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FORMATION OF GIBBSITE SCALE IN THE BAYER PROCESS ON METAL SURFACES

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ABSTRACT

Alumina that feeds the smelter for the production of aluminum is extracted from bauxite ore mainly by the Bayer process. The whole process operates from saturated to supersaturated concentration for most of its components (aluminates, silica and carbonate). Since the caustic solution is continuously supersaturated with respect to sodium aluminates, scale is present in many parts of the process.

In this paper, the scale formation in the Bayer process was examined in order to improve the understanding of the early stages of scale formation and potentially find a solution to this problem. Noble metals were used in comparison with mild steel because they have much lower possibilities to form surface oxides or hydroxides in Bayer conditions. Prior to each scaling experiments, each metallic surface was first characterized by scanning electron microscopy and atomic force microscopy. Scaling measurements were made by plotting mass gain against time for coupons dipped in supersaturated solution. Finally, characterization techniques were used to determine if there is gibbsite adsorption onto studied metals that can explain the scale formation.

INTRODUCTION

Scaling in alumina refineries is a natural consequence of supersaturated solutions that are generated throughout the Bayer Process. The accumulation of scale reduces the efficiency of heat exchangers considerably and may generate other problems such as pipe blockages and probe malfunction. Many researchers have been challenged by fouling problems. They explained scale formation phenomenon using different techniques or hypotheses. Our group investigates some mechanisms in order to explain why gibbsite scale is present on metallic surfaces. Breault and Bouchard (2008) studied scaling in dynamic cell (turbulence flow of Bayer solution on mild steel surfaces), and they demonstrate that the passivating layer on the surface of mild steel or copper is responsible for the scale adherence to the metallic surface and that removing the oxide layer prevents scaling. Brisach et al. (2011) studied scaling in static cell (where metal coupons were introduced in a thermostatic cell without agitation of Bayer solution) and they suggest an apparent global nucleation mechanism in solution, which combines cementation and sudden particle showering.

Scaling of gold probes suggested that gibbsite scale can be formed on noble metals. However, according to their Pourbaix (1974) diagram, noble metals such as gold, platinum and palladium, do not form surface oxides or hydroxides so easily as iron in Bayer conditions.

The objective of the study is to improve the understanding of formation of the gibbsite scale in the Bayer process on oxide free metals. Based on the work of Breault and Bouchard (2008), we studied the gibbsite scaling rate on various metals such as mild steel, copper and some noble metals. Previous results from our study reveal that nucleation times are similar for all studied metals with the same supersaturation degree. To explain how scale is formed on oxide free metals, we studied some parameters describing surface properties, as adsorption isotherm, zeta potential, contact angle and surface roughness.

FUNDAMENTALS

Growth measurements

Gibbsite scaling on metallic surface in contact with Bayer solution takes place according to two recognized steps: nucleation of the first gibbsite nuclei followed by growth of gibbsite crystals. A curve plotting the mass gain as a function of time showing both phenomena is depicted in Fig. 1. To compare noble metals with mild steel we need to measure the nucleation time on each metallic surface. Nucleation time is obtained from interpolation between nucleation and growth linear regression (lines 1 and 2).



Fig. 1. Scale growth typical curve. (1) Scale nucleation, (2) Scale growth.

Free Gibbs energy

Several types of isotherms (Brunauer et al. 1940) are known and the most commonly used are Langmuir and Henry isotherms. Henry isotherm is applicable for very low concentrations of product and presents a linear behavior following Eq. (1) in which k_H is the Henry constant (mg/L). It represents the volume of solution needed to desorb one molecule for a given quantity of support. Therefore, the constant is expressed in volume per surface unit.

$$Q_e = k_H C_e \tag{1}$$

High k_H means high adsorption; however, no information about the maximum quantity adsorbed is available with this method. Only a comparison between several isotherm adsorption curves is significant. Data used to calculate the Henry constant, reported in this paper, are measured by a dynamic method that takes advantage of the chromatographic properties of each material. The dynamic determination is a fast and sensitive quantification method, which can detect very low concentration and very low adsorption of molecules when used with sensitive detectors (ppm level) (Chuduck et al. 1981). Chromatographic columns are filled and packed with the desired powdered support and selected molecules or ions are eluted with the solution of interest. Recorded chromatograms allow extracting the calculation parameters (Fig. 2) needed to obtain the concentration of molecules in solution at the equilibrium Eq. (2) and the quantity adsorbed onto the support Eq. (3).



