Deposition of hematite particles on alumina seal faceplates of nuclear reactor coolant pumps – laboratory experiments and industrial feedback

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Abstract

In the primary circuit of pressurized water reactors (PWR), the dynamic sealing system in reactor coolant pumps is ensured by mechanical seals whose ceramic parts are in contact with the cooling solution. During the stretch-out phase in reactor operation, characterized by low boric acid concentration, the leak-off flow has been observed to abnormally evolve in industrial plants. The deposition of hematite particles, originating from corrosion, on alumina seals of coolant pumps is suspected to be the cause. As better understanding of the adhesion mechanism is the key factor in the prevention of fouling and particle removal, an experimental study was carried out using a laboratory set-up. With model materials, hematite and sintered alumina, the adhesion rate and surface potentials of the interacting solids were measured under different chemical conditions (solution pH and composition) in analogy with the PWR ones. The obtained results were in good agreement with the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and used as such to interpret this industrial phenomenon.

Keywords: adsorption, fouling, zeta potential, pressurized water reactor.

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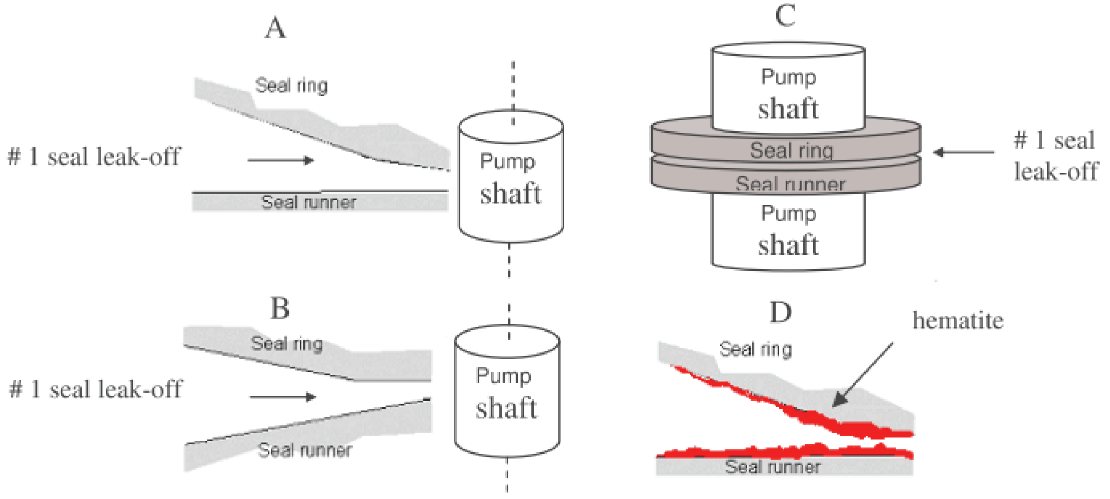

Figure 1. Seal interface diagram: (A) design used in 1300 MW PWR (8 inches seal – the pump shaft is nominally 203.2 mm in diameter), (B) design used in 900 MW PWR (7 inches seal – the pump shaft is nominally 177.8 mm in diameter), (C) scheme of the leakage between the radially tapered seal faces and (D) Deposition of hematite onto seal faceplates.

Reactor coolant pumps (RCP) provide water circulation in the primary circuit of pressurized water reactors (PWR). A chain of three mechanical seals ensures a dynamic sealing system between the primary circuit (155 bars in normal operating conditions) and the reactor building. The first one, the #1 seal (Figure 1), is a hydrostatic film riding over radially tapered ceramic seal faces that operates at temperatures below 95 °C and ensures the main pressure drop. Alumina or silicon nitride are the commonly used ceramics. A significant number of French RCP seals have had operating anomalies during the last few years. The problem has been related to significant changes or trend in #1 seal leak-off flow, which can sometimes exceed the recom-

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mended operating limits of the seal, during the stretch-out phase. The height of the interface near the shaft is equal to 10 μm and the normal operating range is several hundred dm^3/h. The recommended seal injection temperature is maintained near 50 °C.

Boric acid, a weak acid of boron, is used in nuclear power plants as a neutron poison to slow down the rate at which fission is occurring. As the fuel is burned-up, the concentration of boric acid dissolved in the primary reactor coolant decreases (from about 2200 to 5–10 mg dm^{-3}) to maintain 100% power. Lithium hydroxide is used to neutralize the acidity created by the addition of boric acid; it is kept in a specific range with respect to boric acid concentration (pH 6.8 at 50 °C). At the end of the fuel cycle, when the boron content is less than 10 mg dm^{-3}, the average temperature of the coolant fluid is decreased to extend the fuel burn-up. This so-called stretch-out phase is characterized by a slightly higher pH (pH 7.5 at 50 °C). All of these conditions are summarized in the Table 1 [1].

