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ADSORPTION MEASUREMENT OF SCALE INHIBITORS ON STEEL IN BAYER PROCESS

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ABSTRACT

Scaling of mild steel by gibbsite in the Bayer process can be followed by plotting the mass of scale as function of time. It is characterized by two well known steps: an induction period followed by a growth period. The first one can last up to over hundred hours and corresponds to a slow coverage of the surface by scale nuclei. The second one, during which the scale rapidly grows onto nuclei, can be compared to seeded precipitation in the case of gibbsite. The first period involves metal/solution interface. Formation of nuclei can be avoided by adsorption of molecules directly onto the metallic surface. No scale growth will be possible anymore. Above that, these molecules should have no inhibition effect on precipitation.

In this paper, a fast and straightforward dynamic method is presented. It has been improved in our laboratory to determine adsorption strength of molecules by using a high pressure liquid chromatography system. Adsorption measurements of potential scaling inhibitors are exposed. Iron powders in high caustic concentrations are used to simulate mild steel in the Bayer liquor. The adsorption strength of these molecules is correlated to their scaling inhibition effect through scaling and precipitation tests.

INTRODUCTION

The Bayer process was patented more than 100 years ago by Karl Josef Bayer (Bayer, 1888). It has been used since to obtain aluminum oxide from bauxite. The whole circuit operates from saturated to supersaturated concentration for most of its components (aluminate, caustic and carbonate). Since the caustic solution is continuously supersaturated with respect to sodium aluminate and silicate, scale is present in many part of the process. The scale formation has a major impact on the alumina production costs. It decreases the efficiency of heat exchangers (Müller-Steinhagen *et al.*, 2007), reduces the flow in the lines, increases the maintenance costs and lowers the plant productivity. This explains why many researchers have been challenged by scaling problems over the last decades (Fortin and Breault 2003, Gavril *et al.* 2003, Chen *et al.* 2007, Müller-Steinhagen *et al.* 1994, Roach and Cornell 1996).

Scaling of metallic surfaces in contact with supersaturated solutions is characterized by two stages: an induction period (nucleation) and a growth period. The induction period corresponds to a very slow surface coverage by gibbsite nuclei. The kinetics during this induction period is highly governed by metal/solution interactions. In the growth period scale thickness increases rapidly. This stage is governed by scale/solution interaction. So, there are two ways inhibitors can be used. First, some molecules may adsorb onto metallic surface and avoid the formation of nuclei and inhibit scaling (Rossiter *et al.* 1998). Secondly, some molecules may adsorb onto gibbsite scale crystals and slow down or stop the growth period. The goal of Bayer process is to precipitate gibbsite at the end of the process. Thus, precipitation tests are required to know if potential inhibitors have a negative effect on precipitation yields.

In addition, it is extremely interesting to use an analytical technique to discriminate which molecules are potentially adsorbed onto metallic surface. In our laboratory, we use a fast and easy dynamic method to measure adsorption isotherms (Laplante *et al.* 2003, St-Pierre *et al.* 2004, Bouchard *et al.* 2005, Brisach-Wittmeyer *et al.* 2006, Brisach-Wittmeyer *et al.* 2008). We calculate the adsorption strength of some organic compounds on iron powder in high caustic concentration (NaOH 3M). Molecules with the highest adsorption capacity are then studied with respect to their scaling inhibition effect through scaling and precipitation tests.

