

# The Adsorption of Hematite Particles on Steel in Strongly Alkaline Electrolyte

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The adsorption of hematite particles is an important but poorly understood elementary step in the electrolytic preparation of iron metal. In this work, a quantitative method of measuring the quantity of particles adsorbed onto a steel surface from a hematite suspension in concentrated sodium hydroxide electrolyte is proposed. The experimental procedure involves a preadsorption step in a hematite suspension and transfer to a particle-free solution, followed by a potentiostatic reduction of the film of adsorbed particles. The resulting current transient yields a quantitative analysis of the quantity of  $Fe_2O_3$  adsorbed in the original solution. This work demonstrates that adsorption is only weakly dependent on the hematite particle concentration and pH (between 12 and 15). A simple phenomenological model for hematite reduction is proposed based on the form of the current–time transients. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3273198] All rights reserved.

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Iron oxide electrolysis to produce iron metal has been known since the pioneering work of Lloyd in 1929<sup>1</sup> and LeDuc et al. in 1959.<sup>2</sup> A process was patented by Offroy in 1974.<sup>3</sup> However, as the blast furnace is an efficient and mature technology, this work has been very limited in scope and, in particular, the details of iron oxide reduction have received very little attention. Recently, the race to develop new steel-making processes with low greenhouse gas emission has led to a renewed interest in this technology,<sup>4,5</sup> and small scale trials have demonstrated a very high efficiency for direct reduction in alkaline solutions.<sup>6</sup> Nevertheless, it is fair to say that a fundamental understanding of the mechanism of iron ore reduction is still limited. Indeed, to our knowledge, no similar process exists involving the cathodic reduction of a suspension of oxide particles. In general, the reduction of a suspended particle involves at least two elementary kinetic steps: (i) the adsorption or adherence of the hematite particle to the surface, followed by (ii) the electrochemical reduction of the particle. Previous papers<sup>7,8</sup> dealt with the second phenomenon, the mechanism of reduction independent of particle adsorption. In this paper, we make an attempt to investigate the adsorption of the particles to the electrode surface.

The reduction may be carried out in a strongly alkaline aqueous electrolyte (50 wt % NaOH–H<sub>2</sub>O at 100°C) in which finely ground hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, micrometer range) particles are suspended and reduced to iron metal on the cathode.<sup>1-3</sup> The overall net reduction reaction may be written as

$$Fe_2O_3 + 3H_2O + 6e^- \rightarrow 2Fe + 6 OH^-$$
 [1]

The suspension electrolysis process implies a reaction between a polarized surface and an insulating oxide particle with the resulting extraction of oxygen anions and the electrocrystallization of the metal. Though the process efficiency is close to unity in an electrolyte highly concentrated in suspended hematite particles,<sup>2</sup> the electrochemical study of the reaction mechanism for the hematite conversion to metal is hindered by the existence of the hydrogen evolution reaction (HER) as a competing phenomenon on the cathode

$$2H_2O + 2e^- \rightarrow H_2(g) + 2 OH^-$$
 [2]

The evidence of the contact between the particles in suspension and the cathode is difficult to establish because of the opacity of the electrolyte due to the large amount of suspended matter (15 vol %).<sup>3</sup>

Two recent studies have been dedicated to the isolation of the main steps of the reaction, namely, the role of dissolved species<sup>7</sup> and the reaction of a single particle on the cathode,<sup>8</sup> where it was revealed that a hematite particle can macroscopically be converted to

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iron metal when pressed in contact with a polarized surface. The reaction occurs via the local (microscopic scale) production of a magnetite intermediate and the electrocrystallization of iron on the particle surface. An investigation of iron solubility in alkaline electrolyte<sup>7</sup> showed that hematite bulk dissolution is low ( $2 \times 10^{-3}$  mol L<sup>-1</sup>) at 100°C and that the effect of the dissolved ferric ions in the bulk electrolyte on the electrochemical reactions can be neglected in the overall process. This latter study, however, demonstrated that the final electrodeposition step could be obtained from dissolved species in sufficiently reducing conditions, agreeing with the physical theory of crystallization at low temperature and the observation of deposits obtained in the suspension electrolysis process.<sup>6</sup>

These results are important to establish an electrochemical mechanism for the reaction, but the knowledge of the particleelectrode interaction in the suspension process is still lacking. Two limiting cases are possible for the contact mechanism of the hematite reactant according to the residence time of adsorption, as presented in Fig. 1: (a) The particle collides with the cathode surface such that only a fraction of oxide is converted to metal or (b) the particle is adsorbed on the cathode with a residence time sufficient for the entire particle to be reduced to metal.