Amongst the main causes of RCP working anomalies, the deposition of iron oxide particles onto seal surfaces is seen as the most likely explanation for this phenomenon. Even though the alloys used in primary cooling circuit are chosen as less corroded, a release of metallic ions (mainly iron, cobalt and nickel) takes place. Precipitation of these ions also occurs, especially due to changes in temperature, leading to the formation of colloidal particles of metallic oxides. A typical concentration of a few dozens of μg kg^{-1} was found [2]. Indeed, deposits of hematite (α-Fe_2O_3) have been observed on seal faces of French PWRs, as described later in this work. Such deposits can modify the taper geometry, surface roughness and, depending on the location and amount of the deposit, the net convergent angle between the ring and runner faceplates resulting in changes (increase or decrease) in seal leak-off flow. More generally, the deposition of undesired solid particulate matter, or fouling, in industrial equipment where a fluid is circulating is the cause of numerous technical problems and has been thoroughly studied [3–6]. Particle deposition is a two-step process: 1) transport of particles from the bulk solution to the substrate wall, according to hydrodynamics, electrophoresis or thermophoresis and 2) adherence of particles according to physicochemical interactions between the particles and the wall [7]. Moreover, deposition is in competition with the detachment of adhered particles, as a consequence of the drag force [8]. So, the net deposited amount results from the equilibrium between these two phenomena. The physicochemical interactions are described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, where the force of adhesion is the sum of electrostatic forces and the Van der Waals ones, the latter being always positive. The electrostatic forces dictate the attachment step [9–11], as the relative charges of the acting surfaces determine whether the interaction is repulsive (alike charges between particles and wall) or attractive (opposite charges). Isoelectric points (IEP) of particles and of the substrate indicate the pH range where the adhesion might occur, so the chemical prediction needs the knowledge of IEP values for both materials. They are measured by different methods, depending on the solids: mainly by electrophoresis for particles [12], and contact angles [13], streaming potential [14] or latex adhesion [15] for massive substrates.

In industrial systems studied in this work, the correlation between the deposition of hematite and the chemical conditions of the stretch-out phase solution (evolution in boron concentration) has been observed but not yet understood. So, the objective of this work was 1) to determine if the transition from normal operating conditions to those of the stretch-out phase (Table 1) could lead to the deposition of hematite particles, and if so, 2) to elucidate the mechanism of this deposition. To fulfill these objectives, laboratory experiments on a model system hematite–alumina substrate were performed. A previously developed set-up was used to study the influence of the solution pH and composition on the adhesion rate of suspended hematite particles onto the walls of a reactor made of alumina. Two series of measurements were performed, without and with boric acid addition. Also, the effect of H_3BO_3 on the IEP of hematite was investigated.

EXPERIMENTAL

Materials

Hematite, a high-purity powder (99.945%) from Alfa Aesar, was used as received. Scanning electronic microscopy (SEM) image (Figure 2) shows the particles of around 150 nm in size with a high degree of polydis-

Table 1. Main physicochemical characteristics of PWR coolant solution [1]

Parameter	Unit	Normal operating conditions	Stretch-out condition
Boron (as boric acid)	mg kg^{-1}	From 2200 (at the beginning of the cycle) to 10 (at the end of the cycle)[a]	< 10
Lithium (as lithine)	mg kg^{-1}	From 2.2 (at the beginning of the cycle) to 0.5 (at the end of the cycle)[a]	< 0.5
Oxygen	mg kg^{-1}	< 0.010	< 0.010
Hydrogen	cm^3 kg^{-1}	25 to 35	25 to 35

[a] Boric acid and lithine concentrations are coordinated to maintain a pH of 7.2 at 300 °C

persity. The 250 cm^3 reactor made of alumina (Andermann, Germany) had the following characteristics: purity, 99.8% Al_2O_3, bulk density, 3.8 g cm^{-3} and 0% apparent porosity.

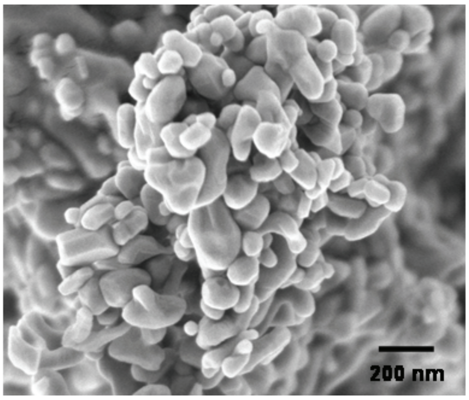

Figure 2. SEM Micrograph of hematite powder particles.