FUNDAMENTALS

Adsorption Isotherms

Several types of isotherms (Brunauer *et al.* 1940) are known and the most commonly used are Langmuir and Henry isotherms. Langmuir isotherm, represented by Eq. (1) is typical of concentrated solutions of solute.

$$Q_e = \frac{Q_{\max} K C_e}{1 + K C_e} \quad (1)$$

In this case, a rapid increase of adsorption occurs, followed by saturation of the surface, this behavior been graphically characterized by an asymptote. Q_e is the adsorbed quantity at equilibrium (mol/g), C_e is the equilibrium concentration (mol/mL), $Q_{\max}$ is the maximal concentration adsorbed (mol/g) and K is a parameter from Langmuir isotherm (ml/mol). Henry isotherm is valid for very small concentrations of product and presents a linear behavior following Eq. (2). k_H is the Henry constant (mL/g). It represents the volume of eluant needed to desorb one molecule for a given quantity of support. Therefore, it is

expressed in volume per mass unit. High k_H means high adsorption.

$$Q_e = k_H C_e \quad (2)$$

However, no information about the maximum quantity adsorbed is available with this method. Only a comparison between several isotherm adsorption curves is significant. For the work reported here, we used a dynamic method to determine the Henry part. The dynamic determination is a very fast and sensitive quantification method, which can detect very low concentration and very low adsorption of molecules when used with sensitive detectors (ppm level) (Chuduk *et al.* 1981). Chromatographic columns are filled with the desired powdered support and selected organic molecules are eluted with the solution of interest as the eluant.

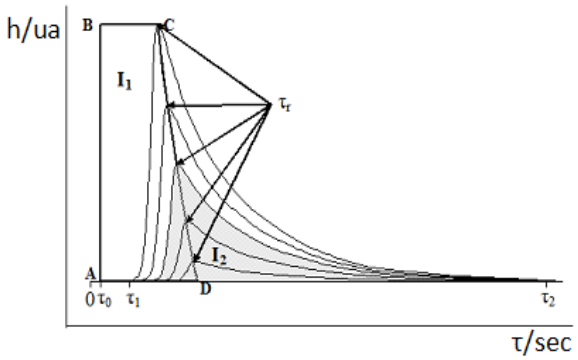


Fig. 1 Determination of chromatographic parameters

The recorded chromatograms allow to extract the calculation parameters (Fig. 1) needed to obtain the concentration of molecules in solution at the equilibrium Eq. (3) and the quantity adsorbed onto the support Eq.(4).

$$C_e = \frac{n_i h_{\max}}{\omega I_2} = \frac{n_i h_{\max}}{\omega \int_{\tau_1}^{\tau_2} h\, d\tau} \quad (3)$$

$$Q_e = \frac{n_i I_1}{m I_2} = \frac{n_i \int_0^h (\tau_r - \tau_0) dh}{m \int_{\tau_1}^{\tau_2} h\, d\tau} \quad (4)$$

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) and m is the mass of support packed into the column (g). I_1 is the integral represented by ABCD where curve AB is connecting the points of peak maxima. I_2 is the peak area integrated from the chromatogram of each amount injected (Fig. 1). One can notice that the retention time (τ_r) is a function of the adsorption capacity for the molecule of interest onto the support. So, it will shift to the smaller values when concentration increases. Q_e is then drawn as a function of C_e and the resulting curve is called the adsorption isotherm.

Growth measurements

Gibbsite scaling on metallic surface in contact with Bayer liquor takes place according to two well known steps: nucleation of the first gibbsite nuclei, followed by growth of gibbsite crystals. A curve plotting the mass gain as a function of time shows both phenomena as depicted in Fig. 2.

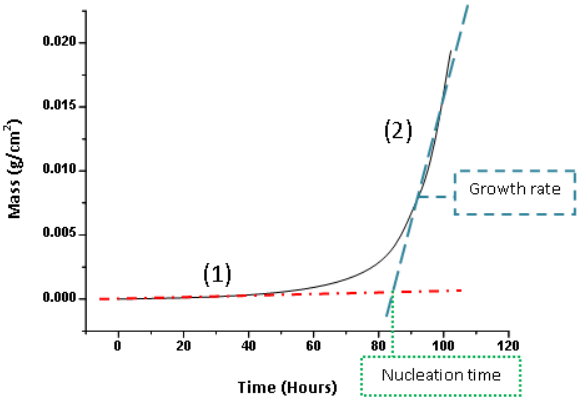


Fig. 2 Scale growth typical curve.
(1) Scale nucleation, (2) Scale growth

To compare inhibitors effects with a typical curve without inhibitor, we need to measure two parameters: nucleation time and growth rate. Nucleation time is obtained from interpolation between nucleation and growth linear regression (lines 1 and 2), and growth rate by the slope from growth linear regression (line 2).

