# “DEPOSITION OF CORROSION PRODUCT PARTICLES ONTO HEAT EXCHANGE SURFACES”

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## ABSTRACT

A program is continuing at UNB Nuclear to investigate the deposition of magnetite particles from suspension in water onto Alloy-800 steam generator tubes. Deposits modify the thermal hydraulic characteristics of the heat transfer surface leading to a decrease in efficiency which is often more severe when boiling or evaporation is involved. We find that the onset of boiling generally enhances the deposition rate. Experiments have been done under sub-cooled boiling conditions, in which microlayer evaporation is believed to be the dominant mechanism and local changes of the chemistry at nucleation sites may affect the particle deposition rate. A continuation of this work is to investigate the effect of bulk boiling on the deposition rate and to examine any additional mechanisms which may be involved. This entails modifying the microlayer evaporation concept to include severe local turbulence effects.

## INTRODUCTION

One aspect of fouling that can have serious consequences is the accumulation of solid particles suspended in a fluid onto a heat transfer surface [1]. The ability to predict and control the rate at which the particles deposit is important, in particular, to the power generating industry. Deposits modify the characteristics of heat transfer surfaces by increasing the resistance to heat transfer and to fluid flow, and may be responsible for harbouring harmful chemicals and increasing radiation levels [2].

Magnetite is the principal corrosion product that forms on the carbon steel surfaces of the piping and equipment around the secondary coolant system of a nuclear reactor. Magnetite is released from these surfaces into the high temperature feed water and is transported to the steam generator tubes, where it deposits on the outside of the tubes. The tube material is typically a nickel alloy, and the CANDU-6 reactors employ Alloy-800.

The fouling process is the net result of two competitive stages acting simultaneously; the deposition stage and the re-entrainment stage, such that the build-up of deposit is given by [3]:

$$\frac{dm_f}{dt} = f_d - f_r = K_d C_b - k_r m_f$$

where the removal coefficient $k_r$ depends on shear stress and is representative of the adhesive and cohesive forces between the particles and the surface.

Under isothermal conditions, the deposition stage is generally modelled as a two-step process, occurring in series [1]. The particles are carried from the bulk liquid to the vicinity of the surface in the transport step. This is followed by the attachment step in which the particles adhere to the surface. The processes are characterized by:

$$\frac{1}{K_d} = \frac{1}{K_t} + \frac{1}{K_a}$$

where $K_d$, $K_t$, and $K_a$ are the deposition, transport and attachment coefficients respectively.

For colloidal particles, diffusion is the dominant transport mechanism. In this regime, the particles move with the fluid and are carried to the surface by Brownian motion of the fluid molecules [1]. For solutions of high Schmidt number, the transport coefficient for diffusion-dominated transport is [4,5]:

$$K_t = \frac{0.084U^*}{Sc^{0.67}}$$

The adhesion process is fundamentally described by considering the surface interactions associated with the depositing particles and the collector surface, the two most important being the London-Van der Waals forces and the electrical double-layer interaction forces. In a single fluid, London-Van der Waals forces between particles and a surface are attractive. Electrical double-layer interaction forces are attractive if the particles and the wall have unlike charges, and repulsive if they have like charges. The charge on each surface is a function of the solution pH. In the pH range where magnetite and Alloy-800 have opposite surface charges, both the electrical double layer and the London-Van der Waals interaction potential will be favourable to deposition and the net surface force will be attractive. In that case, the attachment step is very fast, and the transport step is the limiting stage ($1/K_d \approx 1/K_t$). When double layer repulsions are sufficiently large, the total potential energy will go through a maximum as the particle approaches the wall. This maximum potential energy serves as an energy barrier which must be overcome if the particles are to become attached to the surface. The energy barrier is referred to as the activation energy for attachment which exhibits an Arrhenius temperature dependence [6,7].

$$K_a = k_o \exp(-E/RT_s)$$

In this case, the transport step is very fast, and the attachment step becomes the limiting stage ($1/K_d \approx 1/K_a$). It has been shown that the particle deposition rate for magnetite onto Alloy-800 steam generator tubes will be transport controlled for pH values in the range of 6.5 and 8.3, and will be attachment rate limited outside of this range [2].

