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Characterization of the deposition and transport of magnetite particles in supercritical water

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ABSTRACT

Several online and offline techniques for characterizing the deposition and transport of magnetite particles in supercritical water were investigated using a once-through flow apparatus. Ferrous chloride and ferrous sulfate precursor solutions were injected into a 1.8m heated test section at temperatures ranging from 200 °C to 400 °C. Silver membrane filters of 0.2 μm pore size were used to collect particles under supercritical conditions. Thermal resistance monitoring on the test section showed asymptotic, linear fouling and deposition-removal cycles. A novel method for qualitatively determining the strength of the oxide to the tube surface using a combination of ultrasonic and acid wash procedures demonstrated that at supercritical conditions, a stronger bond is formed which is speculated to be caused by the precipitation of dissolved ferrous species. A comparison between different conditions of pH, heat flux, and precursor were examined using the experimental techniques which are presented in this study. It was found that multiple techniques are needed to characterize the fouling process if the underlying rate-limiting steps are not known a priori.

1. Introduction

Applications of supercritical water (SCW) for the power generating industry have increased with recent developments in ultra-supercritical water fossil-fueled power plants [1–3] and concepts for nuclear supercritical water reactors (SCWR) [4]. Operation of these power plants at higher temperature and pressure increases the thermodynamic efficiency [1], while the higher enthalpy of a supercritical coolant offers an opportunity to decrease the mass flow of the coolant for the same thermal output, resulting in smaller pumps and piping [5]. Technological improvements in materials such as the development of nickel-based alloys and high temperature resistant steels have allowed coal-fired power plants to operate as high as 24 MPa and 600 °C. With nearly two dozen power plants worldwide currently operating at 580–600 °C and 24–25 MPa, there is considerable operational experience with supercritical water in power generation [2]. Despite the operational experience with supercritical water in various applications, transport and deposition (fouling) of corrosion products in this medium remains a significant challenge.

Fouling of oxides onto heat transfer surfaces can be detrimental to power systems, as the deposited material can decrease thermal efficiency and increase the temperature of the heat transfer material promoting earlier degradation [6]. Large amounts of corrosion product deposits are often found on superheater tubes operating above the critical point in a supercritical fossil-fueled power plant, and it is not unusual to find oxide films of several hundred micrometer thickness on these tubes [7]. Such high fouling rates and deposit thicknesses could be problematic, especially for a fuel cladding in an SCWR. Furthermore, fouling in an SCWR could be exacerbated by the complex geometry of the fuel bundle in the reactor core [8].

In addition to deposition, transport of corrosion product particles, whether exfoliated from deposited material or precipitated from the bulk fluid, can be problematic in power generating systems. Once the scale thickness reaches approximately 100–200 μm, oxides on austenitic steel begin to exfoliate due to the differences in thermal expansion between the tube surface and the outer oxide layer, especially during startup and cooling of the boiler [1]. Tube plugging due to exfoliated material buildup can cause overheating in the portion of the tube, resulting in creep rupture of the piping when the pressure due to the fouling buildup exceeds the creep strength of the tubing [1]. In addition, exfoliated material has been found to erode turbine components in a supercritical fossil-fueled power plant if solid particles are released into in the fluid stream. In solid particle erosion (SPE), the protective oxide layer on piping and other components are eroded by particles suspended in the

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fluid stream [9]. SPE can contribute to increased maintenance costs and a decrease in the thermal efficiency of a turbine, which can be very expensive [10]. For an SCWR, transport of radioactive corrosion products can be a significant problem. Corrosion products can form in the reactor core, attaching to fuel cladding and other core components and are then irradiated [11]. Once the particle exfoliates, it can travel to other parts of the system outside the core becoming a source of hazardous radiation to plant operators [6]. Therefore, scale buildup and its resistance to exfoliation is a major concern for any system operating with SCW.

The need for in situ particulate sampling systems can be significant for power plant applications. Information about the properties of the particle such as size, shape, hardness, and strength can lead to information about potential damage that particulates can have on system components [12]. The composition of the particles give an indication as to where they may be coming from (e.g. fuel cladding, piping, etc.), as well as a predicted hardness and strength of the particles.

Sampling at high temperature has been shown to provide better representation of the particulates in the system. Turner and Klimas [13] made measurements of particles on a filter before and after a heat exchanger and found that the concentration of iron was twice as large as when the filter was sampled hot. Turner argued that such a difference is likely due to thermophoresis, where the particles diffuse down a temperature gradient, therefore transported to the colder surface and attaching to the heat exchanger wall. Sampling ports in real power-generating systems are often far away from the line being sampled which can cause further losses in the particulates found at the ports. In a nuclear pressurized water reactor, it was found that 50–75% of particles were lost or dissolved in the solution due to long sampling lines [14].