Precipitation tests

Precipitation inhibition effect of molecules must be verified. Indeed, they may accumulate in the Bayer process and have a negative effect at the precipitation stage. In our laboratory, we use synthetic Bayer liquor cooled down at 65°C by thermostatic control, and we add gibbsite powder as a seed precipitation. To compare inhibitors effects on precipitation, a precipitation ratio variation (P.R.V. in %) is calculated Eq. (5) and then, compared with a blank test without inhibitors (P.R.V.= 0%).

$$\text{P.R.V.} = \frac{\left(A/C_0 - A/C_{inh}\right) - \left(A/C_0 - A/C_{blank}\right)}{\left(A/C_0 - A/C_{blank}\right)} \times 100 \quad (5)$$

A/C ratio (alumina/caustic) is a parameter typical of the Bayer liquor that gives the total concentration of alumina (g/L) dissolved expressed in Al_2O_3 equivalents versus the concentration of dissolved caustic (g/L) expressed in Na_2CO_3 equivalents. A/C_0 is the ratio before precipitation test, A/C_{blank} is the ratio after precipitation test without

inhibitor and A/C_{inh} is the ratio after precipitation with inhibitor.

EXPERIMENTAL

Chemicals

Water used to prepare the eluants was HPLC grade (Fisher Scientific). NaOH 10N (Fisher Scientific), NaOH pellets 99% (Fisher Scientific), Na_2CO_3 (Fisher Scientific), and organic molecules (Aldrich) were used as received. Gibbsite was supplied by Rio Tinto Alcan and used as received to prepare synthetic Bayer liquor. Iron powder 325 mesh, reduced, 98% was purchased by Alfa Aesar. Mild steel coupons (1 and 3 cm diameter) used for the scaling tests were of 1018 type and treated by chemical polishing with hydrofluoric acid (Sigma-Aldrich) and hydrogen peroxide (Anachemia).

Adsorption isotherms

Chromatographic parameters were obtained using Dionex GP 50 equipped with an UV detector, model UVD340U. Dead volume τ_0 was determined by injecting 10 µL of deuterium oxide D_2O. The mobile phases were 3M of NaOH prepared with HPLC grade water. The molecules injected were prepared directly in the eluant at concentrations between 0,0005 and 0,1M. The flow rate was 1,0 mL/min. The columns (15 cm) were filled in with iron powder, which average particle size was between 25 and 45 µm. The parameters used to determine the dynamic adsorption isotherms were collected from the HPLC elution chromatograms and the Henry constants were calculated from Eq. (2).

Synthetic Bayer liquor

The synthetic Bayer liquor solutions were prepared using 150g NaOH pellets, 40g Na_2CO_3 and 180g gibbsite $Al(OH)_3$. The total volume was 1L (distillated water) to give an alumina/caustic ratio of 0,62. The solution was prepared in a pressure reactor (Parr 4843) at 150°C.

Growth measurements

Mild steel coupons (1 and 3 cm diameter) were treated chemically. The chemical treatment was carried out in a solution of 25 mL of water, 25 mL of hydrogen peroxide and 3,5 mL of hydrofluoric acid. The mild steel coupons were plunged into the chemical solution for 15 seconds and then kept in acetone until used. The coupons were fixed to an analytical balance (Mettler Toledo XS64) or to a microbalance (B24 model from Setaram, modified ATG). They were suspended in synthetic Bayer liquor (*A/C* ratio = 0,62) containing various concentrations of potential inhibitors. The mass variations were measured as a function of time.