Experiments

Turbidimetry was the analytical method used to study the adhesion process. The amount of deposited hematite was calculated from the concentration of particles remaining in the suspension, deduced from its turbidity. Adhesion measurements were carried out in a set-up described elsewhere [9]. A hematite suspension (1 mg dm^{-3}) was prepared with KCl (0.01 mol dm^{-3}) as a background electrolyte or with a mixture of lithium hydroxide/boric acid (composition detailed below). It was poured into the reactor and sonicated for a few minutes. Stirring was provided by a four-blade glass propeller. The pH and temperature were continuously measured with a pH electrode and a temperature sensor (Metrohm 6.0228.000). The pH electrode was calibrated at 50 °C with buffers (Metrohm). A continuous flow of nitrogen was kept over suspension to avoid CO_2 contamination. A thermostated double-wall jacket was used to maintain the reactor temperature at 50±0.5 °C.

A Tygon tube plunged into the reactor was used to transfer a suspension aliquot into a turbidity cell by a vacuum line. The experiment consisted of withdrawal of a 30 cm^3 sample, after its 5 min homogenization at a set pH, for turbidity measurement. The analyzed sample was poured back into the reactor. This procedure was repeated typically 4 times during 30 min. Then, the pH conditions were modified (addition of small acid or base amount) and another series of samples withdrawn for turbidity check. The experiments were performed with KCl electrolyte to keep the ionic strength constant, or with a mixture of $LiOH/H_3BO_3$ to obtain the conditions close to those of PWR, Table 2.

Turbidity measurements were performed by using a Hach 2100N turbidimeter. After calibration with formazine standards (Hach), the calibration was checked daily with Gelex secondary turbidity standards (Hach). In each series of turbidity measurements performed at a set pH for a given time, all measured values were normalized to the value of the first, initial measurement.

The zeta potential measurements were carried out by using a Malvern Zetasizer NanoZS instrument. Hematite concentration was optimized at 50 mg dm^{-3}. The ionic strength was fixed at 10^{-2} mol dm^{-3} with KCl, and the pH adjusted with small amounts of HCl and KOH. The influence of boron on the zeta potential of hematite was examined by using 0.1 mol dm^{-3} H_3BO_3. The zeta potential is known to be ionic strength dependent. So, in order to be able to compare the values obtained in the absence or presence of B, the measurements had to be performed at the same ionic strength. Therefore, H_3BO_3 was added into the supporting electrolyte and the experiment performed in the narrow pH range from 3.5 to 7. For the pH values lower than the acidity constant of boric acid, $pKa_{50} = 9.0$ [16], the dominant species is H_3BO_3, which is neutral and does not modify the ionic strength. Contrarily, as pH was raised by KOH, the ionic strength increased due to added K^+ and $B(OH)_4^-$ species formed, resulting from partial neutralization of H_3BO_3. Therefore, the measurements were performed up to pH 7, corresponding to a negligible increase in ionic strength.

RESULTS

Industrial feedback

In recent years, a significant number of French RCP has had seal anomalies during the stretch-out phase. This phase is characterized by a low boric acid concen-

Table 2. Experiments performed in PWR conditions

Composition, H_3BO_3 in 1 ppm LiOH, ppm	Adhesion rate×10^3, min^{-1}	Measured pH	Theoretical pH
0	0.00	9.3	9.4
20	–0.08	7.5	8.0
200	–0.1	6.9	7.0
1000	0.07	6.1	6.1
3000	–0.07	5.3	5.1
5000	0.3	4.7	4.6
10000	0.2	3.9	3.9

tration, less than 10 mg dm^{-3}. Normalized seal leak-off flows versus the number of days from the beginning of the stretch-out operation are shown in Figure 3 for 7 and 8 inch seals. For each seal, the data were collected from different power plants (given in different colours in the diagrams).

