size (0.1μ < particle size < 0.25μ). All the solutions used were 10 ppm in iron concentration (as Fe), pH 10.0. In the experiments

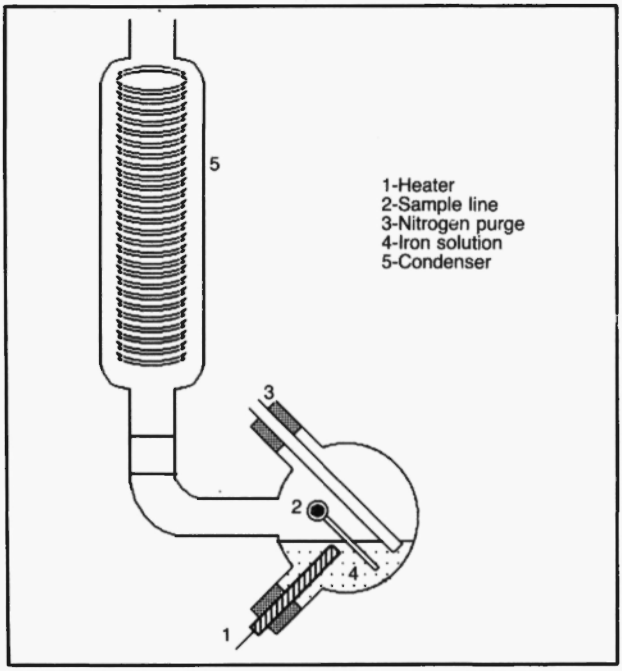

Fig. 1: Experimental apparatus

conducted in presence of an iron dispersing agent, polymer concentrations used were 10-100 ppm as active.

Typical kinetic experiments were conducted by taking samples out of the flask at certain time intervals. At the end of each test, the amount of iron oxide deposited on the heat transfer surface was removed by immersing the heater in a solution containing ferrozine as iron complexing agent and thioglycolic acid as reducing agent. A good mass balance was established between the amount of iron left in bulk water and the amount of iron oxide deposited at the heat transfer area. Therefore, the rate of iron oxide growth at the heated metal surface can be determined by studying the rate of iron removal from the bulk water.

Figure 2 shows a typical kinetic experiment in which the concentration of iron in the bulk water decreases monotonically with time. For a first-order reaction process, the rate of iron removal from the bulk water can be described by the following equation:

$$-d[Fe]/dt = k[Fe] \tag{1}$$

which upon integration yields:

$$\ln [Fe]/[Fe_0] = -k\,t. \tag{2}$$

Figure 3 shows the logarithm of the rate of iron removal from the bulk water, log(–d[Fe]/dt), plotted versus log[Fe]. The slope of this linear plot is close to one, as required by Equation 1, and

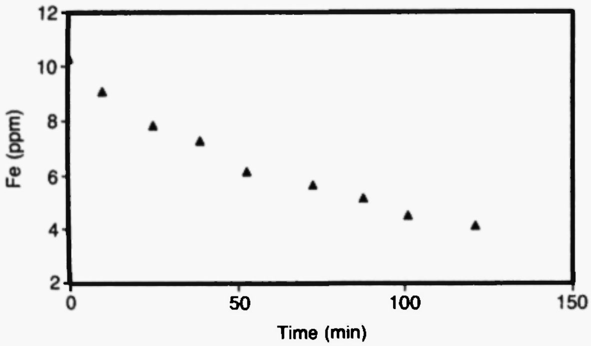

Fig. 2: Rate of iron removal from bulk water. V = 200 ml, A = 12.97 cm^2, unpolished heater. Heat flux = 600,000 W/m^2.