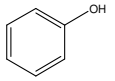
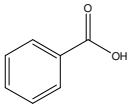
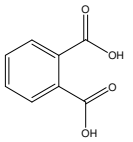
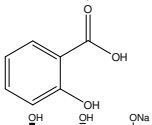
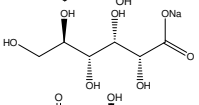
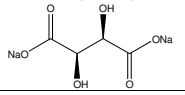
Precipitation tests

The precipitation tests were performed with 500 mL of synthetic Bayer liquor in high density polyethylene (HDPE) bottles at 65°C for 24 hours under continuous agitation at 100 rpm (Phipps & Bird Stirrer 7790-400). After test temperature was reached, the chosen molecules were added (Watling *et al.*, 1999). To start the precipitation process, 80 g/L of $Al(OH)_3$ seed was added. In order to avoid uncontrolled precipitation induced by thermal shock, gibbsite was preheated at 65°C. The *A/C* ratio was determined using an automatic titrator, Metrohm titrino 751 GPD.

RESULTS AND DISCUSSION

Dynamic adsorption isotherm measurements allow fast screening of adsorption power of molecules of potential interest. Molecules with a real effect on gibbsite scale inhibition on iron (used to model mild steel) could be detected. Indeed, a molecule known to cover iron surface and is also known to adsorb on gibbsite and/or to avoid its precipitation might be a good candidate for scaling inhibition.

Table 1. Retention times (min) measured on a same column of potential inhibitors of gibbsite scale onto iron with NaOH 3M used as eluant

Molecule	Formula	Retention time (minutes)
D_2O	-----	1,75
Phenol		1,77
Benzoic acid		1,77
Phthalic acid		1,76
Salicylic acid		1,78
Sodium-D-Gluconate		1,80
Sodium-L-Tartrate		1,81

Injection of many molecules at only one concentration onto a column allowed evaluating their adsorption potential onto iron. Their retention times were therefore compared with a reference molecule that is not adsorbed at all (D_2O). The longer the retention time, the higher the adsorption on iron. The highest among the concentrations of potential inhibitor was injected. Indeed, retention time τ_0 shifts to smaller values when concentration increases (Fig. 1). Retention time shift is a consequence of the adsorption sites saturation in the first centimeters of the chromatographic column. On chromatograms, this phenomenon leads to an asymmetric peak with tailing (Fig. 1). Then, taking these results into account, we made complete dynamic adsorption

isotherm measurements with molecules having a real potential interest. In our case, salicylic acid, sodium-D-gluconate and sodium-L-tartrate were the most interesting molecules of this series. Indeed, they have more than 0,03 min between D_2O and potential inhibitor (0,032, 0,048 and 0,057 minute respectively)(Table 1).

Fig. 3 shows the adsorption isotherms and Henry constants for the three studied molecules. The differences observed in the adsorption tendency (salicylic acid < sodium-D-gluconate < sodium-L-tartrate) may be due to the structure of the molecules (Table 1). On iron some organic molecules with two acidic adjacent functions can replace the –OH groups in $Fe(OH)_2$ by forming a complex (Abd El-Maksoud *et al.* 2005). Aromatic organic molecules can also absorb, via the aromatic ring onto iron oxides, and carboxylates can form a bond with the oxide surface (Bandara, Mielczerski, and Kiwi, 2001).

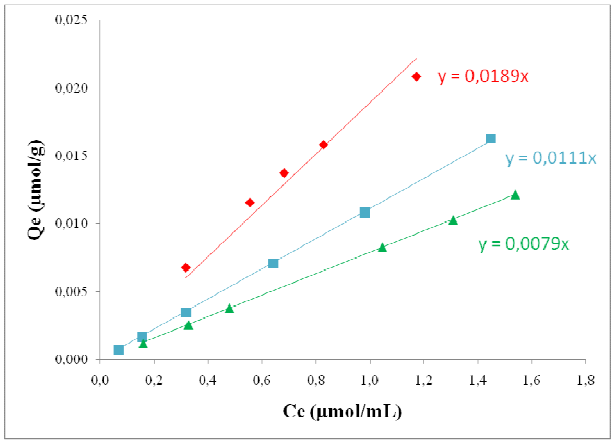


Fig. 3 Effect of molecules structure on adsorption on iron with NaOH 3M for (-▲-) Salicylic acid, (-■-) Sodium-D-gluconate, (-♦-) Sodium-L-tartrate.