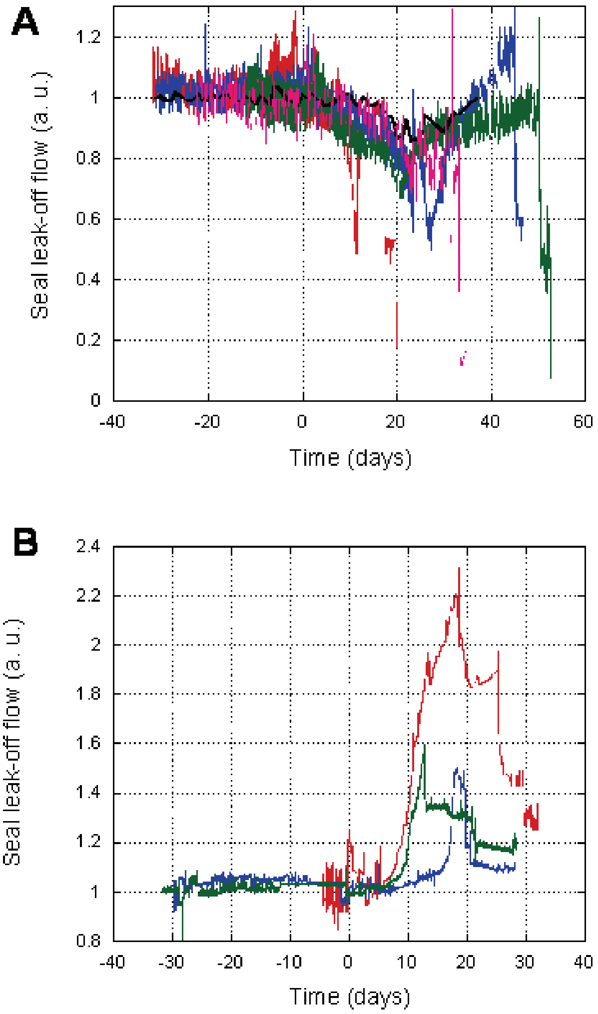

Figure 3. Normalized seal leak-off flows vs. the number of days from the beginning of stretch-out operation for: A) 7 inch seals in 900 MW PWR, and B) 8 inch seals in 1300 MW PWR. Each color corresponds to a different nuclear reactor.

In all examined reactors, the changes in seal leak-off flow started with the stretch-out operation at “0 days” (Figure 3). Before this operation they were constant for both types of seals (designated as “negative days”). In Figure 3A, a decrease in the seal leak-off flow, assumed to be due to modified seal injection water chemistry was observed about six days after the beginning of the stretch-out phase, lasting for about one month (except for the first plant where the decrease was more rapid) until a value approaching low operating limit was reached. A subsequent increase in flow was due to swapping the injection filters of seals with the new ones. In Figure 3B, a sharp increase in seal leak-off flow was observed about six days after the beginning of stretch-out, approaching a high operating limit. The subsequent decrease was also a result of swapping seal injection filters with the new ones.

Several inspections of aluminum oxide seal face-plates upon their removal showed that in all cases, the deposits found on the faceplates surfaces (reddish in color) were predominately composed of iron oxides (hematite).

Turbidity measurements and adhesion rate in laboratory experiments

The adhesion rate of hematite particles onto alumina was studied using a laboratory set-up, according to previously presented experimental protocol. Due to low specific surface area of massive alumina and 0% apparent porosity, the adhesion led to a small decrease in hematite concentration (about 5%). Therefore, the concentration of hematite particles in the suspension has to be very low and measured accurately to determine the adhesion rate. If no agglomeration occurs (assured in our study by use of dilute suspension, low ionic strength and sonication), then the particle concentration can be determined with a high accuracy (error <0.2%) from the suspension turbidity. A linear relationship between the turbidity and the concentration of hematite particles (below 1.2 mg dm^{-3}) was found (Figure 4). The slope represents a turbidity coefficient (α in NTU dm^3 mg^{-1}). As can be seen, the temperature (25 or 50 °C) has no effect on the calibration. In the presence of boric acid, the turbidity coefficient is not modified, but the turbidity is slightly higher. This observation is probably due to insoluble impurities present in boric acid, as the acid concentration is high (0.46 mol dm^{-3} H_3BO_3).

Firstly, the reactivity of alumina reactor walls was tested for different hematite concentrations (0.25 to 1.5 mg dm^{-3}) at pH 3. The turbidity was normalized to the initial turbidity value for each concentration, and the data were fitted by linear segments. A typical evolution (1 mg dm^{-3}) is given in Figure 5.

The adhesion rate r (min^{-1}) was calculated by the following relation [9]:

$$r = \frac{(T_1 - T_2)}{(t_2 - t_1)} \tag{1}$$

where t_i is the time in min and T_i is the turbidity at time t, normalized to the initial turbidity value.

A linear variation of turbidity versus time is found in numerous adhesion studies [9], and corresponds to the low coverage of the surface. The same adhesion rate (0.0020±0.0002 min^{-1}) was found for hematite concentrations between 0.5 and 1.5 mg dm^{-3} at pH 3 (raw data not shown).