Studies of hematite colloidal particle deposition on a stainless steel substrate have been conducted in an electrolyte at a pH value ranging from 2 to 12.<sup>9</sup> The zeta potentials for hematite and stainless steel at pH 12.8 (pH and ionic force being fixed by NaOH concentration) have been evaluated at -48 and -40 mV, respectively, confirming the existence of an electrostatic repulsion between both surfaces in alkaline conditions. However, the use of an electrolyte at a higher ionic strength enhances the deposition of colloids on surfaces of a similar negative charge because of a reduction of the doublelayer thickness. Interactions governing the adhesion of the particle to the substrate are therefore short-range forces, which may be evaluated through the Delaguin-Landau-Verwey-Overbeek<sup>10</sup> (DLVO) theory. The deposition of particles can also be enhanced at a higher temperature<sup>11</sup> or in the presence of a magnetic field.<sup>12</sup> The deposition of particles with repulsive electrostatic interactions (similar charge) cannot be predicted accurately with existing theories although models are under development, which, in addition, take into account the effect of hydrodynamics.<sup>13</sup> As a matter of fact, the experimental results available do not concern the strongly alkaline and high temperature range of the suspension electrolysis process under evaluation and cannot be directly extrapolated to predict the contact mode between the suspended particles and the electrode surface.

From these considerations, a simple experiment is proposed in this work to assess the contact properties between the hematite particles and an iron cathode. The method involves an exposure of the steel surface to the hematite particle suspension in a preliminary

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Figure 1. (Color online) Possible particle/electrode interactions in the suspension electrolysis process: (a) Collision and (b) adhesion of the particle on the cathode.

step, followed by an electrochemical characterization step where the reduction of hematite to metal is obtained. This methodology is used to characterize hematite particle adsorption as a function of suspension composition and exposure conditions.

# Experimental

*Materials.*— Hematite particles from Prolabo (batch 0507825) with less than 1% impurities were used in this work. A particle size distribution analysis (Malvern Mastersizer type S) revealed two size distribution peaks at 0.4 and 10  $\mu$ m, as illustrated in Fig. 2a and b. A mild steel plate, typical of a packaging application, was used for the adsorption substrate, as indicated in Fig. 3a.



Figure 2. (a) Particle size distribution and (b) SEM observation of the starting hematite particles.



Figure 3. (Color online) Steel surfaces used as cathode for (a) studying the electrochemical potential effect and for (b) observations.

For the microscopic analysis, the mild steel substrate was embedded in an epoxy resin holder to expose a square area of about 1 cm<sup>2</sup> (Fig. 3b), polished with 1200 and 2400 grade emery papers and thoroughly rinsed with distilled water before immersion. So-dium hydroxide solutions were prepared by dissolving NaOH (Prolabo 97% purity, maximum 2.5% Na<sub>2</sub>CO<sub>3</sub>) in purified water (Millipore system, resistivity 18.2 M $\Omega$  m).

*Hematite adsorption.*— The suspension was prepared from a sodium hydroxide and water solution at 110°C in a glass beaker (V = 0.4 L), in which the desired amount of hematite particles had been added. Concentrations in particles are given in the volume fraction of hematite, which is readily calculated from the amount of particles introduced ( $m_p$ ) and the hematite density ( $\rho$ )

vol 
$$\% = \frac{m_{\rm p}}{\rho} \frac{1}{V} 100 = 47.5 m_{\rm p}$$

A magnetic stirring device, which also acted as a heating system, was placed at the bottom of the vessel. Hematite adsorption was carried out by immersing the electrode in the suspension for 3 min.