Sodium-L-tartrate and sodium-D-gluconate are well known to be able to form complexes with iron (Ivanov & Kosoy 1975, Sawyer 1964). It can be seen that the three molecules have all adjacent hydroxyl groups. The difference between sodium-L-tartrate (0,0189 mL/g) and sodium-D-gluconate (0,0111 mL/g) may be attributed to the presence of two carboxylic groups for sodium-L-tartrate. So it may able to form a stronger complex with the metal ion (Abd El-Maksoud *et al.* 2005) than sodium-D-gluconate. Salicylic acid (0,0079 mL/g) is the less adsorbed onto iron. Indeed, it has only one carboxylic group and one hydroxyl group, so less possibility to adopt the best conformation for forming an iron-complex. This structure is also more rigid if compared with sodium-D-gluconate and sodium-L-tartrate. Their long chain can move more easily.

To improve the adsorption tendencies observed for isotherm measurements, we carried out scale growth tests. A metallic coupon is plunged in synthetic Bayer liquor and the mass gain is measured as a function of time. As said before, the nucleation period represents the time necessary for a complete coverage of the surface with nuclei. This nucleation period is followed by a growth period during which the gibbsite crystal growth occurs.

In Bayer plant, some cleaning methods to remove the scale are already used. Nevertheless, it cannot be excluded that metallic surfaces of plant piping are partially covered by scale nuclei. Then, we have to find out if the molecule used as potential inhibitor totally avoids nucleation or only slows down the growth rate of scale.

For this purpose, we performed scale growth tests in two different ways. Firstly, the potential inhibitor was added before plunging the mild steel plate into the synthetic Bayer liquor. This test allowed the determination of the potential inhibition of scale nucleation. Secondly, potential inhibitor was added after the crystal growth had begun. This test allowed the determination of the potential inhibition of scale growth when the metallic surface was already covered by scale nuclei. It could be interesting to perform dynamic adsorption isotherm measurements onto gibbsite in addition to that done onto iron (Brisach-Wittmeyer *et al.* 2008, Bouchard *et al.* 2005). However, concentrated solutions of NaOH cannot be used because gibbsite has a good solubility in high caustic solutions. Although adsorption isotherm could be measured at lower NaOH concentrations onto gibbsite support. Growth tests when the potential inhibitor is added after the crystal growth had begun must be performed.

Salicylic acid presents no inhibition effect for both periods, whether added before plunging the coupon into the solution or after the crystal growth had begun. However, when sodium-D-gluconate or sodium-L-tartrate were added as inhibitors (Fig. 4a and b), we observed two distinct behaviors. When they were added before plunging the coupon into the solution, the nucleation time was lengthened by more than 70 hours for sodium-D-gluconate and sodium-L-tartrate. When they were added after the crystal growth had begun, we observed a change in the growth rate. That indicates that the mass gain is lower than without inhibitor. If no inhibitor was added, the growth rate Table 3) was 0,12 mg/cm^2/hour but with addition of sodium-D-gluconate it decreased to 0,026 mg/cm^2/hour. With addition of sodium-L-tartrate, it decreased to 0,040 mg/cm^2/hour. Thus, these scaling tests confirmed that the molecules identified as potential inhibitors by isotherm adsorption measurements avoid gibbsite growth. They even slow down the initial metallic surface coverage.

Precipitation inhibition effect of these molecules must be verified because they may be found later in Bayer process at the precipitation stage. The precipitation ratio variation was calculated by determining the alumina concentration [A] of two samples: the first sample, without any organic molecules ($[A]_{Blank}$) and the second with a given amount of organic molecules ($[A]_{inh}$).

