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ORIGINAL PAPER

Selective electrochemical reactions of an alumina hydrate crystallization inhibitor

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Abstract Selective reactions of catechol have been studied in regard to its inhibition properties towards alumina hydrate crystallization. Electrochemical reactions of the inhibitor leading to products without inhibition behaviour have been obtained using different conditions. First, a pure sodium hydroxide solution (1.0 M NaOH) was used to electrochemically react the catechol. The inhibitor reactions were then carried out in both saturated and supersaturated sodium aluminate solutions ($NaAl(OH)_4$). Electrocatalytic hydrogenation (ECH) of the aromatic ring over rhodium-based catalysts leads to the saturated non-inhibiting molecule, 1,2-cyclohexanediol. Temperature shows no significant influence on the ECH process within the temperature range where the alumina hydrate crystallization is normally carried out. The presence of aluminate ions in solution has, however, a detrimental effect on the current efficiency. Electro-oxidation of the catechol produces muconic acid by cleavage of the carbon-carbon bound. It also produces other oxidation products and, eventually, may lead to total mineralization of catechol into carbonate, which is a less inhibiting molecule. A detrimental effect of the presence of aluminate on the electro-oxidation is also observed. Electrochemical techniques are proposed as new pathways for organic control in caustic medium.

Keywords Alumina hydrate · Crystallization · Electrocatalytic hydrogenation · Electro-oxidation · Inhibition

1 Introduction

Crystallization of alumina hydrate as gibbsite, $Al(OH)_3$, has been widely studied because of its implication in aluminium production. Crystallization inhibitors such as acyclic polyols are often reported [1–4]. The studies on these model compounds brought to light the important role of vicinal hydroxyl groups in the inhibiting behaviour of polyols in gibbsite precipitation. From a thorough analysis of solutions in which plant precipitated gibbsite was dissolved, Picard et al. [5] suggested that aromatic carboxylic acids and hydroxycarboxylic acids are the main organic impurities in crystallizers. Armstrong [6] studied vicinal hydroxyaromatic molecules and suggested that catechol (1,2-dihydroxybenzene) is an inhibitor of gibbsite precipitation.

In a previous study [7], it was proposed that selective reaction of catechol into 1,2-cyclohexanediol and muconic acid would prevent the inhibiting effect of catechol. This study shows that the adsorption on gibbsite seeds of the two selectively modified molecules, derived from catechol, is weak compared to the adsorption of the catechol. This study also shows that the decrease in yield of precipitation with those molecules, at the same concentration, is negligible compared to the decrease observed with catechol.

Oxidation of catechol is already known because of its occurrence in the oxidation products of phenol [8]. The first oxidation product of catechol, *o*-benzoquinone,

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can be further oxidized to muconic acid and, depending on the working conditions, the first oxidation is reversible but not the second one [9]. However, muconic acid can be oxidized leading to shorter aliphatic acids such as acetic acid or, in the end, to totally decompose in sodium carbonate.

The advantage of electro-oxidation over ‘‘wet oxidation’’ is that the reactive species is generated in situ. Other techniques usually need the injection of reactive species such as O_2 and O_3. Adapted electrodes can generate these molecules as well as hydroxyl radicals ($\cdot OH$) [10]. Organic molecules can also be directly oxidized at the electrode or by means of a higher oxide form of the metal [11, 12].

Electrocatalytic hydrogenation (ECH) of unsaturated molecules is an alternative for hydrogenation processes. It has been used for hydrogenation of aromatic molecules such as phenol over various catalysts. The electrode system, proposed by Laplante et al. [13], is a system where powdered catalysts are agglomerated in reticulated vitreous carbon (RVC). This technique allows the testing of a broad family of catalysts in a short period of time. It was also possible to show a correlation between adsorption of the molecules on the catalyst and hydrogenation efficiencies [14].