Fig. 2. Determination of chromatographic parameters

$$C_{e} = \frac{n_{i}h_{\max}}{\omega I_{2}} = \frac{n_{i}h_{\max}}{\omega \int_{\tau_{1}}^{\tau_{2}} hd\tau}$$
(2)

$$Q_e = \frac{n_i I_1}{msI_2} = \frac{n_i \int_0^h (\tau_r - \tau_0) dh}{ms \int_{\tau_1}^{\tau_2} h d\tau}$$
(3)

 n_i is the injected quantity of solute (moles), h_{max} is the height of the peak (arbitrary units), ω is the flow rate of the elution (mL/sec), m is the mass of support packed into the column (g) and s is the specific surface of the support (m²/g) measured by BET isotherm. I_1 is the integral represented by ABCD where curve CD is connecting the peaks maxima. I_2 is the peak area integrated from the chromatogram of each amount injected (Fig. 2). One can notice that the retention time (τ_r) is a function of the adsorption capacity for the molecule of interest onto the support. Q_e is then drawn as a function of C_e and the resulting curve is called the adsorption isotherm.

Zeta potential

The zeta potential (ξ) is a measure of the effective charge on a particle caused by ions gathered in its surrounding layer. The zeta potential is well known to affect some processes such as scaling, corrosion, precipitation and flocculation. It affects the ions adsorption at surface but also influences the impurities attracted to the surfaces (Fôrster et al., 1999; Bott, 1995). One of the most convenient methods for obtaining ξ is called microelectrophoresis. This technique uses the property of charged particles that, under the influence of an applied electric field, will move at some constant, limiting velocity. The electromobility (μ) of a colloid, which is its speed (*u*) divided by the applied electric field (*E*), is measured using this sensitive method.

Contact angle

Contact angle is the study of wetting and non-wetting liquids on a clean solid surface. Using an optical microscope, it is possible to observe and measure a finite contact angle (θ) as the liquid interface approaches the three-phase-contact perimeter of the drop (Fig. 3).



Fig. 3. Diagram of a droplet onto metallic surface

The thermodynamic equilibrium is described by means of the angle of wetting θ between a droplet of synthetic Bayer solution and the studied metallic surface. The hypothesis is that the scale formation depends on the wettability of the surface by the Bayer solution.

EXPERIMENTAL

Synthetic Bayer liquor

The synthetic Bayer solution was prepared using 150 g NaOH pellets (Fisher Scientific), 40 g Na₂CO₃ (Fisher Scientific) and 180 g gibbsite (Al(OH)₃) supplied by Rio Tinto Alcan and used as received. The total volume was 1 L (distillated water) to give an alumina/caustic ratio of 0.62. The solution was prepared in a pressure reactor (Parr 4843) at 150°C. The solution was then cooled and maintained at 65°C to give a constant supersaturation.

Growth measurements

Mild steel (1018 type) coupons (1 and 3 cm diameter) and copper coupons (30x30 mm) were treated chemically. The chemical treatment was carried out in a solution of 25 mL of water, 25 mL of hydrogen peroxide, 30% solution (Anachemia) and 3.5 mL of hydrofluoric acid 48% (Sigma-Aldrich). The coupons were treated into the chemical solution for 15 seconds and then kept in acetone until used.

Gold foils (0.1 mm thick, 99.95%, 25x25 mm, Alfa Aesar), palladium foils (0.1 mm thick, 99.9%, 25x25 mm, Alfa Aesar) and platinum foils (0.1 mm thick, Premion 99.99%, 25x25 mm, Alfa Aesar) were washed with water and acetone before used. Coupons or foils were fixed to an analytical balance (Mettler Toledo XS64). They were suspended in synthetic Bayer solution in a thermostatic cell at 65°C without agitation (A/C ratio=0.62). The mass variations were recorded as function of time using interfaced balance.