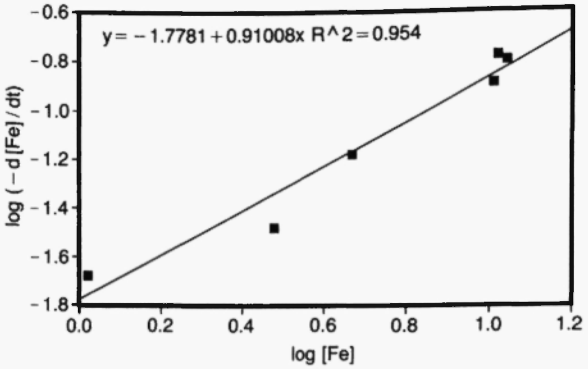

Fig. 3: Plot of log (-d[Fe]/dt) against log [Fe].

Figure 4 shows the excellent linearity of the plot of the integrated form of Equation 1. The data reported on Figures 3 and 4 confirm that the rate of iron removal from the bulk water, and conversely, the rate of iron deposition on the heat transfer area, is a first-order reaction process. For each experiment a kinetic rate constant k, expressed in min^{-1} was determined. Any chemical or physical condition in the system leading to a decrease in the rate constant k leads to a decrease in the rate of iron oxide deposition at the heated metal surface.

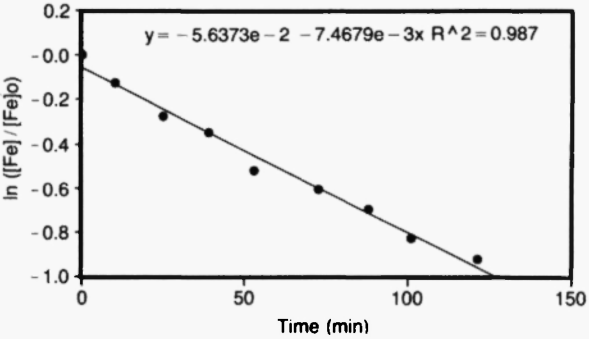

Fig. 4: Ln([Fe]/[Fe]o) as a function of time. V = 200 ml, A = 12.97 cm^2, unpolished heater. Heat flux = 600,000 W/m^2.

3. RESULTS

3 1. Heat Flux Effect

With the stainless steel immersed in the solution and no heat flux applied (boiling of the solution was accomplished by an external heating mantle), no deposition occurs at the metal surface. Increasing heat flux across the heater leads to an increase in the rate of iron removal from the water solution, as shown in Figure 5. Correspondingly, the rate of iron oxide deposition at the heated metal surface increases linearly with heat flux, as shown in Figure 6.

At low heat flux, the number of nucleated iron oxide sites are lower than at high heat flux, as shown in Figures 7 and 8. The fact

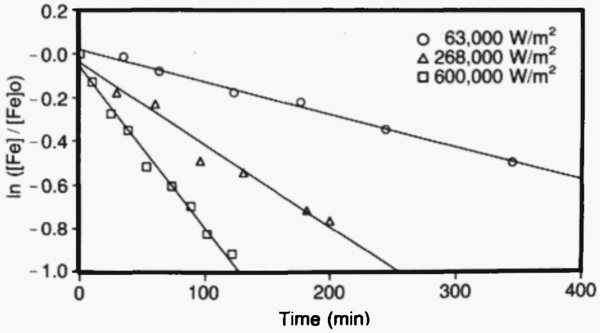

Fig. 5: Rate of iron removal at different heat fluxes. V = 200 ml, A = 12.97 cm^2, unpolished heater.

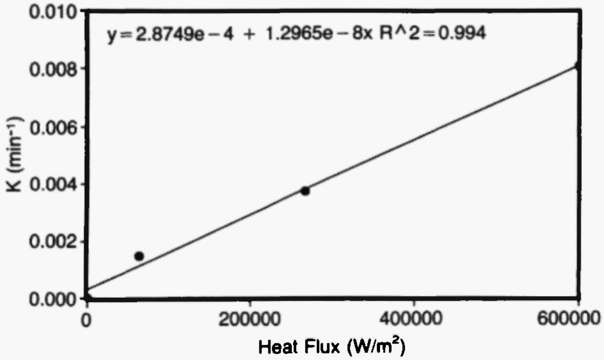

Fig. 6: Rate of iron deposition as a function of heat flux. V = 200 ml, A = 12.97 cm^2, unpolished heater.