Electrocatalytic hydrogenation of unsaturated molecules also takes advantage of the in situ production of the active species. The hydrogen electrochemically generated can react with the C=C bounds. Other hydrogenation techniques usually take place in high-pressure vessels where gaseous hydrogen is injected at high temperature [15].

Thornber et al. have suggested an electrochemical method of oxidizing model organic species in caustic medium [16], where ferrate ions are generated in situ, from the consuming of the iron anode. This paper presents an alternative approach using electrochemistry to control organic molecules that show an inhibiting behaviour towards alumina hydrate crystallization from sodium aluminate supersaturated solution.

2 Experimental

Precipitation tests were conducted using an aluminate supersaturated solution prepared with 188 g L^{-1} of $Al(OH)_3$, 150 g L^{-1} of NaOH and 40 g L^{-1} of Na_2CO_3. All components were mixed together in a high-pressure vessel at 150 °C. Measurements of the species in solution were done using titrimetric methods [17].

Electrochemical experiments were carried out in an H-type cell. The anodic compartment was separated from the cathodic one by a cationic membrane (Nafion 117, Dupont technologies). For potentiometric and cyclic voltammetry measurements, the electrolytic contact between the reference electrode, a saturated calomel electrode (SCE), and the working electrode was done using a Luggin capillary.

Electrolyses were carried out in 28.0 mL of 1.0 M NaOH prepared with demineralized water (18.0 MΩ) and high purity NaOH (99.99%). A solution of 0.15 M catechol in 1.0 M NaOH was prepared and 2.00 mL of this solution were added to the electrochemical cell just before the electrolyses. Potentiostatic and galvanostatic electrolyses were conducted using PAR273A and PAR173 respectively. A constant flow of nitrogen was maintained during the electrolysis to avoid oxygen dissolution in the solution.

Electrolyses were also carried out in aluminate supersaturated and saturated solutions. Supersaturated solutions were the same as those used for precipitation tests. Saturated solutions were obtained by seeded precipitation of supersaturated solution over several months. Solutions were filtered through Whatman 40 filter paper and stored at room temperature in HDPE bottles.

The working anodes were made from a sheet of nickel of 2.0 × 1.0 cm. The cathode was made from a suspension of 200 mg of the catalyst (Rh/Al_2O_3 5%, Alfa Aesar) circulating through a RVC foam (2.0 × 2.5 × 0.7 cm) of 80 pores per inch, from Electrolytica Inc. A nickel wire was used as the counter-electrode.

Analyses of electrolysis products were performed with a high performance liquid chromatograph (HPLC Agilent 1,100 Series) equipped with a refraction index detector. Standard solutions for quantitative analysis were prepared using products from manufacturers without further purification.

The experiments on the influence of electrolysis on precipitation yield were carried out in a 600 mL thermoregulated cell. The anode was a 7.2 × 1.75 × 0.2 cm piece of nickel. The cathode was made from a stainless steel 316 gauze of 20 meshes. The anode was placed at the centre of the cell and was totally surrounded by the cathode. The anodic current density was 400 mA cm^{-2}. This high density, in the oxygen evolution zone, was chosen to allow the oxidation of catechol in a minimum period of time to the detriment of current efficiency. The solutions were stirred with a magnetic agitator. Precipitation tests and yield measurements of the electrolysed solutions were described in a previous paper [7].

3 Results

Earlier work has shown that if a precipitation inhibitor like catechol can be modified, either by an oxidation or reduction reaction, its detrimental effect on precipitation could be eliminated [7]. This is shown in Fig. 1 where the effect of catechol on the yield of alumina hydrate precipitation is compared to its oxidation and hydrogenation products, which have no effect on precipitation yield. Thus, two electrochemical pathways, ECH and electro-oxidation (Fig. 2), were investigated to determine if these approaches could lead to the desired reactions of precipitation inhibitors. Saturated and supersaturated aluminate solutions were chosen and tests were performed with 10 mmol L^{-1} of catechol. Precipitation tests were carried out in supersaturated aluminate solution with 25 mmol L^{-1} of catechol.

