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Determination of isoelectric points of metals and metallic alloys by adhesion of latex particles

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ABSTRACT

A set-up and a method were developed to determine the isoelectric point of metals and metallic alloys samples (stainless steels, inconel, zircaloy, aluminum and dural) by measuring the adhesion rate of negative latex particles. The concentration of polystyrene spheres with surface carboxylate groups (initially 0.5–1 mg L^{-1}) in contact with metallic samples was measured as a function of pH and time by turbidimetry. The simulation of measurements by a model predicting the sticking coefficient based on DLVO theory was used for the determination of the isoelectric point from experimental results. It was found that the isoelectric points of aluminum (8.7) and dural (9.1), treated by boiling water, are close to those of hydrated aluminum oxides powders. For stainless steels, inconel and zircaloy, the values of isoelectric points were found to be between 2.4 and 3.0, far below the isoelectric points measured for metallic oxides constituting the alloy surface layer. This difference was explained by two different charging mechanisms: (1) deprotonation of hydroxyl groups on the surface of the metal oxide in suspension or as a thick layer, (2) adsorption of hydroxide ions on a metal surface covered by a thin oxide layer, as observed on hydrophobic surfaces.

1. Introduction

Deposition of particles in industrial equipment with a circulating fluid is the cause of several technical problems. For example, such a process induces fouling of filters and heat exchangers [1,2], and produces radioactive contamination of cooling circuits of nuclear reactors. The transport of particles from the bulk of the solution to the walls depends on its hydrodynamics, but, in the vicinity of the wall, chemical interactions between the particle and the wall must also be taken into account. According to DLVO theory [3], the interaction can be calculated as the sum of the electrostatic and the van der Waals forces, the last term being always attractive. The electrostatic forces are dominant during the deposition phase, and hence the relative charges of the surfaces are the determinant parameters indicating whether the interaction is repulsive or attractive. Values of the isoelectric points (IEP) of particles and substrates indicate the pH where the zeta potential is equal with zero and the range where the adhesion is favored. Thus, a prediction requires the knowledge of the values of IEP for both materials. For particles, electrophoretic methods (mainly zetametry) have been widely used [4]. For massive substrates, a few methods have been developed, based on the influence of pH on (1) the contact angle of a drop of solution on the surface [5], (2) the adhesion rate of latex particles on a reactor wall [6], and (3) the streaming potential recorded between the inlet and the outlet of a solution flowing between plates [7–13] or through a tube [14]. The streaming potential method has been used for several insulating materials as Teflon [12] or polyethylene [13], but also for metals. This method applied to stainless steels or iron alloys of different compositions has given values of IEP in the pH range 3–5 [7–9,14] (Table 1). These values, which correspond to the surface reactivity of the oxide layer covering the metals, are much lower than the mean value of IEP of metallic oxides (powder \samples): chromium (hydr-)oxides (between 6 and 8.5 [4]), nickel (hydr-)oxides (between 10 and 11.5 [4]), magnetite (between 6 and 7 [4]) and ferric (hydr-)oxides (between 8 and 9 [4]). This difference in IEP's may indicate a charging mechanism, which is not based on the acido-basic properties of the hydroxyl groups, as usually described in surface complexation models (2-pK [4], MUSIC [15]).

In circuits of pressurized water nuclear reactors (PWR), the deposition of colloidal corrosion products on metallic parts was observed, and its understanding and modeling require the knowledge of IEP's of these massive substrates [16,17]. The circuit network is built of stainless steels, the steam generator is made of tubes of inconel (nickel-based alloys), while fuel rods are made of zircaloy (high-zirconium alloy) [18]. To our best knowledge, IEP values for inconel and zircaloy have not been published yet

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Table 1
Literature review of isoelectric points of massive metallic substrates measured by the streaming potential method.

Metal or alloy[a]	Treatment	Surface composition	IEP
304 SS [7]	Polishing in water/oxidation by room atmosphere	Fe/Cr = 3	4.2
304 SS [8]	Annealing in H_2/washing HNO_3 0.2 M 70 °C	Cr/Fe = 1.7	4
304 SS [8]	Annealing in H_2/polishing/aged 24 h in atmosphere	n.d.	3.2/4.1
304 SS [14]	As received or washed by acetone, boiling NaOH, HNO_3	n.d.	4–5
347 SS [14]	As received	n.d.	3–4
FeCr 18% [9]	Ageing 17 h at pH 8	Fe/Cr = 2	3
FeCr 18% [9]	Ageing 17 h at pH 4.5	Fe/Cr = 0.9	5
FeCrSi 18–1% [9]	Annealing in H_2	SiO_2	3.5
FeCrAl 20–5% [9]	Annealing in air	Al_2O_3–SiO_2	3
Ti_6Al_4V [10]	Oxidation by room atmosphere	TiO_2–Al_2O_3 5 nm thick	4.4
Aluminum [11]	200 nm layer deposited on glass, UV/ozone oxidation	n.d.	5.4
Gold [11]	100 nm layer deposited on glass	n.d.	4.1