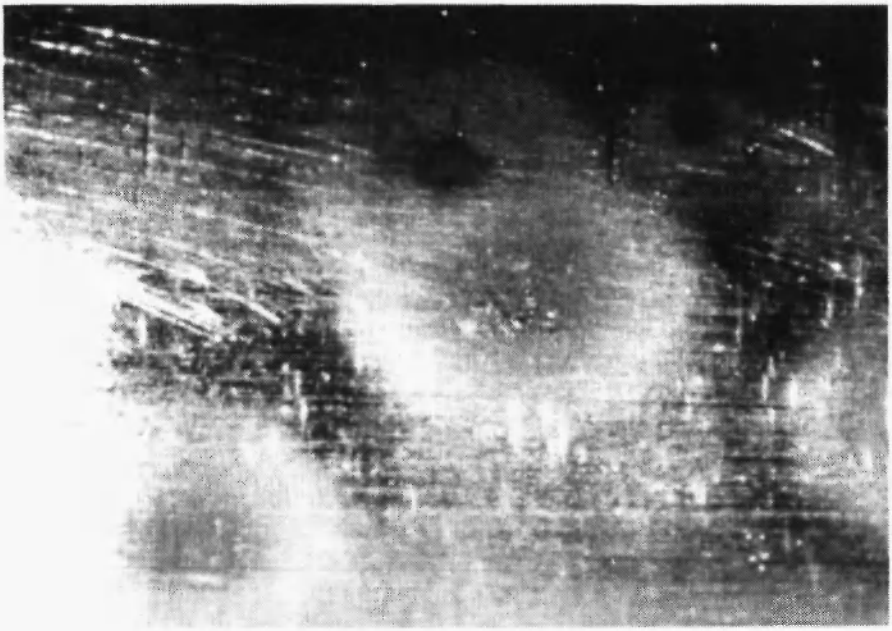

Fig. 7: Iron oxide deposited at the heat transfer surface after 2 hours (X12 magnification). Heat flux = 67,370 W/m^2. unpolished surface.

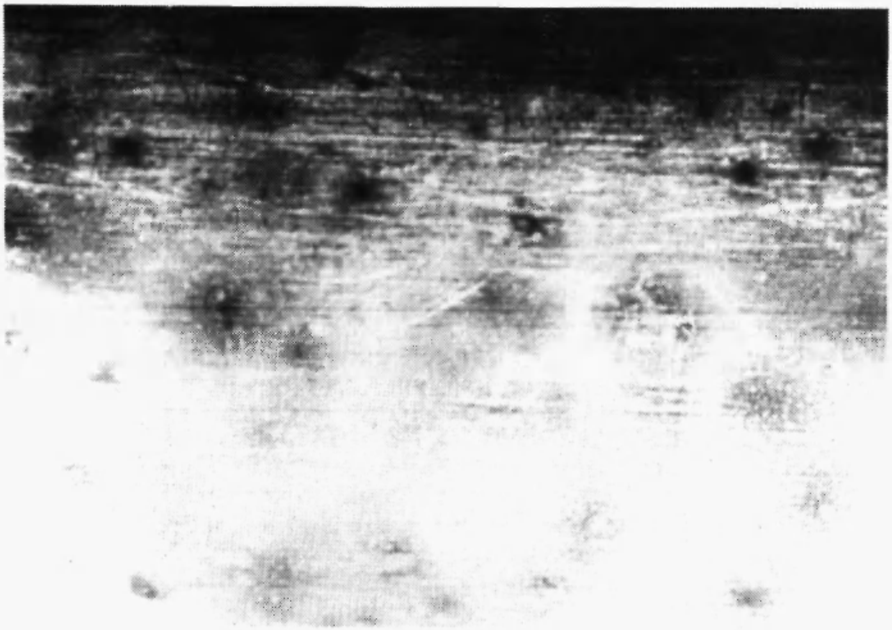

Fig. 8: Iron oxide deposited at the heat transfer surface after 2 hours (X12 magnification). Heat flux = 433,700 W/m^2, unpolished surface.