*Electrochemical analysis step.*— Particles adsorbed during the adsorption step were detected and quantified by potentiostatic reduction in a separate particle-free electrolyte. Following the adsorption step, the electrode was directly transferred to the analysis cell without rinsing. The analysis electrolyte solution consisted of an unstirred, 50 wt % NaOH/water electrolyte at  $110^{\circ}$ C (pH<sub>25°C</sub> 15.3) in a glass beaker (0.4 L). A new solution was used for each electroreduction experiment to guarantee replication. A large-area platinum cylinder counter electrode and a HgO/Hg/KOH (10 M) reference electrode were used, with the steel/adsorbed hematite electrode as the cathode. A constant potential of -1.2 V vs Hg/HgO was applied to the steel electrode by a Solartron 1286 potentiostat in chrono-amperometric mode. Current transients were measured during the cathodic polarization.

The transfer of the electrode from the adsorption electrolyte to the analysis electrolyte required approximately 3 s, and polarization began approximately 5 s after the immersion in the analysis electrolyte. The surface was neither rinsed nor dried during the transfer; therefore, it remained exposed to the alkaline solution throughout. Nonadsorbed hematite particles, present in the electrolyte film after the removal from the adsorption electrolyte, were in this way redispersed in the analysis electrolyte. Therefore, only the particles that were strongly adsorbed on the surface were analyzed.

Scanning electron microscopy observation.— After the electrochemical reduction in the analysis step was achieved, the electrode was removed from the analysis cell, rinsed with purified water, and dried in an oven at 40°C under a N<sub>2</sub> atmosphere. The electrode surface was observed using a JEOL JSM-840 microscope. For each



**Figure 4.** (Color online) Current variation at  $E_{\text{cathodic}} = -1.2$  V after immersion (a)  $\bigcirc$ , in 15 vol % hematite suspension and (b)  $\triangle$ , in blank NaOH.

observed sample, approximately 10 pictures were randomly recorded to represent the whole electrode surface from a statistical viewpoint.

*IFM characterization.*— An interferometric microscope (IFM, Microxam 100HR ADE Phase Shift) was used to obtain the topography of the electrode surface.

#### **Results and Discussion**

The adsorption and reduction of hematite particles.— Figure 4 gives a typical example of the coulometric reduction of adsorbed hematite particles [(a), circles] after immersion in a 50 wt % NaOH–H<sub>2</sub>O solution at 110°C for 3 min with 15 vol % of hematite. A blank measurement [(b), triangles] after immersion under identical conditions in a solution without hematite particles is also shown. The analysis electrolyte was 50% NaOH at 110°C and was carried out at an imposed potential of -1.2 V vs Hg/HgO. Following previous studies of hematite reduction,<sup>8</sup> this potential is sufficient to reduce the hematite particles while minimizing the hydrogen formation reaction.

At least three distinct kinetic regimes are observed in the current transients whether or not hematite particle adsorption has occurred: (*i*) fast current decrease for approximately 1 s, (*ii*) transient current regime where either a distinct peak or a slow decay with a shoulder is observed, and (*iii*) steady-state current after 30 s until the end of the experiment. As shown in Fig. 4, the effect of the adsorbed particles is essential in the second kinetic regime. Figure 4a and b shows a start with a sharp decrease in the current density, which ends after approximately 1 s ( $t_p$ ) although the initial current is increased by a factor of 2 in the presence of adsorbed particles. Similarly, the steady-state current obtained after approximately 30 s is nearly identical for Fig. 4a and b. As the background current in the blank electrolyte is no doubt due essentially to the HER reaction, these results demonstrate that this reaction is not markedly affected by the presence of the adsorbed hematite particles.

By contrast, the second kinetic period is markedly affected by the presence of hematite particles. The blank (Fig. 4b) shows only a slight increase in the current, obtaining a steady state after approximately 4 s. The current transient for the sample immersed in the particle suspension shows a strong increase in current, passing through the maximum value of 95 mA at about 7 s, forming a well-defined peak, and then declines to a steady-state value, very similar to that measured for the blank experiment at  $t_{end}$  (28 s).