The particle deposition rate is generally enhanced by the onset of boiling [8,9,10]. Under flow-boiling conditions, it is proposed that the deposition flux can be expressed as the sum of two separate fluxes acting in parallel: one arising from forced convective transport of the particles from the bulk fluid to the heat transfer surface and the second from boiling convection [9,11]. Thus,

$$K_d(2f) = K_d + K_b$$

It is generally accepted that microlayer evaporation is the dominant mechanism for the initial deposition process under boiling conditions. Vapour bubbles grow at active nucleation sites leaving, as they grow, a very thin “microlayer” of liquid beneath the bubble. This thin layer is totally evaporated leaving the solid content of the deposit on the surface. The bubble detaches and unsaturated liquid contacts the surface again. A new bubble forms and the process is repeated [12]. As a result, a deposit is expected to show concentric rings [13,14].

## EXPERIMENTAL METHODS AND APPARATUS

### Synthesis of Magnetite

The magnetite particles used in the experiments are synthesized using a sol-gel method [14,15]. This method involves the aging at 90$^{o}$C of a ferrous hydroxide gel in an oxygen-free environment. Scanning electron microscopy and X-Ray analysis are then performed to confirm the formation and morphology of magnetite. The end product is magnetite particles which are monodisperse, colloidal (0.6 m) and nearly spherical in shape.

### Recirculating Loop

A recirculating water loop operated at atmospheric pressure and temperatures up to the boiling point is used to conduct the experiments. The loop is mainly constructed of stainless steel and is equipped with a vertical glass test section. The test section houses an Alloy-800 steam generator tube which is equipped with a cartridge heater capable of obtaining a heat flux of 240 kW/m$^2$. The pH of the coolant is set by the addition of dilute nitric acid or potassium hydroxide. To maintain a constant concentration of magnetite in the coolant, samples are regularly tested using atomic absorption spectrometry; additions/dilutions are made accordingly. A radiotracing technique is also available to monitor deposition continuously online. A schematic of the apparatus follows.

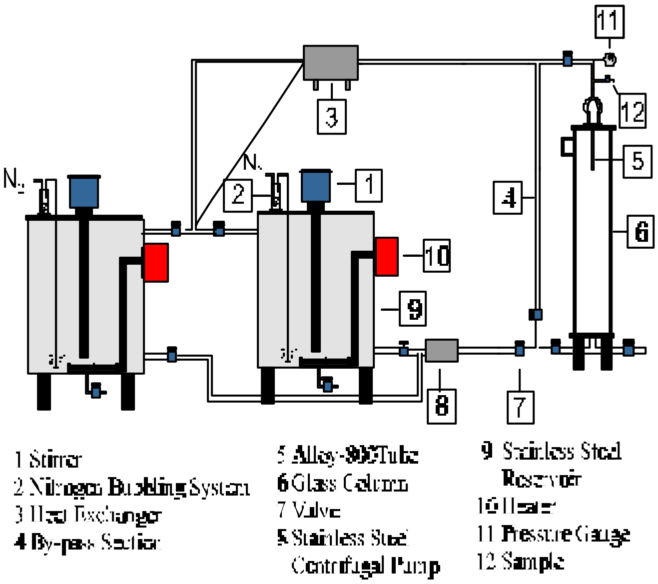

**Figure 1: Recirculating Water Loop Schematic**

## PRELIMINARY RESULTS

In a preliminary sub-cooled boiling experiment (bulk water temperature of 90 $^{o}$C, nominal heat flux of 100 kW/m$^2$) the heat transfer on the Alloy-800 tube was found to be unevenly distributed. The resultant deposition mass of magnetite particles per unit area was determined to be approximately a factor of 10 higher than that given in the literature [14]. Along the tube, three zones of different heat transfer characteristics were observed.

Near the “nose” of the tube, a wide ring (1 inch thick) of relatively stagnant bubbles, with relatively large diameters and long residence times was present. These bubbles were roughly spherical in shape and did not collapse instantaneously after the heat flux was removed.

Near the top of the tube, another smaller ring of bubbles was noticed. These bubbles were also roughly spherical in shape, but had a much smaller diameter than those on the bottom of the tube. They appeared to be stationary and tended to collapse on the surface; however, did not collapse instantaneously when the heat flux was cut at the end of a run.

In the middle section of the tube, bubbles were much smaller in diameter. They nucleated very rapidly and appeared to slide along the tube before collapsing in the flow. These bubbles instantly disappeared once the heat flux was cut from the tube.