that at higher heat flux a higher rate of iron oxide deposition is observed at the heated metal surface is, therefore, probably related to the number of active sites present at the metal surface. It can be inferred that iron oxide particles nucleate preferentially at the site of continuous steam bubbling at the heated surface. Steam bubble volume and growth rate at the heated metal surface vary with the heat flux applied. As shown in Figures 7 and 8, iron oxide growth covers a larger area, per active site, at lower heat fluxes than at higher ones. Thus, once nucleation has taken place, iron oxide growth at the heated metal surface is a process that appears to be controlled by the surface area of the steam bubble leaving the surface. This explanation is in agreement with the model proposed by Asakura /4,5/ and Rabah /6,7/ based on microlayer evaporation and drying out phenomena that occur in the nucleate boiling bubble.

3.2. Specific Surface Area Effect

The rate of iron oxide deposition at heated metal surfaces is directly proportional to the surface area exposed to the solution containing the iron hydroxide, as shown in Figure 9. This is in agreement with the results presented above since, provided the heat flux is constant, a higher surface area provides a higher number of nucleation sites. Similarly, for a surface-controlled process, the rate of iron oxide growth is also inversely proportional to the solution volume used, as shown in Figure 10. A combination of the data of Figures 9 and 10 is presented in Figure 11 where the

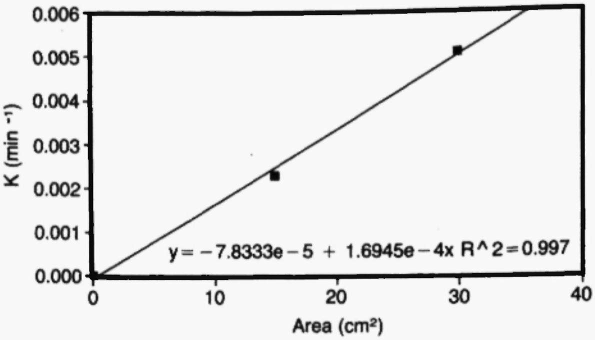

Fig. 9: Rate of iron oxide deposition as a function of heater area. V = 370 ml. Heat flux = 245,000 W/m^2. Heater surface polished with #240 grit emery paper.

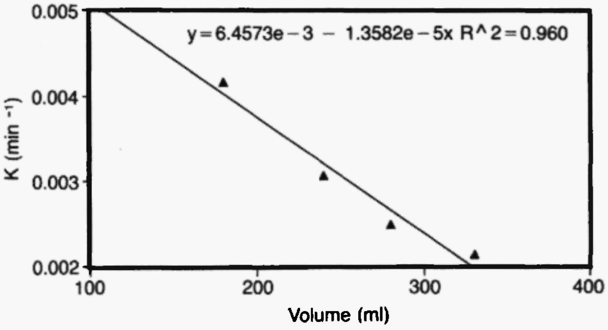

Fig. 10: Rate of iron oxide deposition as a function of solution volume. A = 14.96 cm^2. Heat flux = 245,000 W/m^2. Heater surface polished with #240 grit emery paper.