That the current maximum observed during the second period in Fig. 4a is due to the reduction of the hematite particles has been confirmed by scanning electron microscopy (SEM) performed after



Figure 5. Surface of the steel electrode after immersion in the suspension and reduction at -1.2 V/HgHgO.

the current transient has returned to the background. A typical example is shown in Fig. 5. The grains appearing on the surface have been identified as pure iron metal by energy-dispersive X-ray analysis (>90% Fe, <1% O). A detailed understanding of the current transients in the first period is beyond the scope of this work, but some comments are in order. The initial decrease during the first few seconds cannot be attributed to double-layer charging, which has a time constant of less than a second.<sup>14</sup> This current might be attributed to the reduction of an oxidized layer on the steel plate. From the determined charge (0.2 C for the blank and 0.4 C for hematite, from raw current integrated between t = 0 and  $t_p$ ), the thickness of the equivalent oxide layer (considered as hematite) is on the order of 100 nm, which agrees acceptably with the results obtained in such a concentrated electrolyte and high temperature, where iron oxide films form quickly.<sup>15</sup> While this proposition requires additional studies for verification, it does set a lower limit to the thickness of oxide films that can be measured with this technique.

The relatively slow increase in the current observed in the current transient for the blank (Fig. 4b) after  $t_p$  may be due to an increase in the electrochemically active surface linked with the removal of the insulating passivation layer. A larger concentration in the reactant (water) provided by the fresh electrolyte might also be responsible for such a behavior. This increase is much more pronounced in the surface immersed in the suspension. The charge difference between  $t_p$  and  $t_{end}$  can be converted to the quantity of Fe(III) by Faraday's law according to Reaction 1. The slow decay of the current for both experiments after  $t_{end}$  is commonly attributed to the diffusion limitation for aqueous species (water or ions) in a stagnant electrolysis configuration such as this.

Influence of hematite particle concentration .- The raw data of current transients at -1.2 V vs Hg/HgO for various concentrations of hematite particles in the suspension reactor are shown in Fig. 6a. The current increases with the hematite concentration, though the shape of the curves is not strictly identical throughout the trials. The first seconds of current decrease noticed in the plate electrode studies (shown in Fig. 3a, current transient in Fig. 4) are not observed in this configuration (electrode shown in Fig. 3b). To obtain an evaluation of the overall reaction kinetics, the derivative of the current is plotted as a function of time in Fig. 6b. Characteristic values are taken at the inflexion of these curves for each concentration. The corresponding reaction rate, presented in Fig. 7a, increases with the hematite concentration and agrees with the assumption of a rate limited by the amount of hematite particles. However, the reaction rate reaches a plateau, suggesting the saturation of the surface by iron oxide. To evaluate the charge related to the adsorbed hematite particles, the steady-state background obtained for the blank has been systematically subtracted. The overall charge obtained by integrating the corresponding current-time transient is also presented in Fig. 7a. It increases monotonically with the concentration of hema-



Figure 6. Effect of the hematite volumic fraction in suspension on the (a) electrochemical signals and (b) corresponding derivative.

tite particles in the suspension reactor. A rough estimation of the number of adsorbed particles as a function of hematite concentration in the suspension may be obtained from the total charge by assuming a particle diameter of 2  $\mu$ m, as illustrated in Fig. 7b. Scanning electron micrographs of the electrode surface after electrolysis in suspensions with various hematite concentrations are presented in Fig. 8. The amount of metal observed on the surface increases with the concentration of hematite, but the surface coverage remains low. The results suggest that the number of nucleation sites remains relatively constant with hematite concentration, though the cluster size increases markedly.