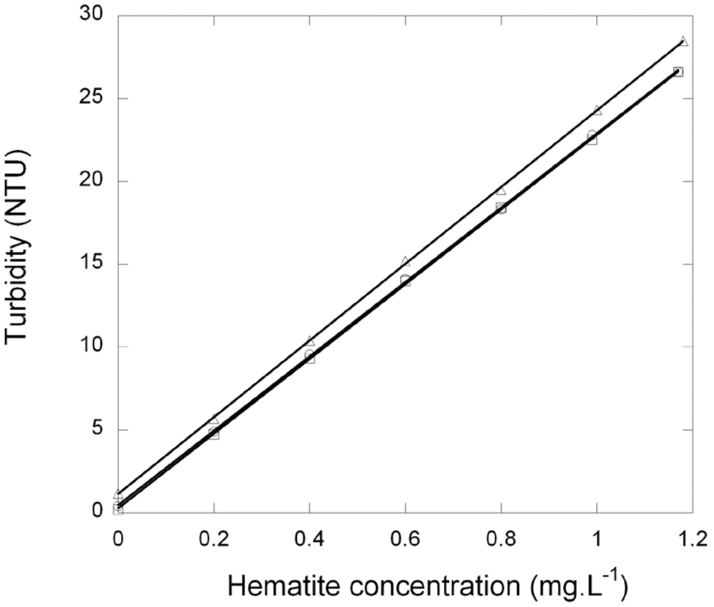

Figure 4. Calibration curves: turbidity measurement vs. hematite particle concentration at 25 °C without boric acid (□), 50 °C without boric acid (○), and at 50 °C with 0.46 mol dm^{-3} H_3BO_3 (5 g dm^{-3} B) (△).

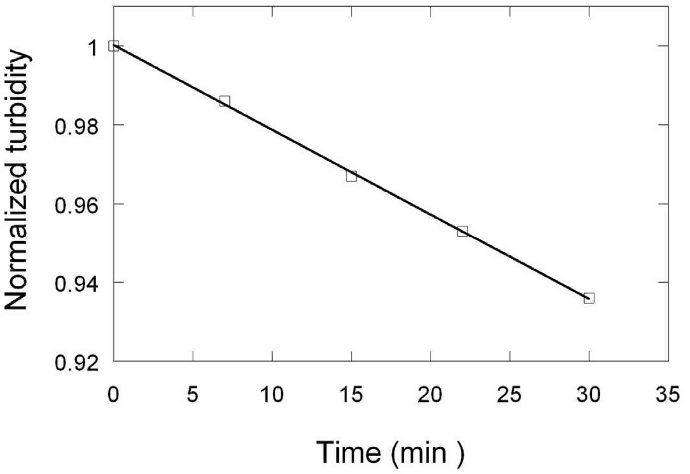

Figure 5. Evolution of turbidity of hematite suspension (1 mg dm^{-3}) with time in an alumina reactor (KCl 10^{-2} mol dm^{-3}, pH 3, T = 50 °C).

Thus, it was proven that the adhesion rate is independent on hematite concentration as expected, since normalizing turbidity is a simple division by initial concentration. This result allows one to represent the adhesion reaction by the following Eq. (2):

$$\mathrm{A} + \overline{\mathrm{S}} \rightarrow \overline{\mathrm{SA}} \quad (2)$$

where A represents the particle, $\overline{\mathrm{S}}$ the reactive site, and $\overline{\mathrm{SA}}$ the particle adsorbed at the surface.

As high energy is required to remove particles from the surface, the detachment step is negligible under hydrodynamic conditions of the experiment. The rate of reaction (2) is:

$$R = k[\mathrm{A}]^a[\overline{\mathrm{S}}]^b \quad (3)$$

where k is the rate coefficient, and a and b are reaction orders for particle and surface, respectively. As the surface coverage is very low, $[\overline{\mathrm{S}}]$ can be considered constant. Also, our previous results [9] have shown that the rate is linearly dependent on the particle concentration, *i.e.*, $a = 1$, leading to the simple relation $R = k'[\mathrm{A}]$ with $k' = k[\overline{\mathrm{S}}]$.

After Eq. (1), the adhesion rate can be written:

$$r = \frac{1 - T/T_i}{\Delta t} = \frac{\Delta[\mathrm{A}]}{[\mathrm{A}]_i \Delta t} \quad (4)$$

where $[\mathrm{A}]_i$ is the initial concentration of hematite and T_i is the initial turbidity of suspension. The relation between the rate of reaction and rate of adhesion is:

$$R=\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=r[\mathrm{A}]_i \tag{5}$$

Thus, R is proportional to $[\mathrm{A}]_i$, *i.e.*, the adhesion reaction can be considered to be pseudo first order, dependent only on the concentration of particles.

Effect of pH and boric acid addition on adhesion rate of hematite

Once the protocol to interpret the experimental results was defined, several experiments were performed to determine the effect of pH and boric acid on the adhesion rate of hematite (1 mg dm^{-3}). Experiments done using a simple electrolytic solution (0.01 mol dm^{-3} KCl) illustrate alumina surface reactivity towards hematite (Figure 6). The observed trend indicates that the adhesion increases at low pH values, decreases with increase in pH, and drops to zero at pH 10. The scattering of experimental values is rather large, as often observed in adhesion studies [3–5].