[a] SS: stainless steel.

and their determination is amongst the purposes of the present work. To perform this measurement, the influence of the pH on the deposition rate of negative latex particles on massive samples of metals and alloys was studied. Kallay et al. [19–21] determined IEP's of several pure metallic powders and stainless steels via adhesion of latex particles in a packed column. However, this technique requires samples as powders or beads, and the preparation of such samples from massive metallic plates (using a file for example) could disturb the surfaces and modify their reactivity. In a previous work [6], it was shown that the adhesion of particles on a reactor wall could be followed by turbidimetry, despite low surface area of the substrate, which leads to a small deposited amount.

Our aim, described in this paper, was to develop a new set-up to follow the adhesion of latex particles on metal and metallic alloys samples on the bottom of a glass reactor, in order to measure the IEP of metal and metallic alloys surfaces. The principle of this measurement is based on the pioneered works by Kallay et al. [19–21]. From a simulation based on DLVO theory, the obtained adhesion rates were related to the IEP of substrates. The values of IEP and the charging mechanism were discussed.

2. Experimental

2.1. Materials

Carboxylated latex (Estapor-Merck) consists of polystyrene spheres (300 nm) with carboxylate groups to ensure negative surface charge in a wide pH range. Several metallic substrates were investigated (Table 2). They were in the shape of discs with a diameter of 60 mm and 1 mm thick. The samples were polished with SiC 2400 (LamPlan) in the presence of water, then sonicated in ethanol and washed in high purity water. A chemical treatment, intended to control the nature and the thickness of the oxide layer on the surface, was performed on several samples for two reasons: (1) the surface of aluminum or stainless steel in industrial applications is often treated to increase its efficiency against corrosion, and (2) the chemical treatment and the nature of the oxide layer may have an effect on IEP. The aluminum samples were immersed in boiling high purity water for 30 min in order to allow the growth of a pseudo-boehmite film [22]. The passivation of a stainless steel sample was performed with nitric acid (6 mol L^{-1}) at 60 °C for 1 h [23].

2.2. Set-up

Adhesion measurements were carried out by a set-up shown in Fig. 1. The metallic sample was on the bottom of a 250-mL glass reactor filled with 200 mL of a suspension of 1 mg L^{-1} latex particles in $NaNO_3$ 10^{-3} mol L^{-1}. The stirring was provided by a three-blade glass propeller, at 240 rpm. The pH and temperature were continuously measured with a combined glass electrode and a temperature sensor (Metrohm 6.0228.000). Aliquots of the suspension were withdrawn to measure the remaining concentration of latex particles by turbidimetry. Adhesion experiments were carried out under a continuous flow of nitrogen over the suspension to avoid carbon dioxide contamination. A thermostated double-wall jacket allowed a temperature control at 25 ± 0.5 °C.

2.3. Experiments

An aliquot of the suspension was withdrawn at regular time intervals (typically every 7 min during 30 min) from the reactor and put into a cell for turbidity measurement. Then, it was poured back into the reactor. The pH was modified during the experiment by addition of HNO_3 0.1 or 0.5 mol L^{-1}.

Table 2
Characteristics of studied samples and measured values of isoelectric points.

Material[a]	Major element	Specification or composition[b]	Treatment[c]	IEP measured by extrapolation
Glass	–	–	None	2.2
Aluminum	Al	–	Polishing + oxidation in boiling water	8.7
Dural	Al	Cu 4%	Polishing + oxidation in boiling water	9.1
304L SS#1	Fe	Cr 20%, Ni 12%, Mn 1.8%	Polishing	3.4
304L SS#1	Fe	Cr 20%, Ni 12%, Mn 1.8%	Polishing + passivation in HNO_3	3.0
304L SS#2	Fe	Cr 17–20%, Ni 9–12%, Mn 2%	Polishing	3.0
316L SS	Fe	Cr 16–18%, Ni 10.5-13%, Mo 2–2.5%, Mn 2%	Polishing	2.8
Zircaloy-4	Zr	Sn 1.5%	Polishing	2.4
Inconel 690	Ni	Cr 27–31%, Fe 7–11%	Polishing	2.4

[a] Two different samples of 304L SS were studied (#1 and#2), coming from two dealers.
[b] Composition comes from chemical analysis for 304L SS#1.
[c] The procedure of chemical treatments are detailed in the text.