Knowing the initial A/C_0 ratio, the precipitation ratio variation is calculated from Eq. (5). In the absence of inhibition effect, $[A]_{inh}$ is the same as $[A]_{Blank}$ and the precipitation ratio variation is 0%. With an inhibition effect, $[A]_{inh}$ is higher than $[A]_{Blank}$ and the P.R.V. is less than 0%. In the case of a molecule that enhances the precipitation process, the P.R.V. variation is higher than 0%.

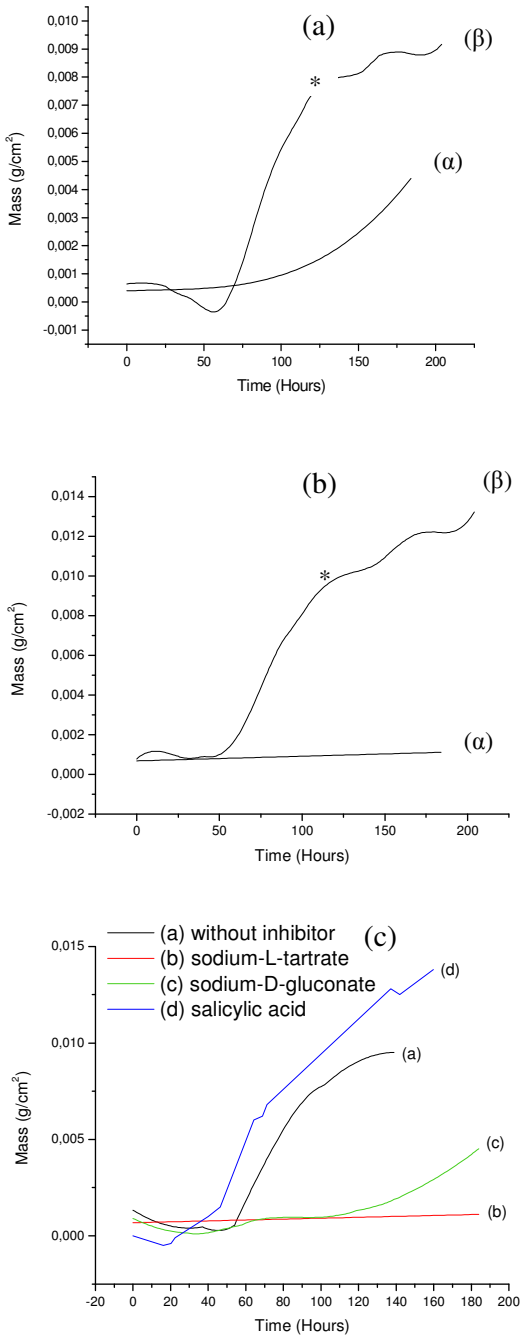


Fig. 4 Scale growth tests in synthetic Bayer liquor with addition of potential inhibitors: (a) Sodium-D-gluconate (1 mmol/L), (b) Sodium-L-tartrate (5 mmol/L), (c) comparison of all inhibitors; where inhibitors were added (α) before plunging the plate into the solution, (β) after the crystal growth had begun (*)

Salicylic acid has no effect on the precipitation rate of gibbsite because the P.R.V. is always 0% whatever the concentration of inhibitor in the solution. We cannot test higher concentrations because of the limit of solubility of salicylic acid into synthetic Bayer liquor solution.