3.1 Electrocatalytic hydrogenation (ECH) pathways

Catechol ECH in 1.0 M NaOH with a commercial catalyst of Rh/Al_2O_3 5% is shown in Fig. 3. Under these conditions, it takes 375 °C to totally hydrogenate the catechol compared to 173 °C for a 100% current efficiency. This gives a current efficiency of 46%. The detection of the two isomers (*cis* and *trans*) of the cyclohexanediol suggests the presence of intermediate products. This particular aspect is the subject of another article from our group [18].

For temperatures between 25 °C and 65 °C, no significant effect on the ECH of catechol was observed under the conditions tested, as shown in Fig. 4. This suggests that ECH process could be done at the precipitation temperature of 65 °C.

The effect of the presence of aluminate ion on ECH can be seen in Fig. 5. The current efficiency of the ECH process drops to 20% in saturated aluminate solution. The effect of the aluminate ion is more important in the supersaturated solution where the efficiency drops to less than 10%. Studies have shown that adsorption of organic molecules on the catalyst is a key parameter of ECH [14]. In situ modification of the catalyst surface by adsorption of molecules greatly influences the efficiency of ECH [19]. Adsorption of aluminate ions on the alumina surface may be responsible for the current efficiency reduction.

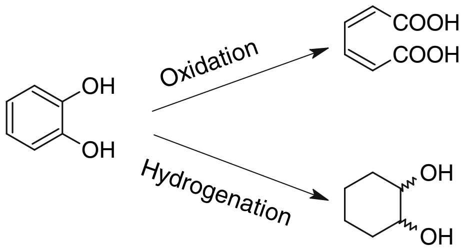

Fig. 2 Selective reaction pathways

3.2 Oxidation pathway

Cyclic voltammetry with a nickel working electrode in pure 1.0 M NaOH solution containing 13 mM of catechol shows that the oxidation of the catechol occurs directly on the nickel at a potential of –0.100 V versus SCE (Fig. 6). The absence of a reduction peak suggests that the oxidation is irreversible. This can be explained by the further oxidation of *o*-benzoquinone, the primary oxidation product, to muconic acid. Ryan et al. also suggest the possible dimerization of *o*-benzoquinone with the catecholate ions in solution [20].

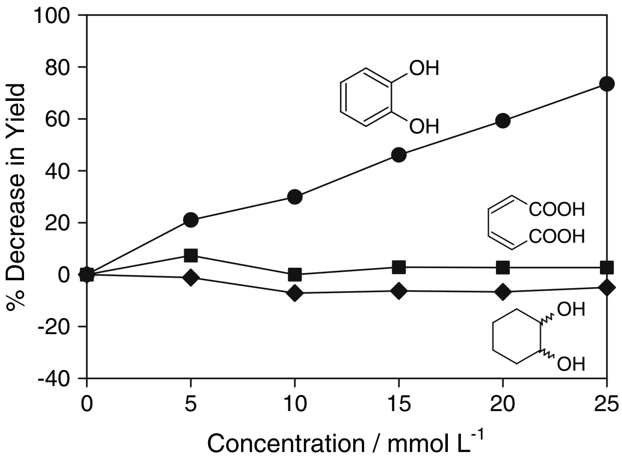

Fig. 1 Effect of the concentration of selected molecules on the alumina hydrate precipitation yield. ●—catechol, ◆—1,2-cyclohexanediol (*cis*-*trans* mixture), ■—muconic acid