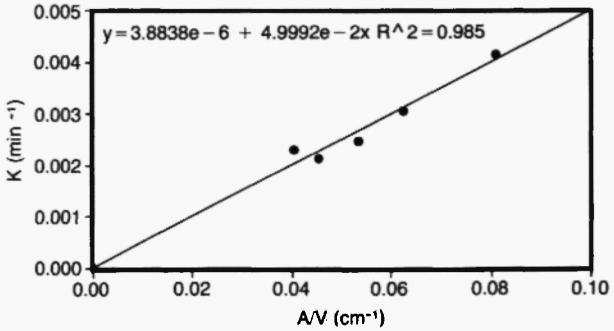

Fig. 11: Rate of iron oxide deposition as a function of specific surface area, A/V. Heat flux = 245,000 W/m^2. Heater surface polished with #240 grit emery paper.

rate of iron oxide deposition at the heat transfer surface is plotted as a function of the area to volume ratio, A/V, or specific surface area. The linear dependence of k on A/V clearly demonstrates that the rate of iron oxide growth at heated metal surfaces is a surface-controlled process /10/.

3.3. Surface Effect

The stainless steel heaters were polished with different grades of emery paper and the rate of iron oxide growth was evaluated for many different polished surfaces. Figure 12 shows the rate of iron

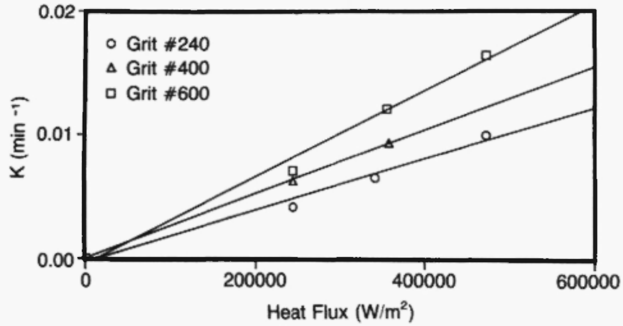

Fig. 12: Rate of iron oxide deposition as a function of heat flux for different surface polished heaters. V = 200 ml, A = 12.97 cm^2.

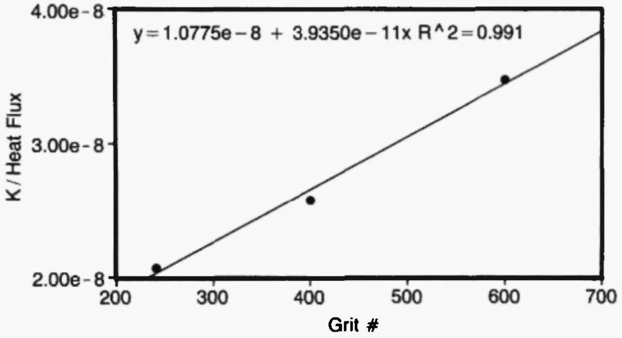

Fig. 13: Dependence of the rate of iron oxide deposition on surface roughness.

oxide deposition as a function of heat flux for different surface polished heaters. When the rate of iron oxide deposition was normalized to the heat flux across the heater and plotted versus the grit emery paper used, the data of Figure 13 were obtained. As the heated metal surface becomes smoother, the rate of iron oxide deposition increases accordingly. This indicates that very highly polished surfaces have a very high number of active sites, per unit area, on which steam bubbles can be generated and iron oxide nucleation can occur. This is visually shown in Figures 14 and 15.

The effect of surface metal composition on the rate of iron oxide deposition at heated metal surfaces was evaluated by using a carbon steel sleeve on top of the stainless steel heater. The data

