Degradability of aluminum in acidic and alkaline solutions

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ABSTRACT

The processes of aluminum degradation in HCl, H_2SO_4, HNO_3 and NaOH solutions were investigated in static and agitated media. The effects of concentration, temperature, and mixture of acids were studied. The dissolution of aluminum was faster in NaOH and HCl than in H_2SO_4 and HNO_3. The activation energies were 86.5 and 52.4 kJ/mol for Al dissolved in HCl and NaOH respectively. An inhibiting effect on Al dissolution was observed with the mixture HCl + HNO_3 regardless of the conditions used while a synergetic effect was observed with the mixture H_2SO_4 + HCl using acids at 4 M.

1. Introduction

The natural concentration of metals in the environment has been increased over time by human activities. Some metals such as aluminum, iron and zinc are largely used in domestic as well as in industrial purposes. Aluminum for example is used in cans, food plates, doors, automotive and construction [1]. The increasing severity of the environmental legislations has forced the recycling of aluminum to give a reasonable final destination [2,3]. However, a part is still found in solid waste landfills. The study of the potential release of aluminum when deposited in landfill is of a great importance to predict its long term behavior in nature. In the region of Annaba large amounts of aluminum are present in municipal solid waste. The recycling industry of metals in our region is not yet developed. This is problematic because various reactions can be occurring when aluminum comes into contact with some industrial liquid effluents enough acid or alkaline to initiate the dissolution reactions and pollute the environment [4]. The behavior of aluminum was extensively studied in the context of corrosion where the research was focused on the protection of the metal from chloride attack [5–8]. Aluminum dissolution was also studied in term of hydrogen production [9–11]. In fact, gaseous hydrogen is considered as an environmentally friendly fuel with high calorific value which can be generated from the corrosion of aluminum in alkaline solutions. Thus, due to its amphoteric character aluminum may be dissolved in acidic or in alkaline solutions. However, only two studies were found in the literature dealing with the comparison of aluminum dissolution in both environments. Oguzie [12] investigated

the inhibiting effect of leaf extracts of *Sansevieria Trifasciata* on the corrosion of aluminum in 2 M HCl and KOH using the gasometric technique. He found that the organic extract exhibited good inhibition efficiency during Al corrosion in both solutions and that the corrosion of Al in KOH was faster than in HCl. Garcia-Garica et al. [13] studied the effect of nickel on the corrosion of Al and Al alloy AA1050 in HCl and NaOH solutions that are employed in lithographic industry. They found that the addition of nickel enhanced the dissolution rate of Al in both solutions. In this study also, the dissolution rate of Al in NaOH was found to be greater than that in HCl. However, the first paper was focused on the protection of aluminum from corrosion and the second one on its acceleration rather than on the comparison of Al dissolution in both environments under the same conditions. In this study a special attention is paid to the kinetic of aluminum dissolution in HCl, H_2SO_4, HNO_3 and NaOH under the same experimental conditions. The influence of the operation conditions on the resultant morphology of aluminum was also considered.

2. Experimental methods

H_2SO_4 (96–98%, Biochem), HNO_3 (60%, Cheminova), HCl (37%, Carlo Erba) and NaOH pellets (99%, Biochem) were used as leaching reagents. Al specimens in the form of disc (6 mm of radius, 2.46 mm of thickness and 99.999% purity) were supplied by Sigma–Aldrich. The composition of aluminum is given in Table 1. All specimens were used without further polishing but for experiments, they were degreased in acetone and rinsed with deionized water. All reagents were used as received. Deionized water was used to prepare all aqueous solutions. Tests of Al dissolution were performed in a Pyrex glass reactor heated in a water bath and

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Table 1
Chemical impurities of aluminum used in this work (ppm by mass).

Fe	Si	Cu	Mn	Mg	Cr	Ni	Zn	Ti	V	Zr	Al
2	2.5	2	0.2	2.8	0.3	0.3	0.3	0.8	0.8	0.1	Balance

equipped with a return-flow cooler. SEM images were taken with the Environmental Scanning Microscopy instrument (XL 30, Philips, Netherlands). Two scenarios were investigated in which aluminum was in contact with static solutions (without external agitation) and dynamic solutions (agitated magnetically). The experiments were performed by contacting one disc of aluminum (0.75 g) with 200 mL of the desired solution. The volume of 200 mL was chosen to avoid the saturation of the solution and preventing a solubility-control phenomenon in the leachate. Al^{3+} present in aqueous solutions was determined by reverse titration of zinc sulfate solution with EDTA using xylenol orange as indicator [14]. The data presented are an average of two tests replicates with an error of 5%. Aluminum dissolved was calculated in term of weight loss using the expression:

$$\text{Aluminum dissolved} = \frac{C \times V \times M}{A} \quad (\text{mg/cm}^2) \tag{1}$$

where C is the concentration of Al^{3+} analyzed in the solution (mol/L), V is the volume of the solution (0.2 L), M is the molar mass of Al (26.982 g/mol) and A the surface of the disc (0.927 cm^2).