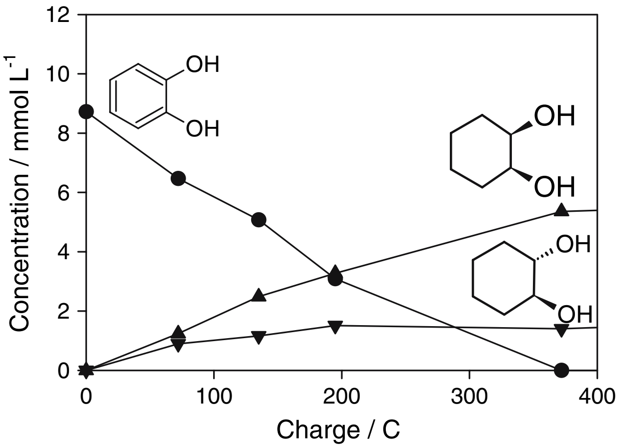

Fig. 3 ECH of catechol on Rh/Al_2O_3 5% in 1.0 M NaOH, I = 10 mA. ●—catechol, ▼—*trans*-1,2-cyclohexanediol, ▲—*cis*-1,2-cyclohexanediol

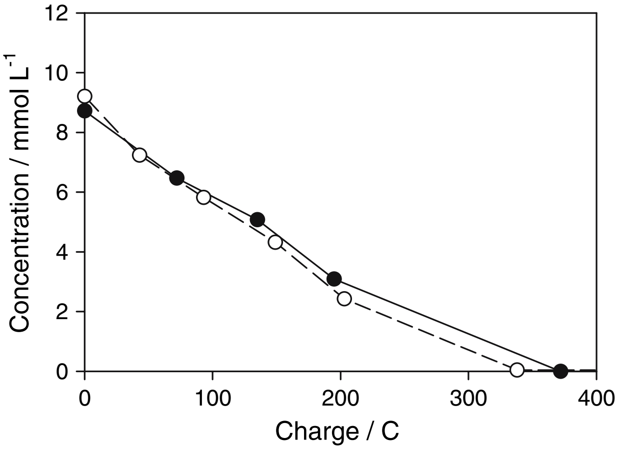

Fig. 4 Influence of temperature on the ECH of catechol on Rh/Al_2O_3 5% in 1.0 M NaOH; I = 10 mA ●—room temperature, ○—65 °C

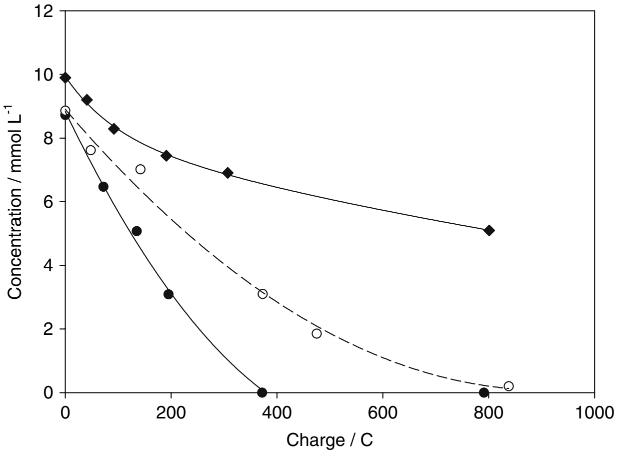

Fig. 5 Influence of aluminate concentration on the ECH of catechol on Rh/Al_2O_3 5%: ●—without aluminate (1.0 M NaOH), *o*—saturated aluminate solution and ◆—supersaturated aluminate solution

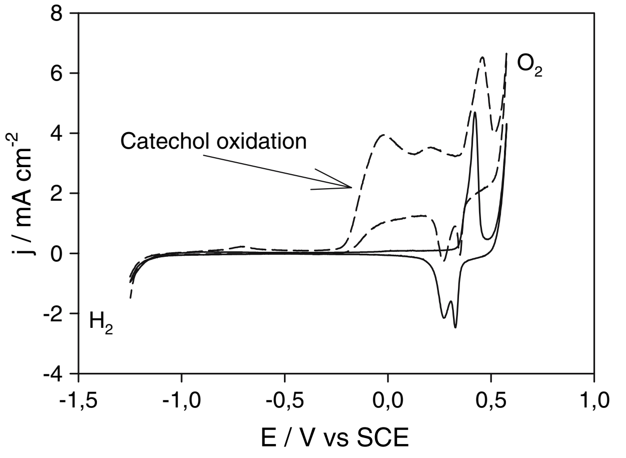

Fig. 6 Cyclic voltammetry of nickel electrode at 50 mV s^{-1} in: (——) pure 1.0 M NaOH and (– –) 13 mM catechol. (reference electrode : SCE)