The topography of the electrode surface in such conditions is presented in Fig. 9 where the increase in iron deposition is confirmed, especially up to a 6.5% volumic fraction of hematite. These observations confirm the low surface coverage with metal and the three-dimensional (3D) growth of the iron clusters with increasing



Figure 8. Surface of the electrode after electrolysis for various volumic fractions of hematite in suspension. Figures indicate the volumic fraction in hematite. Scale bar: 10  $\mu$ m.

particle concentration. The average size of the clusters is on the order of a few micrometers, but their height can reach 10–30  $\mu$ m. The reason for such 3D growth requires further investigation, but the heterogeneous aggregation of the colloidal hematite particles seems a fair explanation. The movement of the particles on the electrode surface occurs because of the H<sub>2</sub> bubbles and other electrohydrodynamic phenomena.<sup>16,17</sup> As a matter of fact, such morphology cannot be attributed to the conventional mechanisms of electrocrystallization involving adions because the dimensions of the iron clusters are much larger than the diffusion distance for adions.

The relationship between the concentration in particles and the amount of metal deposit demonstrates that iron formation occurs by a direct reduction of the hematite particles, suggesting the hematite particles are adsorbed on the steel surface for a period of time sufficient for total particle reduction to occur. The contact phenomena involved are then of the type depicted in Fig. 1b. Such deposition of negatively charged hematite particles on a negatively charged surface is surprising in view of DLVO theory results, and hydrodynamic aspects (kinetic energy of the particle) are invoked to justify the overcoming of short-range repulsion forces.<sup>13</sup>

For the diluted suspensions, the amount of metal produced increases with the hematite concentration, which agrees with a mass-transfer limitation to the electrode. In concentrated suspensions (>5%), the saturation of the surface by the adsorbed particles is observed, and the hematite concentration does not significantly affect the amount of metal produced.

Influence of immersion time and hydroxide ion concentration.— The effect of sodium hydroxide concentration in the suspension reactor has been studied in the  $2.4 \times 10^{-2}$  to  $18.6 \text{ mol } \text{L}^{-1}$  range (corresponding to pH<sub>25°C</sub> 12.3–15.3) for 15 vol %. hematite. As presented in Fig. 10a, no significant variation in the electrical charge can be measured even if a tendency toward a larger extent of adsorption at a higher pH can be observed. Further, no significant effect of the immersion time in the suspension was observed, as shown in Fig. 10b. These results imply that the stability of the suspension against homogeneous aggregation is ensured even at pH values as low as 12, which agrees with previous studies of hematite suspensions in which the pH of zero charge was pH<sub>pzc</sub> ~ 9.<sup>18</sup> The



Figure 7. (Color online) (a) Variation in the charge and initial derivative of current density and (b) the number of 2  $\mu$ m diameter adsorbed particles with hematite concentration.



Figure 9. (Color online) Observations of the electrode surface with optical interferometry microscope. Numbers in bold indicate the volumic fraction in hematite. (Observed surface of  $410 \times 410 \mu$ m.)

steel surface is quickly saturated with hematite particles, and no transient phenomena are detected on the time scale studied within the experimental error.

The reduction of the adsorbed particles.— Although the focus of this work is on the adsorption of the hematite particles during immersion in the suspension reactor, it is of interest to investigate the influence of the potential on the reduction reaction so as to better understand the analytical process and perhaps shed light on the overall reduction mechanism. Using the steel plate as a cathode (Fig. 3a), the effect of the polarization during the electrochemical analysis step has been studied. The immersion step has been conducted for each experiment in a concentrated suspension of hematite at 15 vol %.

Figure 11a presents the variation in the HER reaction for the blank at different potentials, while Fig. 11b gives the variation obtained in the presence of adsorbed particles. A strong variation in both reactions is observed to occur with applied potential. The steady-state HER reaction was measured as an average value near the end of the experiment in Fig. 11. The initial rate of hematite particle reduction is difficult to establish from the visual inspection of the curves in Fig. 11; therefore, a simple model was developed, which permits an interpretation of the entire data set after the subtraction of the background HER reaction. The model proposed for the hematite particle reduction assumes an increase in the total current due to particle reduction,<sup>8</sup> linked to the hematite/electrode active surface area increase under iron metal production. On the contrary, the background current is assumed constant throughout the experiment, as exemplified in Fig. 4, where the very first current values are the same as the final steady-state values.

The total current is then the sum of two contributions

$$I = I_{hem} + I_{background}$$

the latest term being constant in the chronoamperometric experiments, while the first one varies with hematite consumption.