Agglomerates of magnetite were visible on the surface of the bubbles in both the top and bottom rings of bubbles on the tube. In these areas, it was also observed that the fluid boundary layer was extended around the stagnant bubbles.

Samples were taken from the tube after a run, in which the magnetite from the three zones was removed and tested separately. The measurements confirmed the observations, in that the heaviest deposit was in the region of the top ring of bubbles, a somewhat lighter deposit occurred at the bottom ring while the centre section had the lightest deposit of all.

## DISCUSSION

The onset of boiling generally enhances the deposition rate [8,9,11,12,14]. It is observed that under boiling conditions, deposits are exclusively formed at the sites of bubble nucleation [14] which suggests that the deposition rate is closely related to the density of nucleation sites and mainly controlled by the mechanisms associated with bubble formation.

According to Thomas & Grigull [8], the initiation, growth and release of a bubble causes turbulence in the laminar boundary layer adjacent to the tube wall, resulting in an influx of water towards the wall to replace the space occupied by the leaving bubble and thereby raising the probability of deposition. A high nucleation frequency also suggests that removal of deposit is important. Particles that are collected on or under the bubble surface will be released as bubbles leave the surface. This may produce a levelling-off effect in which the rate of deposition eventually balances the rate of removal.

Since deposits are formed at the sites of bubble nucleation, trapping of particles at the bubble surface and microlayer evaporation are generally accepted as the dominant mechanisms when boiling is involved. Trapping of particles was visible in both the top and bottom rings of bubbles on the tube. These bubbles have a higher residence time on the surface and have a relatively large diameter, thus, the quantity of magnetite collected on the surface of the bubble is important and deposition by microlayer evaporation will be low. In the middle section of the tube, the residence time of a bubble on the tube surface is insufficient to allow for substantial trapping of particles on its surface, therefore, the quantity of magnetite collected is mainly due to microlayer evaporation.

The bubbles present in the top and bottom rings on the tube exhibit a high degree of stability. It is suspected that nitrogen has diffused inside these bubbles enhancing their stability and impeding their collapse when the heat flux is removed from the tube. Bubbles in the middle section of the tube have a high nucleation frequency and collapse easily; they are believed to contain only vapour.

As the fluid flows along the tube in the vertical direction, it is expected that the surface temperature and the fluid temperature at the interface will vary. Near the “nose” of the tube, the fluid temperature at the interface will still be close to the inlet temperature. As fluid flows along the tube, its temperature in the vicinity of the surface increases and the thermal boundary layer thickens, thereby enhancing bubble nucleation.

The localized extensions of the laminar boundary layer around the larger bubbles present in both the top and bottom rings of bubbles may be a result of dead flow zones in which the shearing force may become very small or even zero [8]. As a result, in these zones, the particles reaching the wall at the beginning of deposition will have the greatest probability of depositing.

## CONCLUSION

A program is continuing at UNB Nuclear to investigate the deposition of magnetite particles from suspension in water onto Alloy-800 steam generator tubes. A preliminary sub-cooled boiling experiment has been done in which the density of bubble nucleation sites may have an effect on the particle deposition rate. A continuation of this work entails studying the effect of bulk boiling and examining any additional mechanisms which may be involved. It is expected that the rate of particle deposition will be enhanced even more under these conditions due to severe local turbulence effects.

## NOMENCLATURE

| | | |
|---|---|---|
| $C_b$ | bulk concentration of particles | $kg/m^3$ |
| $E$ | activation energy of adhesion | J/mol |
| $k_o$ | constant in equation (5) | |
| $k_r$ | removal constant | $s^{-1}$ |
| $K_a$ | attachment rate coefficient | m/s |
| $K_b$ | deposition coefficient associated with boiling | m/s |
| $K_d$ | deposition coefficient for single phase flow | m/s |
| $K_d(2\ )$ | deposition coefficient for two-phase flow | m/s |
| $K_t$ | transport rate coefficient | m/s |
| $m_f$ | mass of fouling deposit per surface area | $g/m^2$ |
| $R$ | universal gas constant | J/(mol K) |
| $Sc$ | Schmidt number | |
| $T_s$ | surface temperature | K |
| $U*$ | friction velocity | m/s |

### Greek Letters

| | | |
|---|---|---|
| $_d$ | particle deposition flux | $kg/(m^2\ s)$ |
| $_r$ | particle removal flux | $kg/(m^2\ s)$ |

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