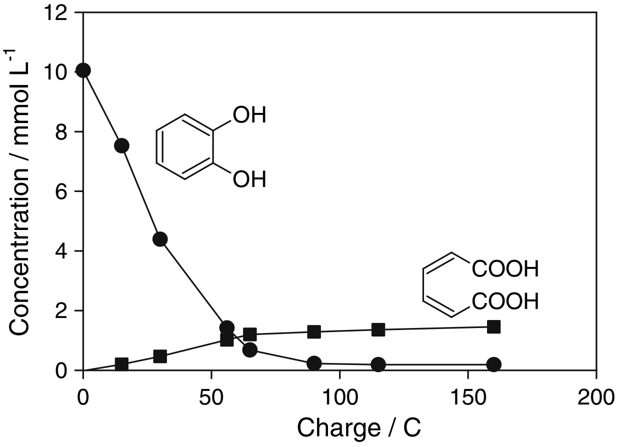

Fig. 7 Galvanostatic oxidation of catechol on nickel anode in 1.0 M NaOH, j = 1.25 mA cm^{-2}. ●—catechol, ■—muconic acid

Results of the oxidation of catechol on a nickel anode in 1.0 M NaOH are shown in Figs. 7 and 8. Galvanostatic experiment was conducted at low current density, 1.25 mA cm^{-2}, to optimise current efficiency. The potential chosen for the potentiostatic experiment was 0.100 V, which is directly after the first oxidation wave on the cyclic voltammogram (Fig. 6).

Galvanostatic electro-oxidation of catechol was then carried out in supersaturated and saturated aluminate solutions (Fig. 9). Here again the presence of aluminate has a detrimental effect on the current efficiency of the reactions.

Cyclic voltammetry on a nickel anode in the three different solutions shows that the presence of aluminate shifts the oxidation wave of catechol to more positive potentials (Fig. 10). In supersaturated solutions the oxidation potential has shifted to the same potential as for nickel oxidation.

This shift of the oxidation potential of catechol, when aluminate ions are present in solution may explain the current efficiency reduction under galvanostatic condition (Fig. 9). The shift to more positive values leads to additional side reactions reducing the current efficiency for catechol oxidation.

3.3 Precipitation versus electro-oxydation at 400 mA cm^{-2}

Electrolysis of supersaturated aluminate solution containing 25 mmol L^{-1} of catechol over a nickel anode shows that, at the precipitation temperature, i.e., 65 °C, the loss in alumina hydrate precipitation yield decreases with electrolysis time (Table 1). This shows

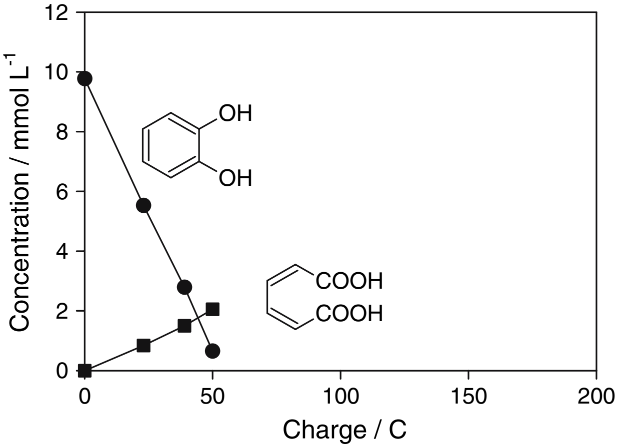

Fig. 8 Potentiostatic oxidation of catechol on nickel anode in 1.0 M NaOH, $E = 100$ mV versus SCE. ●—catechol, ■—muconic acid

that 30 min of electrolysis is sufficient to increase the yield of precipitation of alumina hydrate by almost 25%.