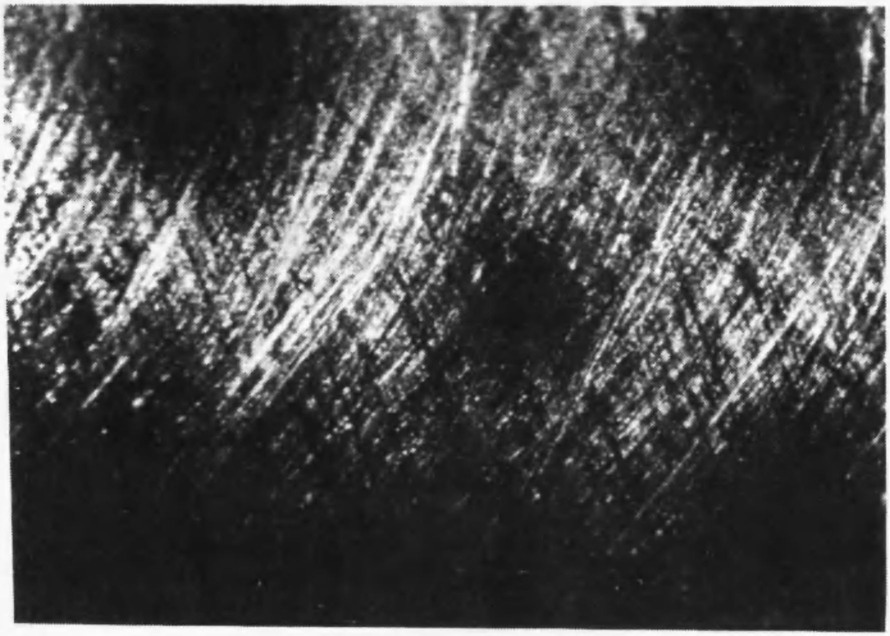

Fig. 14: Iron oxide deposited at the heat transfer surface after 2 hours (X25 magnification). Heat flux = 430,000 W/m^2. Heater surface polished with #240 grit emery paper.

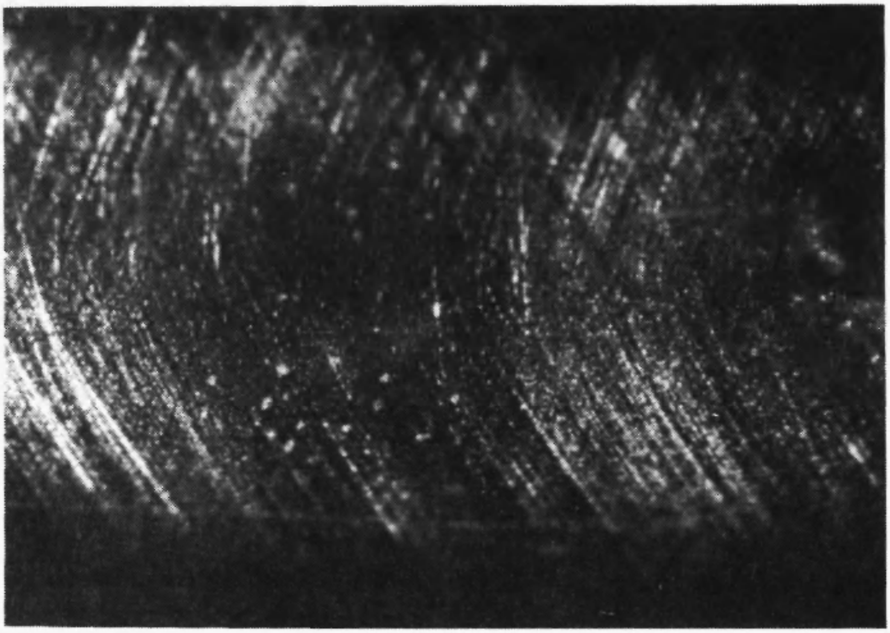

Fig. 15: Iron oxide deposited at the heat transfer surface after 2 hours (X25 magnification). Heat flux = 430,000 W/m^2. Heater surface polished with #600 grit emery paper.

obtained were normalized to the specific surface area and are reported in the last column of Table 1. For the same heat flux, specific area (A/V) and surface roughness, the rates of iron oxide deposition differ by 5%, which is within the experimental error. Therefore, the rate of iron deposition at metal heated surfaces, although dependent on the surface active number of sites, appears to be independent of the surface metal nature, at least at atmospheric pressure.