The present work examines four techniques for measuring and monitoring fouling and transport of magnetite in supercritical water. The intention is to determine the effectiveness of these techniques in observing the various particle size, deposition rate, and adhesive strength of the particle to the wall in supercritical water under various heat flux, temperature, and pH conditions.

2. Experimental method

2.1. Apparatus

The once-through flow apparatus shown in Fig. 1 was used for all experiments reported in this study. The majority of the system tubing is constructed from 1/4″ seamless AISI stainless steel 316L. A 20 L plastic tank and a glass flask were used for the primary feedwater tank and the injection solution tank, respectively. It was important to keep the oxygen content low in the system favoring the formation of magnetite, and therefore, the tanks were deaerated by vigorously bubbling nitrogen into the water.

A high-pressure positive-displacement pump with a pulsation damper delivered the majority of the fluid. Three preheaters (combined total 8.6 kW) are located between the main pump and the test section. A secondary pump injects the ferrous precursor solution into the main stream 14 cm before the test section. Flow passes through a perforated metal disc with 0.5 mm diameter holes to ensure good mixing prior to the test section. The 1/8″ tube test section is heated uniformly by electric current running through the tube walls.

Eleven K-type Chromel/Alumel thermocouples were spot welded to the 1/8″ test section tubing on the outside wall. These thermocouples were placed on the top of the tube, however, buoyancy effects were found to be negligible using calculations developed by Bazargan et al. [15], and the results of these calculations are given by Karakama [16]. Bulk fluid temperatures were measured using Inconel sheathed, ungrounded probes which were inserted at the tees with the probe end approximately at the center of fluid flow.

Temperature measurements of the test section thermocouples were recorded using 16-bit resolution (3.12 μV or 0.1 °C). Temperature is sampled at 20 kHz but 5-s averages are used in all post processing and reporting. The temperatures were quite stable (std = 0.7 °C for experiment #1) and therefore, any temperature differences due to fouling can be measured with an accuracy of 1 °C.

Three filters were constructed and installed at various locations in the system to collect particles formed in supercritical water. After each experiment, the filters were removed and analyzed using SEM (scanning electron microscope) and EDX (energy-dispersive X-ray spectroscopy) with the objective of determining particle size, shape, and composition. After the test section, a final tee splits the stream toward a secondary line consisting of a high-temperature, high-pressure filter and the primary line connecting directly into a heat exchanger. Sintered silver membranes (SPI Supplies; absolute retention pore size of 0.2 μm and thickness of 50 μm, product #01170-CF) were used for high-temperature sampling. The thinness of the filter makes it ideal for higher flow rates and the conductive properties of the silver membrane make it excellent for SEM/EDX and XRD (X-ray diffraction) analysis. The secondary line has its own heat exchanger and a needle valve to cool and depressurize the fluid to room temperature and ambient pressure. A low-temperature, low-pressure (LTLP) 25 mm Swin-Lok filter holder filter with glass fiber membrane (Millipore; 0.7 μm pore size; product #APFF02500) is located after the needle valve in the secondary line.

On the primary line, a 2.0 m long tube and shell heat exchanger cools the hot supercritical fluid flowing in the tube side with cold water flowing in the shell side. After the primary heat exchanger, there is a low-temperature high-pressure (LTHP) filter followed by a TESCOM back pressure regulator. The LTHP filter holder body was constructed from stainless steel 316L and the same glass fiber filters used in the LTLP filters were also used for the LTHP filter. The LTHP filter was used to collect particles in the primary line after the heat exchanger as well as to protect the back pressure regulator which was sensitive to particulate fouling. Pressure was monitored with a GP-50 pressure transducer (P-1 in Fig. 1), calibrated by the manufacturer with an accuracy of ±0.1 MPa.

Before each experiment, the primary pump was turned on and the system was flushed with deionized water for about 1 h. Primary and injection tanks were continually sparged with nitrogen. An Omega DOB21 measured the dissolved oxygen (DO) content in the two feedwater tanks. The DO measurement has a relative accuracy of 0.02% FSO. After 1–2 h of sparging, the DO reached a nominal value of 0.00 ppm.

After the desired flow rate and pressure were achieved at room temperature, the system was heated to supercritical conditions. The injection pump was momentarily turned off in order to switch the injection tank from deionized water to the precursor solution. This point would be observed in the temperature measurements by a momentary increase in the temperature profile of the test section due to reduced flow rates. Once the tank with the precursor solution was connected, the injection pump was turned on once again and the temperature of the test section dropped to its original temperature. Each experiment ran for approximately 40 min, with the exception of the low-concentration ferrous chloride experiment which lasted for 400 min. The total mass of the iron injected was kept constant in all experiments.

Some experiments were done at a higher pH of ~9 since the majority of current CANDU reactors run under an alkaline water chemistry using LiOH [17]. The pH is known to affect both the morphology of the magnetite particles formed in aqueous solutions [18], and the attachment of particles onto heated walls in high