Free adsorption energy of Gibbs

Chromatographic parameters were obtained using Agilent 1100 Series equipped with a refractive index detector, model G1362A. Dead volume τ_0 was determined by injecting $5 \,\mu$ L of phenol $\geq 99\%$ (Sigma-Aldrich) solutions of 5 mM. The mobile phase were 0.01 M or 0.1 M of NaOH prepared with NaOH 1N (Fisher Scientific) and HPLC grade water (Fisher Scientific).

Table 1. Characteristic of studied metallic powders

Metals powder	Company	Particle size	Purity (%)	Specific surface (m²/g)
Iron	Alfa Aesar	6-10 μm	99.5	n/a
Copper	Aldrich	-45 μm	99	n/a
Mild steel	ATOMET	20-45 µm	n/a	0.08
Gold	Alfa Aesar	-200 mesh	99.9	0.01
Palladium	Alfa Aesar	-200 mesh	99.95	0.16
Platinum	Alfa Aesar	-200 mesh	99.98	0.07

The molecules injected were prepared directly in the mobile phase at concentrations between 4 and 20 mM. The flow rate was 0.5 mL/min. The columns (15 or 25 cm) were filled in with selected powder of Table 1. The parameters used to determine the dynamic adsorption isotherms were collected from the HPLC elution chromatograms and Henry constants and free Gibbs energy were calculated (St-Jean et al. 2009).

Zeta potentials

Zeta potential measurements were performed on gibbsite powder (supplied by Rio Tinto Alcan and used as received), mild steel powder (ATOMET), iron powder (Alfa Aesar), copper powder (Aldrich) and palladium powder (Alfa Aesar) suspensions in NaOH 0.01 M and 0.1 M solution at 15°C. Suspensions were prepared in high density polyethylene (HDPE) bottles at room temperature for 24 hours under continuous agitation before cooling down at 15°C. Metallic suspensions were about 5% (m/V) for mild steel, iron and copper, and 3% (m/V) for palladium. Zeta potentials were taken using a ZetaProbe Colloidal Dynamics instrument.

Contact angles

Contact angle measurements were performed on same coupons or foil that for growth measurements (with same treatment), using a FTA200 First Ten Angstroms instrument. Contact angles were obtained from the angle between coupons surface and a drop of synthetic Bayer liquor.

Surface characterizations

Scanning Electron Microscopy (SEM) images were taken using a HITACHI S-4700 instrument. Samples were analyzed for surface composition using a Si(Li) Energy-Dispersive X-ray Spectrometer (EDS) INCA Oxford instrument coupled with HITACHI S-4700. Surface roughnesses were obtained using an atomic force microscope (AFM) instrument from Veeco NanoScope IIIa in contact mode. The value of roughness (Ra) is obtained from the arithmetic average of the absolute value of the surface (20x20µm) height deviations measured from the mean plane.

RESULTS AND DISCUSSION

First, surface characterizations of metal coupons were made by scanning electron microscopy before they were used for growth measurements. In this way, we wanted to observe surface roughness of metal coupons. Fig. 4 shows SEM images for each studied metals.

Several surface defects are observed on mild steel coupon (Fig. 4a). It seems that intergranular microstructures become visible after the chemical attack. Palladium and platinum (Fig. 4d and Fig. 4e) seem to possess the smoothest surfaces if we compare with gold (Fig. 4c). These observations can be confirmed by AFM roughness measurements (Table 2 and Fig. 5).

Table 2. Surface roughness from AFM measurements and nucleation times

Metal coupons	Roughness (nm)	Nucleation time (hour)
Gold	185	71 ± 22
Mild steel	60	71 ± 20
Palladium	9	85 ± 21
Platinum	16	106 ± 13
Copper	134	104 ± 18

It is important to note that each metal coupon used in this study did not have the same surface roughness.

Next step carried out was scale growth measurement tests. All metallic coupons were dipped in temperature controlled synthetic Bayer solution, at 65°C in order to keep a constant supersaturation. The mass gains were recorded as a function of time. Fig. 6 shows the mass gain of each metallic coupons used. There are some differences between the nucleation times of metals.



Fig. 4. SEM images of each metal coupons. Mild steel chemically treated (a), copper chemically treated (b), gold (c), palladium (d) and platinum (e).