As discussed earlier, in the PWRs the primary circuit solution is characterized by the presence of boric acid and lithine. Some typical physicochemical conditions are listed in Table 1. To simulate the industrial conditions, a series of adhesion measurements was performed using mixed $\mathrm{LiOH{-}H_3BO_3}$ solutions, with a fixed concentration of lithium (Li 1 mg dm^{-3}) and different concentrations of $\mathrm{H_3BO_3}$. Solution compositions are given in Table 2. As can be seen, incremental increase in boric acid concentration causes a gradual decrease in pH from 9.3 to 3.9. Contrary to experiments without boron, no adhesion of hematite onto alumina reactor walls was observed from the mixed Li/B solution, whatever the solution pH and chemical composition (Table 2), taking into account that the absolute error can be estimated to $\pm 10^{-3}$ min^{-1}.

Surface potential of solids

Electrostatic interactions play a dominant role in adhesion. For example, the following equation was used to simulate results of AFM (atomic force microscopy) [17] forces for a sphere/plane system, F_{el}:

$$F_{\mathrm{el}}/R=\frac{\varepsilon\varepsilon_0 4\pi\varphi_1\varphi_2\exp(-\frac{d}{\lambda})}{\lambda} \tag{6}$$

where R is the radius of the spherical particles, d the separation distance, ε the dielectric constant of water, ε_0 the permittivity of free space, φ_i the potential of solid i, and λ the Debye screening length.

Thus, to understand the interactions, it is necessary to characterize surface potentials of the interacting solids, in our case – hematite and massive alumina.

The zeta potential of hematite particles was measured as a function of pH in the 4–11 range (Figure 7). The isoelectric point (IEP) was determined around pH 9. Previously published studies indicated IEP between 6 and 10 [18]. Our value lies amongst the highest reported ones, in accordance with high purity of the solid. Indeed, contamination by synthesis compounds (sulfates or carbonates) can shift the IEP of iron oxides to lower pH values. This is important as the contamination of the solid surface affects the formation of weak surface complexes, and the presence of such contaminants could decrease or hinder the role of boric acid in surface potential [19]. The effect of boric acid on zeta potential of hematite is clearly seen: a zeta potential versus pH curve is shifted toward lower pH values. In the presence of 0.1 mol dm^{-3} boric acid, the IEP is ca. 4 pH units lower than the value measured in a simple electrolyte (KCl 0.01 mol dm^{-3}). The zeta potential was measured at 25 °C, whereas a higher tempe-

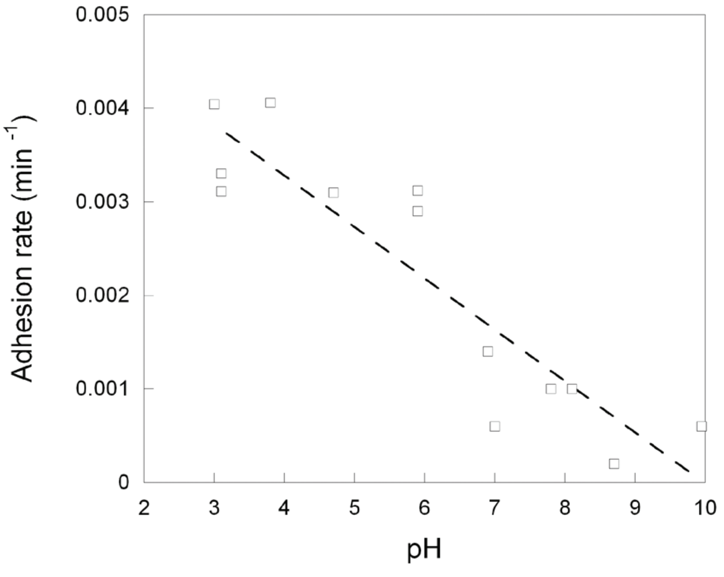

Figure 6. Adhesion rate of hematite particles onto alumina (KCl 0.01 mol dm^{-3}, 50 °C). Dashed line is a guide for the eye.