The concentration of the solutions used for the dissolution of aluminum was varied from 0.5 to 4 M and the temperature from 40 to 80 °C under 350 rpm. The dissolution kinetic was examined according to the heterogeneous reaction models and the best fitted equation to the experimental data was determined. The point of zero charge (pH_{PZC}) of Al was determined by a method used elsewhere [15,16]. This method consisted on mixing 1 g of the solid with 20 mL of CO_2-free distilled water. The sample was manually agitated over a period of 48 h after which, the pH of the solution was taken as pH_{PZC}.

3. Results

3.1. Static media

The dissolution reaction of aluminum in highly acidic and alkaline solutions may be written in term of cathodic and anodic reactions [17,18]. The cathodic reaction in acidic solution is the discharge of proton while the main cathodic reaction in alkaline solution is the reduction of water to hydrogen:

$$H^+ + e^- \rightarrow 1/2H_2 \tag{2}$$

$$H_2O + e^- \rightarrow 1/2H_2 + OH^- \tag{3}$$

The anodic reactions taking place in the corrosion of aluminum in acidic and alkaline solutions are:

$$Al + 3H^+ \rightarrow Al^{3+} \tag{4}$$

$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^- \tag{5}$$

The overall reactions may be written for both solutions as follows:

$$Al + 3H^+ \rightarrow Al^{3+} + 3/2H_2 \uparrow \tag{6}$$

$$Al + 3H_2O + OH^- \rightarrow Al(OH)_4^- + 3/2H_2 \uparrow \tag{7}$$
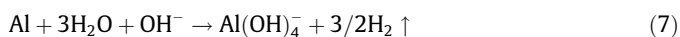
The reactions (6) and (7) are true for the aluminum dissolution in HCl and H_2SO_4 while with HNO_3 the nitrates are reduced by aluminum through the following reaction [19]:

$$Al + NO_3^- + 4H^+ \rightarrow Al^{3+} + NO + 2H_2O \tag{8}$$
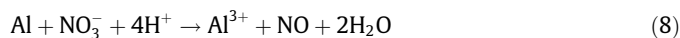
In this case ionic aluminum is also formed but not the gaseous hydrogen. Depending on the volume of gas formed, hydrogen evolution may agitate the interface, dispersing the corrosion products and reducing thereby the importance of mass transport limitation. With NaOH as a large excess of the solution was used, no precipitation of aluminum was ever observed.

Aluminum was contacted with HCl, HNO_3, H_2SO_4 and NaOH solutions at three concentrations (0.5, 1 and 2 M) at ambient temperature (25 °C) and in absence of stirring. The results show that in all cases the release of aluminum increased with increasing the concentration of the solutions except in the case of HNO_3. Higher amount of Al was released with NaOH compared to HCl with the three concentrations (Fig. 1a and b). The dissolution of Al in H_2SO_4 and HNO_3 was remarkably slower than that observed with HCl and NaOH (Fig. 1c and d) and was not greatly dependent on their concentrations. Furthermore, increasing the concentration of HNO_3 led to decrease Al release as shown in Fig. 1d.

The release of aluminum started after the elapses of a certain time from the contact with all solutions. This time is identified as the induction period which is the time needed by the solution to destruct the oxide film and start the dissolution of the metal [8,20]. The induction periods were 4320, 1440 and 750 min with HCl and 330, 150 and 90 min with NaOH at 0.5, 1 and 2 M respectively. The induction periods observed with NaOH with the three concentrations were shorter than those observed with HCl. Thus, despite the presence of chlorides and H^+ known for their aggressiveness (initiation of pitting) both ions were not sufficiently efficient to dissolve Al as OH^- ions did. Dissolution of metals occurs via heterogeneous reactions which include the transfer of reactants and chemical reactions. In this study, the results of aluminum dissolution were analyzed using the shrinking core model. SCM was chosen because it approximates real particles more closely than does the other conversion models in a wide variety of situations. In this model the reactant is considered to be nonporous and is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid. This model used the following expressions to describe the dissolution kinetics of the process [21]:

$$\text{For liquid film diffusion control}: \quad x = kt \tag{9}$$

For film diffusion control through product layer:

$$1 - 3(1-x)^{2/3} + 2(1-x) = kt \tag{10}$$

$$\text{For surface chemical reaction control}: \quad 1 - (1-x)^{1/3} = kt \tag{11}$$

where x is the amount of aluminum dissolved at time t and k is the apparent rate constant (min^{-1}). The overall rate of dissolution is controlled by the slowest of these sequential steps.

The kinetic calculations show that a satisfactory fitting of the model controlled by the chemical reaction was obtained with 2 M HCl over the whole reaction time (Fig. 1e). With 1 M HCl the chemical reaction controlled the dissolution in range 570–7200 min and transport through boundary layer in range 7200–28,800 min while transport through boundary layer controlled the dissolution over the whole reaction time with 0.5 M HCl. The dissolution of Al in NaOH was controlled by chemical reaction with the three concentrations (Fig. 1f) and the rate constant of Al dissolved in 2 M NaOH (3×10^{-4} min^{-1}) was 15 times higher than that obtained with HCl at the same concentration (2×10^{-5} min^{-1}).

The surface of aluminum was examined by SEM analysis. The morphology of Al surface obtained after contacting 0.5 M HCl for