Platinum

Fig. 5. AFM images of surface roughness of different metallic surfaces.

Surprisingly, some noble metals, like gold, scaled as fast as mild steel (Table 2). According to Pourbaix diagrams (Pourbaix 1974) three different areas can be observed: corrosion, passivation and immunity. These areas depend on the pH and surface potential of each metals used. As Breault and Bouchard (2008) said, under Bayer working conditions, mild steel is essentially stable because the solution is already saturated with $HFeO_2^{-1}$ ions, preventing any further corrosion, and the mild steel surface is covered by a passivating iron hydroxide layer. In the case of gold, palladium and platinum, they are in the immunity zone under Bayer working conditions. However, all of them have scale formation at their surface even if they are in the immunity zone. The case of copper is different because according to his Pourbaix diagram, copper is in the corrosion zone under Bayer conditions. As Gassa et al. (1998) have reported, dissolution of copper is observed under some conditions.



Fig. 6. Scale growth tests in synthetic Bayer liquor. Mild steel (a), gold (b), palladium (c), copper (d) and platinum (e)

During the scaling trials with copper, two observations confirm that, under Bayer working conditions, there is dissolution of the copper. Firstly, after 160 hours of scaling the solution of synthetic Bayer solution turn deep blue. Secondly, as displayed on Fig. 6, we observe loss of mass before the growth period. At this point scaling is more important than the copper dissolution.

According to all these results, it would seem that the scaling in the Bayer process is not only connected to the physical or chemical properties of the metals. Since supersaturation was constant in each trial, we suggest a solution phenomenon to explain scaling on metallic surface. Some other results allow us to support our hypothesis, like complete dynamic adsorption measurements on studied powder metals.

As expected by Breault and Bouchard (2008), where they demonstrate that the surface oxide/hydroxide layer forming the passivating layer is responsible for the gibbsite adherence on a passivated mild steel surface, highest adsorption of gibbsite is measured on mild steel.

Results obtained at 25°C in a NaOH 0.01 M solution show gibbsite adsorption onto studied metals (Fig. 7).

Results obtained allow us to conclude that gibbsite adsorption onto metallic powder decrease when increasing the sodium hydroxide concentration of the mobile phase. These results suggest a competition between the ions OH^- and $Al(OH)_4^-$ for a same adsorption site on the metal surfaces.

Zeta potential and contact angles were also measured. The nucleation period is mainly influenced by the interfacial free energy crystal/heat transfer surface since the adhesion phenomenon strongly depends on interfacial interactions.



Fig. 7. Gibbsite adsorption onto metallic surfaces with NaOH 0.01 M. (-•-) Mild steel (---) Platinum, (-•-) Palladium and (\blacktriangle -) Gold.

Similarly charged particles with a significant zeta potential will repel each other and the particles will remain dispersed. On the other hand, particles with a small zeta potential magnitude can join together if there are sufficiently small repulsive forces between the particles. Karakyriakos and Patrick (2005) published a report on the industrial applications using improved measurements of particle surface charge. They explain why in concentrated caustic solutions, the measurement of zeta potential is inadequate. It is difficult to measure the zeta potential in high ionic strength solutions because the surface charge is mostly neutralized by counter ions in the 1 to 5 M sodium hydroxide solutions resulting in only very low zeta potential magnitudes and correspondingly small zeta potential changes. This hypothesis also explains why the measurement of adsorption isotherm in high caustic concentrations gave immeasurable results.

Table 3 shows some shifts in the zeta potential between metallic surfaces without gibbsite and with gibbsite. Higher shift is observed with NaOH 0.01 M solutions. So we can conclude that it has no specific binding of the aluminates anions at the metallic surfaces, no alteration on the bulk solution properties by solubilized gibbsite or hydrophobic alteration of the surfaces.