4 Discussion

Electrochemical results demonstrate the opportunity of selective reaction of catechol in a caustic medium. The ECH pathway shows the greatest selectivity. The reduction of catechol gave cyclohexanediol without any other reduction product. Temperature does not show any major influence on the efficiency of the process, suggesting that ECH can be done at precipitation temperatures.

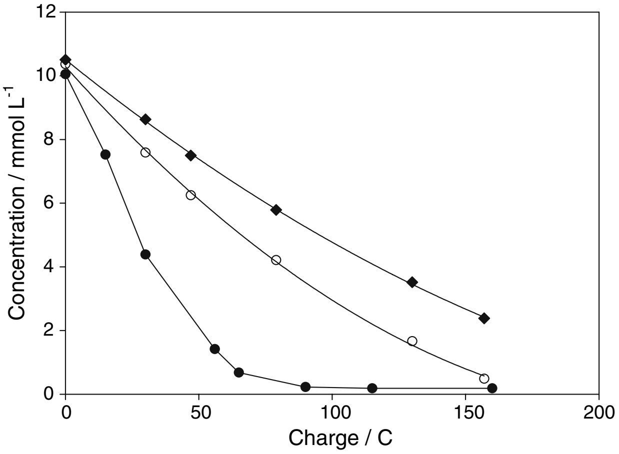

Fig. 9 Influence of aluminate concentration on galvanostatic electro-oxidation of catechol, $j = 1.25$ mA cm^{-2}: ●—without aluminate, *o*—saturated aluminate solution and ◆—supersaturated aluminate solution

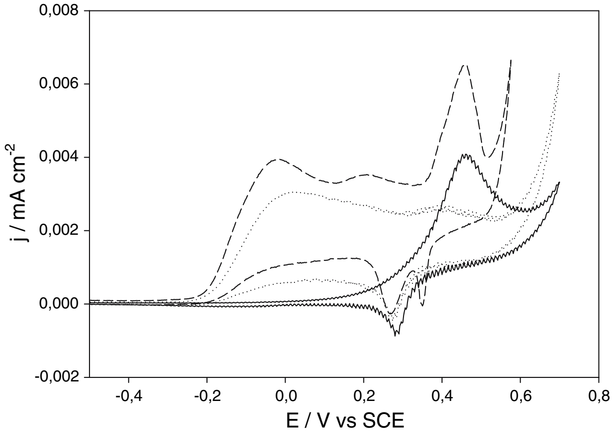

Fig. 10 Cyclic voltammetry of different 13 mM catechol solution at 50 mV s^{-1}; (- - -) 1.0 M NaOH, (· · ·) saturated aluminate solution and (—) supersaturated aluminate solution. (reference electrode : SCE)

The presence of aluminate ions is of great interest due to its influence on ECH of catechol. In the chosen range of temperature, the coulombic efficiency of ECH drops to 20% or less, in both saturated and supersaturated sodium aluminate solutions. The adsorption of aluminate ions on the catalyst surface in both saturated and supersaturated solutions explains this efficiency loss. By adsorbing on active sites of the catalyst, aluminate ions modify the adsorption behaviour of the catalyst towards the catechol. This effect is more significant in supersaturated aluminate solution and it induces alumina hydrate crystallization.

Since the presence of the catalyst induces the crystallization of alumina hydrate in supersaturated solutions, the effect of ECH on the precipitation yield cannot be conducted under those conditions.