Therefore, one can individually evaluate the hematite/iron metal electrochemical reaction kinetic, thanks to the use of the derivative of the current

$$\frac{dI}{dt} = \frac{dI_{\text{hem}}}{dt} + \frac{dI_{\text{background}}}{dt} = K_{\text{hem}}(V)\frac{dS_{\text{hem}}}{dt}$$

Evaluating the derivative of the current is then a simple method to evaluate the variation in the reaction kinetic with the electrode potential ( $K_{\text{hem}}$ ), assuming that the initial number of adsorbed hematite particles is constant between the experiments. The derivative



**Figure 10.** Influence of (a) sodium hydroxide concentration and (b) immersion time ( $[NaOH] = 20 \text{ mol } L^{-1}$ ) in the suspension on the electrochemical charge attributed to iron production.

Figure 11. Current transients for various potentials at  $110^{\circ}$ C and 50% NaOH in the (a) absence of hematite particles and in the (b) presence of adsorbed particles after immersion in 15 vol % of hematite, as described in the text.

or



**Figure 12.** (Color online) Tafel plot from current densities determined in Fig. 11 for HER (current,  $\Box$ ) and adsorbed particles (derivative of the current,  $\bigcirc$ ).

has been evaluated at the inflection point of curves presented in Fig. 11b. The full derivation of such a model is given in the next section, leading to a current density value solely linked with hematite particle reduction.

In Fig. 12, a Tafel slope of 127 mV/dec is obtained for the HER reaction, which may be compared with that of Ref. 19. By contrast, two Tafel slopes of 59 and 186 mV/dec are obtained for particle reduction at low and high current densities, respectively. The value at a low current density could be related to one electron transfer limiting step, but there may be synergistic effects between the HER and the particle reduction because particle movement on the surface may be associated with the hydrogen gas formation, as mentioned in the previous section. Nevertheless, the fact that particle reduction and hydrogen formation show different Tafel slopes demonstrates that particle reduction is not controlled entirely by surface particle movement. Also, by comparison, with the commonly assumed mechanisms for high temperature formation and reduction of oxides, it might seem reasonable to propose oxygen ion diffusion within the solid as the rate limiting step. However, the low diffusivity of oxygen ions at this temperature range makes this highly unlikely for the rapid reaction rates observed here.

Phenomenological model for particle reduction.— In this section, we propose a simple model to account for the contribution of adsorbed hematite particle reduction to the total current transient. A truly predictive model is, of course, beyond the scope of this work; however, even a simple model makes a useful point of comparison for the experimental data. We consider the surface to be partially covered with  $N_p$  hematite spherical particles of initial radius,  $r_o$ , and the particles are reduced from their outer surface toward their center with an electrochemical kinetic coefficient  $k_{\text{Fe}}$ . The electroreduction of hematite via Reaction 1 is conducted at the  $j_{\text{Fe}}$  current density

$$k_{\rm Fe} = \frac{j_{\rm Fe}}{6F} (\text{mol } \text{m}^{-2} \text{ s}^{-1})$$
 [3]

on the surface of the particle ( $S_p = 4\pi r^2$ ). Faraday's law predicts the variation in the particle volume as follows

$$dV = -\frac{M}{\rho}k_{\rm Fe}4\pi r^2 dt$$

$$dV = 4\pi r^2 dr$$

so that after integration



Figure 13. (Color online) Current variation with time at various potentials. Experimental data are shown as points; the solid curve is a fit to Eq. 5.

$$r = r_{\rm o} - \frac{M}{\rho} k_{\rm Fe} k_{\rm Fe}$$

The fraction of the current for each particle is calculated from

 $i_{\rm p} = k_{\rm Fe} 4\pi r^2$ 

$$i_{\rm p} = k_{\rm Fe} 4\pi \left( r_{\rm o} - \frac{M}{\rho} k_{\rm Fe} t \right)^2$$
 [4]