Table 3. Zeta potential measurements in NaOH 0.01 M and 0.1 M

Madal	NaOH 0.01 M		NaOH 0.10 M	
Metat powder	Without	With	Without	With
powder	Gibbsit	Gibbsite	Gibbsite	Gibbsite

	e (mV)	(10mM) (mV)	(mV)	(10 mM) (mV)
Iron 5%	+0.7	-3.0	+1.3	+0.4
Mild Steel	+2.0	-3.6	+0.8	-0.9
5%				
Palladium	-1.1	-3.9	+1.2	n/a
3%				
Copper 5%	+4.2	-7.0	+3.4	-4.7

Table 4 shows the results obtained for the measurements of contact angles. A metal surface entirely free from oxides would have a higher surface energy than an oxidized metal. So it is concluded that clean metal, such as gold, is hydrophilic but just a partial monolayer of carbonate contamination will turn it into hydrophobic (Smith, 1980; Bewig and Zisman, 1965). However, it is difficult to prepare a clean metal surface and maintain its cleanliness at atmospheric pressure long enough to measure the contact angle.

 Table 4. Contact angle measurements with synthetic Bayer liquor solution

Metal coupons	Contact angles (°)	Nucleation time (hour)
Gold	78	75 ± 22
Mild steel	30	71 ± 20
Palladium	67	85 ± 21
Platinum	41	106 ± 13
Copper	32	104 ± 18

Thus our results show that metal surfaces are not entirely free from oxides or carbonate contamination. In fact, because we made measurements after exposure to atmospheric air, we have a carbonate contamination of metallic surfaces from carbon dioxide (Smith, 1980; Vachon, 2009). In addition, comparison between each contact angle of metal is complicated because each coupon did not have the same roughness.

It is important to note that each metal is wetted by synthetic Bayer solution but more easily in the case of mild steel and copper.

Some researchers suggested a nucleation mechanism by means of cementation of physical particles that appear in solution by catastrophic secondary nucleation (Brisach et al., 2011). They suggested a mechanism in which the scale is formed in bulk solution and not directly at the interface solution/substrate. Their hypothesis is linked with the measurement in the present work.

Results from adsorption isotherms and zeta potentials allow us to conclude that gibbsite adsorption on different metallic surfaces was negligible in our experiments even if we can measure it. So we know that gibbsite does not have a noteworthy adsorption onto metallic surfaces and we know that all studied metals scaled approximately as fast as each other. The results showed no correlation between scaling by gibbsite adsorption but we can show the relationship between nucleation time and surface roughness (Fig. 8). Copper was removed from this graph because, as explained earlier, copper can be solubilized in Bayer conditions.

Results allow us to propose that the nucleation mechanism is produced by the combination of two phenomena like Brisach et al. (2011) demonstrated, supported by Li et al. (2005) and Qian et Botsaris (1997). First phenomenon is a densification leading to the nucleation of aluminum trihydroxide. Second phenomenon is the catastrophic secondary nucleation leading to the formation of a sudden shower of nuclei. These nuclei can be approached near the metallic surface and may penetrate some surface defects (roughness) and then be trapped by cementation and growth of crystal.



Fig. 8. Relationship between metallic surfaces roughness and nucleation time

This mechanism is similar to the one that is taking place during gel permeation chromatography. According to the pores diameter, nuclei can penetrate more or less in the pores. Once in the pores the nuclei can grow up and be trapped, so the scaling can occur with different bindings at the surface. It seems to be almost the same results that Brisach et al (2011) obtained when they studied the nucleation time as function of the particle sizes. In their study, the substrate always has the same roughness but the nuclei sizes were different. In our case, the substrate does not always have the same roughness, but the nuclei size is almost the same.

Moreover, other factors can also influence the scaling in Bayer process. Influence of impurities or the oxide layer at the metallic surface can play an important role in the adherence mechanism of scale (Gavril et al., 2003, Breault and Bouchard, 2008). Indeed, gibbsite scale is more difficult to remove on the steel or copper coupons than on the coupon of noble metals where a simple friction of fingers allows removing the scale.

CONCLUSIONS

According to our study in the same working conditions of supersaturation, temperature and static measurements:

- 1. Scale growth measurements were made on palladium, platinum, gold, mild steel and copper. Even if they were nobles, scale forms onto each surface.
- 2. Results obtained demonstrate that at constant supersaturation, even if there is gibbsite adsorption on the studied metals, determining factor in scaling phenomenon for the Bayer process is the surface roughness (in static cell).
- 3. Scaling of metals in Bayer process is, at first sight, a solution phenomenon, where first nuclei are produced then they can be trapped at the metallic surfaces.

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