The electro-oxidation of catechol on nickel demonstrates that it is possible to totally modify the molecule. However, compared to ECH, this technique is less selective if we take into account the formation of the predicted product, muconic acid. In the best case, only 20% of muconic acid was observed after the total modification of the catechol. This can be explained by the further oxidation of muconic acid to shorter

Table 1 Influence of electrolysis of catechol on yield of precipitation of alumina hydrate

Time/ Min	Decrease in yield/ %	Catechol concentration/ mmol L^{-1}	Muconic acid concentration/ mmol L^{-1}
0.0	74.4	25.8	0.0
15.0	60.4	22.9	0.4
30.0	49.8	14.8	0.7

aliphatic acid and to carbonate. The presence of aluminate in solution has a detrimental effect, as in the case of ECH. Galvanostatic experiments show that increasing the aluminate concentration decreases the efficiency of the oxidation. Cyclic voltammetry showed that the oxidation wave of catechol is more positive when the solution is saturated with sodium aluminate. In the case of supersaturated aluminate solution the wave is at the same potential as for nickel oxidation. This shift of the oxidation potential of the catechol explains the current efficiency reduction by allowing side reaction to take place.

Electro-oxidation of catechol in supersaturated aluminate solution allows an increase in precipitation yield. These results are in agreement with the precipitation results shown in Fig. 1. Oxidation for 30 min diminishes the concentration of catechol to 14.8 mM and the decrease in yield is 49.8%, which is very close to the original test done with 15.0 mM of catechol (Fig. 1). This result suggests that, even if catechol is not converted into muconic acid only, it is nevertheless transformed into non inhibiting molecules.

5 Conclusion

Selective electrochemical reactions of catechol, a known alumina hydrate crystallization inhibitor, have been achieved in caustic solutions and in saturated and supersaturated aluminate solutions. Two possible pathways were investigated showing that catechol is electrochemically active at the electrode for both the hydrogenation and the oxidation reactions.

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References

1. Watling H, Loh J, Gatter H (2000) Hydrometallurgy 55:275
2. Watling H (2000) Hydrometallurgy 55:289
3. Watling HR, Townsend R, Loh JSC (1999) Industrial Crystallization, 1
4. Smith PG, Watling HR, Crew P (1996) Colloids Surf A Physicochem Eng Asp 111:119
5. Picard F, Audet D, Boily H, Larocque J (2002) Identification of hydrate active organics (HAO) present in spent bayer liquors by state-of-the-art analytical methods, Proceedings of the 6th International Alumina Quality Workshop, Brisbane, Australia, p 46
6. Armstrong L (1993) Bound soda incorporation during hydrate precipitation, Proceedings of the 3rd International Alumina Quality Workshop. HunterValley, Australia, p 283
7. Bouchard NA, Breault R, Picard F, Chouinard Y, Ménard H (2005) Light Metals, 197
8. Joglekar HS, Samant SD, Joshi JB (1991) Water Res 25:135
9. Nematollahi D, Alimoradi M, Husain SW (2004) Electroanalysis 16:1359
10. da Silva LM, De Faria LA, Boodts JFC (2003) Electrochim Acta 48:699
11. Fleischmann M, Korinek K, Pletcher D (1971) J Electroanal Chem 31:39
12. Sharifian H, Kirk DW (1986) J Electrochem Soc 133:921
13. Laplante F, Brossard L, Menard H (2003) Can J Chem 81:258
14. Laplante F, Bouchard NA, Dube P, Menard H, Brossard L (2003) Can J Chem 81:1039
15. Nishimura S (2001) Handbook of heterogeneous catalytic hydrogenation for organic synthesis. J. Wiley, New York, p 340
16. Thornber M, Woods G, Vernon C, Brown M (2000) Oxidation of bayer organic species in situ using ferrate., CHEMECA, 28th Australasian Chemical Engineering Conference, Perth, Australia, 9–12 July
17. Watts HL, Utley DW (1953) Anal Chem 25:864
18. Brisach-Wittmeyer A, Bouchard NA, Breault R, Menard H (2006) Can J Chem 84:1640
19. Cirtiu MC, Oudghiri Hassani H, Bouchard NA, Rowntree P, Ménard H (2006) Langmuir 22:6414
20. Ryan MD, Yueh A, Chen W-Y (1980) J Electrochem Soc 127:1489