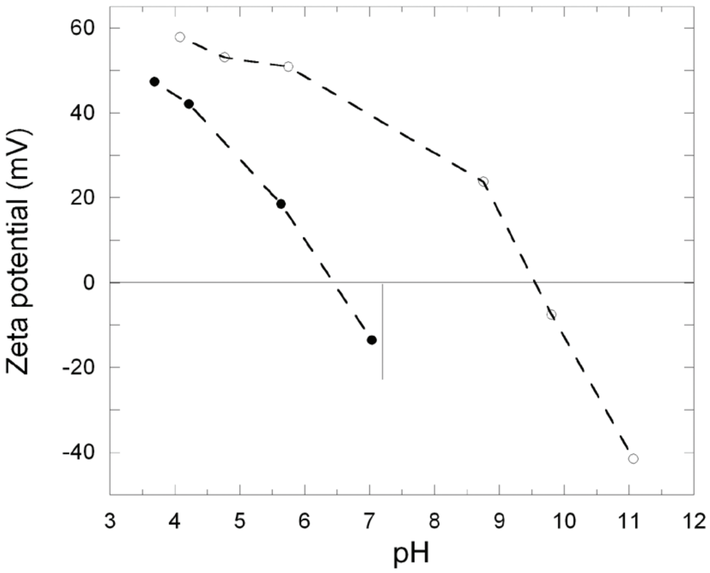

Figure 7. Zeta potential of hematite in: KCl 10^{-2} mol dm^{-3} (○), and in KCl 10^{-2} mol dm^{-3} + H_3BO_3 0.1 mol dm^{-3} (●). The vertical line shows the limit of the range corresponding to a constant ionic strength.

rature (ca. 50 °C) corresponds to both adhesion experiments and PWR conditions. A very weak effect of temperature on the amount of boron sorbed onto ferric oxy-hydroxide between 10 and 70 °C was reported [20,21]. Therefore, the shift in IEP should be attributed to the sorption of boron only. Moreover, values measured at 25 °C can be used to interpret the adhesion data recorded at slightly higher temperatures. These results show that the presence of concentrated boric acid leads to a charge reversal of hematite particles in a wide pH range (6.5 to 9.5). As adhesion is ruled by electrostatic interactions, a large effect on the behavior of hematite toward alumina can be expected.

Contrary to hematite particles, it was much more difficult to perform a measurement of the surface potential of alumina reactor wall, as a massive sample. We have developed a method [9,15] where the surface potential of a massive reactor is probed by adhesion of particles with a known surface potential. Applied to the alumina reactor, it was found that its IEP is located below pH 3. This value is much lower than that measured for alumina powder samples [18], but close to literature values obtained for massive samples [22], as discussed below.

DISCUSSION

To gain information about the fouling of RCP seals, we performed experiments to study the adhesion of hematite onto sintered alumina reactor walls, since direct work with alumina seals was not possible.

The obtained results are discussed in the light of DLVO theory. So, the energy of interaction between two charged bodies in the polar media is a summation of attractive Van der Waals force and electrostatic ones. In the case of metal oxides in water, the latter are predominant [9,11]. Indeed, when placed in water, the surface hydroxyl groups on iron oxide powder (>FeOH) react with H^+ or OH^- at low and high pH, respectively, creating a positively ($>FeOH_2^+$) or negatively ($>FeO^-$) charged surface, following the 2-p*K* model [23]. The isoelectric point corresponds to the pH where the net surface charge is zero.

As already discussed, the surface potential of hematite (IEP ≈ 9), measured in this work (Figure 7), accords well with previously published studies [10,18], but the surface potential of alumina (*IEP* < 3) is much more tricky. Indeed, zetametry of alumina particles, whatever the crystallographic phase or hydration state (*α*, γ-Al_2O_3, boehmite, gibbsite, etc.), has indicated an *IEP* > 8 [18]. A discrepancy in IEP values exists in literature (see [22] and references herein), depending on whether the alumina is present in the form of a powder or a massive substrate [23]. The *IEP* values as low as 3–4.2 were found by several researchers for *α*-alumina sapphire single crystals [22]. This behaviour is still not fully understood but indicates a difference in charging mechanisms. It could be assumed that the surface charge of massive alumina is acquired via a process different from acid-base reaction with hydroxyl. Accumulation of hydroxide/hydronium ions in the interfacial water layer could be another explanation [15,22].

The main experimental result of this study – the effect of pH and boric acid addition on the adhesion rate of hematite is illustrated in Figure 6 and Table 2. In pure electrolyte solution (Figure 6), a decrease in adhesion with an increase in pH can be interpreted by a decrease in electrostatic attraction between hematite particles, which positive surface potential drops to 0 at around pH 9, and alumina surface, negatively charged over the whole pH range studied. On the other hand, the experiments performed in the boric acid/lithine containing electrolyte solution revealed totally different adhesion behavior. The effect of lithium on the surface potential of alumina and hematite is expected to be negligible, knowing that this cation interacts weakly with metallic oxides [24]. Contrarily, boric acid is known to sorb on iron oxy-hydroxides in the pH range 4–12 [24–26]. This phenomenon causes a decrease in surface potential of particles by several mechanisms. Determination of real speciation of sorbed boric acid would demand a complex study out of the scope of this work. However, reactions (7)–(9) are several examples of possible mechanisms taking place at the hematite surface, from low to high solution pH, representing: neutralization of the surface (Eq. (7)), charge reversal (Eq. (8)) or the formation of a negative surface charge (Eq. (9)):

$$\rangle \mathrm{Fe-OH_2^+ + H_3BO_3 \rightarrow \rangle Fe-O-B(OH)_2 + H_3O^+} \tag{7}$$

$$\rangle \mathrm{Fe-OH_2^+ + B(OH)_4^- \rightarrow \rangle Fe-O-B(OH)_3^- + H_3O^+} \tag{8}$$

$$\rangle \mathrm{Fe-OH + B(OH)_4^- \rightarrow \rangle Fe-O-B(OH)_3^- + H_2O} \tag{9}$$