3.4. Effect of Iron Dispersing Agents

Water soluble polymers are extensively used in internal boiler treatment in order to condition iron oxide particles returned as corrosion products from the condensate and preboiler system and prevent their further agglomeration. The effect of an acrylic acid/acrylamide copolymer extensively used in boiler treatment /11/ on the rate of iron oxide growth was evaluated in the experimental apparatus at different polymer concentrations and the data obtained are reported in Figure 16. At a ratio of 1/1 ppm polymer active/ppm Fe, no effect on the rate of iron deposition was observed. However, further increase in polymer concentration leads to a decrease in the rate of iron oxide growth. At a 10/1 ppm polymer active/ppm iron, the rate of iron oxide growth is 50 times lower in the presence of polymer treatment.

Since iron oxide particles are finely dispersed by the copolymer, particle agglomeration at the nucleate boiling steam bubble is

TABLE 1

Effect of surface metal composition on the rate of iron oxide growth

$V = 200$ ml, Heat flux = 410,000 W/m^2
Heater polished with #240 grit emery paper

Surface	Area (cm^2)	k(min^{-1})	$K' = kV/A$ (cm/min)
Stainless steel	14.96	$8.1 \bullet 10^{-3}$	0.1083
Carbon steel	17.67	$1.0 \bullet 10^{-2}$	0.1132

minimized, thus iron oxide growth at the heated metal surface is highly reduced. In addition, since polyelectrolytes used as iron dispersing agents are also surface active agents /12/, another possible explanation for the inhibition of iron oxide growth at the heated surface is that the copolymer is able to alter the surface tension of the steam bubbles leaving the heat transfer surface. A direct comparison between iron oxide growth at heated metal surface in absence (reaction time = 2 hours) and presence of iron dispersing agent (reaction time = 15 hours) is shown in Figures 17 and 18.

4. CONCLUSIONS

Iron oxide particles nucleate preferentially at gas-liquid interfaces provided by gas bubbles leaving the heated surface and subsequently grow by a surface-controlled process. The rate of iron oxide growth at the heat transfer area is a first-order reaction process and is a function of the following parameters:

- It increases by increasing heat flux.
- It appears to be similar in mild steel and stainless steel heated surfaces, at least at atmospheric pressure.
- It is dependent on the heat transfer area surface roughness, or number of active nucleation sites.
- It is directly proportional to the specific surface area exposed, A/V.

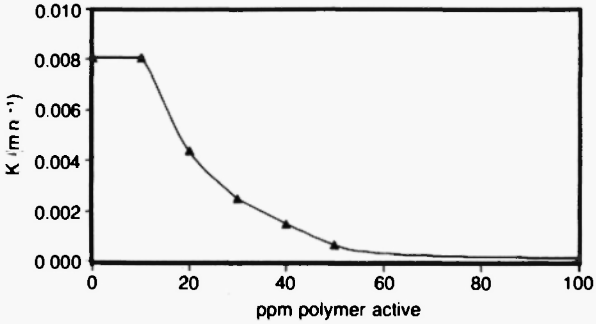

Fig. 16: Rate of iron oxide deposition as a function of polymer concentration. V = 200 ml, A = 12.96 cm^2 unpolished heater. Heat flux = 600,000 W/m^2.