Table 2. Influence of organic molecules as inhibitors on the precipitation rate (P.R.) of alumina hydrate

Molecule	Concentration (mmol/L)	Precipitation rate (± 3 %)
Blank	-	0
Sodium-D-gluconate	1	-10
	2	-22
	5	-98
	10	-99
	100	-100
Sodium-L-tartrate	1	-3
	2	-9
	5	-22
	10	-25
	100	-93
Salicylic acid	0,15-0,55	0

Sodium-L-tartrate and sodium-D-gluconate are already known as good precipitation inhibitors in the Bayer process (Rossiter *et al.* 1996, Watling *et al.* 1999). Results recorded in our laboratory confirm these from the literature. Sodium-L-tartrate is less inhibiting than sodium-D-gluconate. Sodium-D-gluconate totally inhibits gibbsite precipitation with only 5 mmol/L, whereas sodium-L-tartrate has still 86% of gibbisite precipitation at the same concentration. Many papers were published to understand the mechanism of sodium-D-gluconate poisoning of gibbsite precipitation (Rossiter *et al.* 1996, Watling *et al.* 2000, Rossiter *et al.* 1998). They concluded that the growth rate suppression is due to a reduction of the available surface area and not to a change in the activity of the available surface. Sodium-D-gluconate appears to extend the region where primary nucleation is the dominant mechanism by preventing precipitation on the heterogeneous surface.
Nevertheless, with a concentration of 1 mmol/L, sodium-D-gluconate and sodium-L-tartrate present a gibbsite precipitation of 90% and 97% respectively. That is promising for use of these scale formation inhibitors in plant.

In order to improve these promising results, we undertook correlation studies between results from our laboratory using synthetic Bayer liquor and results from Bayer plant using real Bayer liquor.

Table 3 is particularly interesting because even if the results obtained in the plant were not exactly the same as these obtained in the lab, the trends of results are the same. Indeed, in both lab and plant, addition of organic inhibitors lengthened the nucleation time by a factor of at least two. Additionally, growth rate dramatically decreased in both environments. In fact, results are not expected to be exactly the same because experimental conditions are not the same in lab and in plant. For example, in our laboratory we use synthetic Bayer liquor prepared with pure reactants. In the Bayer plant, real Bayer liquor is prepared with bauxite ore and all impurities which it can contain. In the laboratory, we make scaling tests at 65°C whereas in the Bayer plant

the temperature is much higher, approximately 107°C. Also, in the plant the solution flows through pipes while in the laboratory, coupons are immersed in a static solution. Another difference between laboratory and plant is the *A/C* ratio, which is often higher in Bayer plant than in our laboratory (0,72 instead of 0,62 in our conditions).

Table 3. Comparison between laboratory and Bayer plant growth measurements

	Reference (Blank)	Salicylic acid	Sodium -D-gluconate	Sodium -L-tartrate
Concentration (mmol/L)	0	0,60	1,0	5,0
Laboratory nucleation time (hours)	60	45	135	>160
Plant nucleation time (hours)	52	50	>150	116
Laboratory growth rate (mg/cm^2/hour)	0,12	-	0,026	0,040
Plant growth rate (mg/cm^2/hour)	0,69	0,66	0,02	0,28

Salicylic acid is not a good scaling inhibitor in laboratory conditions or in the plant because it doesn't affect either the nucleation time or the growth rate (Table 3). However, sodium-D-gluconate and sodium-L-tartrate lengthened nucleation time significantly in laboratory and plant tests if compared with reference nucleation time (60 and 52 hours respectively). Furthermore, gibbsite growth rate was also modified when these molecules were added after crystal growth had already begun. In this example, growth rates were in the same range in Bayer plant and in laboratory for all the molecules.

CONCLUSIONS

1. A very fast dynamic adsorption isotherm measurement method was developed for adsorption power screening of potential scaling inhibitors.
2. Correlation between adsorption power and scaling inhibition shows that scaling inhibitors should adsorb onto iron with a Henry constant higher than 0,007 mL/g to be efficient.
3. Precipitation and scaling growth tests indicate that at low concentration, sodium-D-gluconate and sodium-L-tartrate might be scaling inhibitors but not precipitation ones.
4. Comparison between scale growth tests done in the laboratory and in the plant shows that inhibitor effects of sodium-D-gluconate and sodium-L-tartrate are almost similar. Results obtained in both environments can be compared and transferred from the laboratory to the plant.

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