Indeed, no adhesion of hematite was measured in the $LiOH/H_3BO_3$ mixtures (Table 2). In the absence of boron this can be explained by high pH due to lithine. In the presence of boron, hematite surface is complexed by boron species, which causes a decrease or reversal of its surface potential, leading to the disappearance of attractive electrostatic forces present previously between positively charged hematite and negative alumina surface, as illustrated in Figure 6. Moreover, the dependence zeta potential–pH (Fig. 7) confirms a charge reversal of hematite after addition of boric acid. From the results obtained in electrolyte and complexing solutions (Figure 6 and Table 2, respectively), it can concluded that the fouling of alumina seals occurs due to the evolution in boron concentration. Thus, the finding can be used to interpret the industrial feedback (Figure 3). A common observation in nuclear power plants is the change in the leak-off flow rate about six days after the beginning of the stretch-out phase. During this period, the boron concentration reaches values below 10 mg mol dm^{-3} that changes the sign of the surface potential of iron oxide particles in the circuit: desorption of boron from particles leads to a neutral or positive hematite surface. This can be represented by Eqs. (7)–(9) from right to left. The affinity of particles toward negatively charged alumina seals is greatly increased, leading to their deposition. Thick particle layers formed then influence the flow rate due to fouling effect. The change in seal roughness by formation of a deposit could modify the hydrodynamic conditions at the surface of the seals, leading to an increase or a decrease of the flow rate (Figure 3).

CONCLUSION

Experiments with model materials (sintered alumina – hematite) have brought to light the influence of solution pH and boron concentration on particle deposition. It was shown that the adhesion process accords well with the DLVO theory. In the absence of boron, the adhesion rate decreases at pH 3–9, along with a decrease in positive surface charge of hematite. In the presence of high boron concentrations (>20 mg dm^{-3}) or lithine only (alkaline pH), repulsive electrostatic interactions prevent the adhesion of hematite particles onto alumina, due to alike (negative) charges. From the industrial feedback for several French PWRs, the correlation between the stretch-out phase and the abnormal evolution of the seal leak-off flow has been observed. Based on laboratory results, we explain this behaviour by low boron concentration characterizing the stretch-out phase solution, which reverses the charge of iron oxide particles from negative to positive and promotes their adhesion onto negatively charged alumina seal faceplates.

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IZVOD

DEPONOVANJE ČESTICA HEMATITA NA POVRŠINU ZAPTIVKI OD ALUMINIJUM-OKSIDA U RASHLADNIM PUMPAMA NUKLEARNIH REAKTORA – LABORATORIJSKI EKSPERIMENTI U SPREZI SA INDUSTRIJOM

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(Naučni rad)

U primarnoj petlji nuklearnih reaktora sa vodom pod pritiskom (PWR), dinamički sistem zaptivanja kod pumpi za hlađenje obezbeđen je mehaničkim zaptivkama čiji su keramički delovi u kontaktu sa rashladnom tečnošću. Tokom faze produženog izgaranja (engl. *stretch-out phase*) u radu rekatora, za koju je karakteristična niska koncentracija borne kiseline, primećeno je nekontrolisano curenje u industrijskim postrojenjima. Najverovatniji uzrok ove pojave je deponovanje čestica hematita, kao produkta korozije, na keramičke zaptivke od aluminijum-oksida, koje su sastavni delovi rashladnih pumpi. Pošto je razumevanje mehanizma adhezije od suštinskog značaja za prevenciju zakrečenja i uklanjanje čestica sa površina, izvedeno je eksperimentalno istraživanje primenom laboratorijskog uređaja. Kao model materijali korišćeni su prah hematita i sinterovani aluminijum-oksid, a brzina adhezije i površinski potencijali ovih materijala u interakciji mereni su pri različitim hemijskim uslovima (pH i sastav suspenzije), analogno uslovima u PWR reaktoru. Dobijeni rezultati su bili u skladu sa Derjaguin–Landau–Verwey–Overbeek (DLVO) teorijom i kao takvi su korišćeni za interpretaciju industrijskog fenomena.

Ključne reči: Adsorpcija • Zakrečenje • Zeta potential • Reaktori sa vodom pod pritiskom