And, the overall total current is  $I = N_{\rm p} i_{\rm p}$ 

$$I = N_{\rm p} k_{\rm Fe} 4 \pi \left( r_{\rm o} - \frac{M}{\rho} k_{\rm Fe} t \right)^2$$
 [5]

The assumption of a homogeneous spherical geometry is obviously not correct; however, it provides an ideal situation by which we can compare the experimental data. The assumption that hematite reduction begins on the outer surface of the particle is consistent with previous experiments.<sup>8</sup>

The adsorption step was the same for all the data in Fig. 11. Therefore, within a statistical variation, we can assume that  $N_p$  is constant for these experiments. The data in Fig. 11, after the removal of the contribution of background processes occurring during the first few seconds and the steady-state HER reaction, have been analyzed using Eq. 5, assuming a constant number of particles  $N_p$ = 2 × 10<sup>6</sup>, with the radius ( $r_o$ ) and the electrochemical kinetic coefficient ( $k_{Fe}$ ) as adjustable variables. The comparison between the model and the experimental results is presented in Fig. 13, with corresponding parameters presented in Table I. The model fairly

Table I. Experimental conditions	and modeling	results from	the
current variation in Fig. 11.			

E (V/HgHgO)	t <sub>max</sub> (s)	<i>r</i> <sub>0</sub> (m)	$(\mathbf{A}^{j_{\mathrm{Fe}}}\mathbf{m}^{-2})$
-1.1	169.6	$1.9 \times 10^{-06}$	197
-1.15	75	$2.1 \times 10^{-06}$	594
-1.18	55.33	$2.3 \times 10^{-06}$	700
-1.2	37.5	$2.0 \times 10^{-06}$	1000
-1.23	33	$2.2 \times 10^{-06}$	1200
-1.25	24.45	$2.0 \times 10^{-06}$	1450
-1.28	17	$1.9 \times 10^{-06}$	1930



**Figure 14.** (Color online) Variation in the  $r_0/j_{\text{Fe}}$  fitted value from Fig. 11 as a function of time  $t_{max}$ 

agrees with the experimental results. Note that from Eq. 5, the  $r_0/j_{\text{Fe}}$ ratio should be proportional to the time  $(t_{\text{max}})$ , at which the current reaches zero, the proportionality constant being

$$\frac{M}{\rho}\frac{1}{6F} = 5.3 \times 10^{-11} \text{ m}^3 \text{ C}^{-1}$$

This is also verified by experimental results, as shown in Fig. 14.

### Conclusion

The stability of the hematite particles in highly concentrated alkaline solution limits the aggregation of such iron oxides in suspension. Physical chemical interactions of such two-phase media enhance the wetting of a steel surface so that particles adhere to the substrate. By the electroreduction of hematite to metal in a separate analysis cell, the corresponding amount of adsorbed particles can be evaluated. The trapped particles have a characteristic length of less than 2  $\,\mu\text{m},$  and a 3D aggregation of iron metal on the steel surface is observed. Compared with the hematite concentration, the influence of the base electrolyte concentration or immersion time on such process indicates that bulk electrolyte/particle interactions are of second order in determining the intensity of adhesion phenomena. A preliminary analysis of the particle reduction rate reveals Tafel-like kinetics for the electroreduction of iron oxide to iron.

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#### List of Symbols

- Tafel slope,  $b_{\rm C} = 2.303 RT/n_{\rm e}F = 0.076$  in V/decade for one elec $b_{\rm C}$ tron transfer at 383 K
- F Faraday's constant, 96,485 C mol-1
- current resulting from the reduction of a single particle. A ip I
- total current attributed to adsorbed particles reduction, A current density for the hematite to metal reduction in Reaction 1, j<sub>Fe</sub>
- $A \ m^{-2}$
- $k_{\rm Fe}$ electrochemical kinetic coefficient, mol m<sup>-2</sup> s<sup>-1</sup>
- М hematite molar mass, 0.1597 kg mol-
- number of particles adsorbed on the surface  $N_{\rm p}$
- radius of the adsorbed particles before reduction, m  $r_{0}$

Greek

hematite specific gravity,<sup>20</sup> 5260 kg m<sup>-3</sup>

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