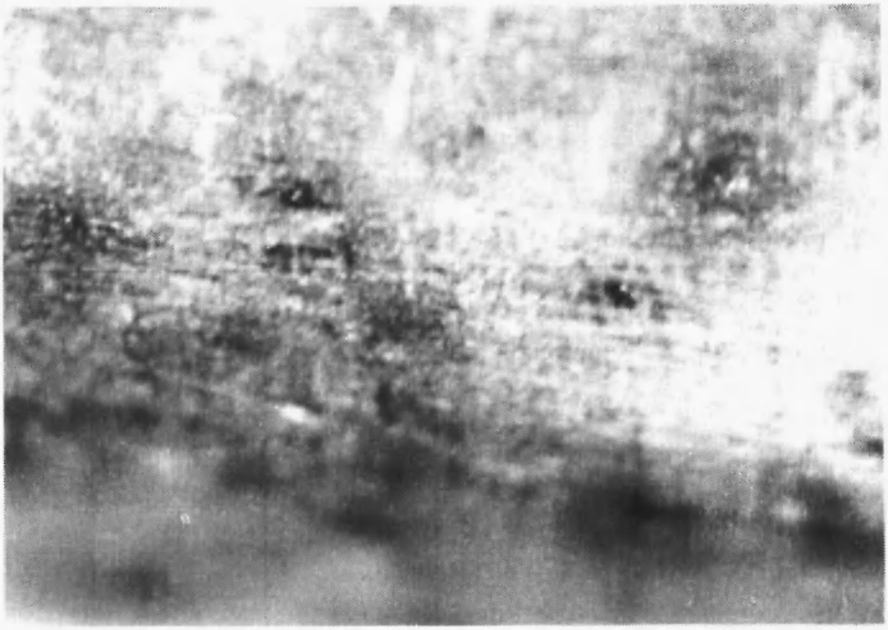

Fig. 17: Iron oxide deposited at the heat transfer surface after 2 hours (X25 magnification). Heat flux = 600,000 W/m^2, unpolished surface. No iron dispersing agent.

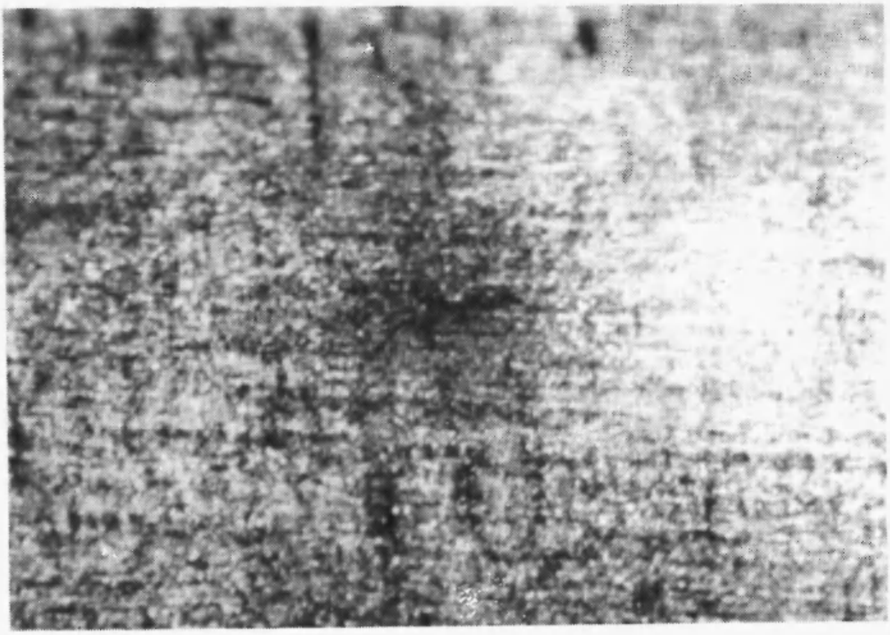

Fig. 18: Iron oxide deposited at the heat transfer surface after 15 hours (X25 magnification). Heat flux = 600,000 W/m^2, unpolished surface. 10/1 ppm polymer active/ppm Fe.

The use of iron dispersing agents dramatically affects the rate of iron oxide growth at heated metal surfaces. At a dosage of 10/1 ppm polymer active/ppm Fe, the rate of iron oxide growth is 50 times slower in presence of an acrylic acid/acrylamide copolymer used as iron dispersing agent in boiler applications. A possible explanation for the inhibition of iron oxide growth at the heated surface is that iron dispersing agents, in addition to keeping iron oxide particles dispersed in solution and minimizing their agglomeration, are also able to alter the surface tension of the steam bubbles leaving the heat transfer surface.

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