Leaching Process Investigation of Secondary Aluminum Dross: The Effect of CO₂ on Leaching Process of Salt Cake from Aluminum Remelting Process

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For the recycling/disposal of aluminum dross/salt cake from aluminum remelting, aqueous leaching offers an interesting economic process route. One major obstacle is the reaction between the AlN present in the dross and the aqueous phase, which can lead to the emission of NH₃ gas, posing a serious environmental problem. In the current work, a leaching process using CO₂-saturated water is attempted with a view to absorb the ammonia formed *in situ*. The current results show that at a solid-to-liquid ratio of 1:20 and 3 hours at 291 K (18 °C), the extraction of Na and K from the dross could be kept as high as 95.6 pct and 95.9 pct respectively. At the same time, with continuous CO₂ bubbling, the mass of escaping NH₃ gas decreased from 0.25 mg in pure water down to <0.006 mg, indicating effective absorption of ammonia by carbonized water. Furthermore, the results in the case of the leaching experiments with synthetic AlN show that the introduction of CO₂ causes hindrance to the hydrolysis of AlN. The plausible mechanisms for the observed phenomena are discussed. The concept of the leaching of the salt cake by carbonated water and the consequent retention of AlN in the leach residue opens up a promising route toward an environment-friendly recycling process for the salt cake *viz.* recovery of the salts, utilization of CO₂, and further processing of the dross residue, toward the synthesis of AlON from the leach residues.

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I. INTRODUCTION

DURING the remelting of aluminum scrap, the rest product formed is the aluminum dross/salt cake. This contains the salt mixture added during melting to prevent the oxidation of aluminum along with products of reaction between liquid aluminum and air, *viz.* Al₂O₃ and AlN. Very small amounts of Al₄C₃ and AlP are also found in the salt cake. The composition of salt cake from secondary aluminum remelting varies depending on the production practice and the alloy of the scrap that is remelted. In addition to the compounds mentioned, the dross may contain even smaller amounts of SiO₂ and MgO, apart from entrapped elemental aluminum.^[1,2] One important process that steps in the treatment of this waste material is the recovery of metallic aluminum by leaching the salts out and separating Al metal. The wastes generated from treatment of the salt cake (nonmetallic products together including some chlorides) are usually landfilled or

disposed without treatment, causing a load on the environment.^[3]

The earliest submitted method for salt cake processing was patented in the 1978 by Papafingos and Lance.^[4] This patent features the equipment for cooling and disaggregating aluminum dross with water to dissolve the salts. However, during the leaching process, AlN, Al₄C₃, and AlP (the latter two compounds are in less significant amounts) will react with water or even with moisture in the air according to the following chemical Reactions [1] through [3]

The terrible smelling ammonia escapes during the process, and also NH₃ is readily soluble in water, increasing simultaneously its pH value up to 9 or higher. As a consequence, the metallic aluminum particles present are more vulnerable to hydrolysis in strong alkaline solution forming hydrogen according to the following reaction^[6]:

According to Yerushalmi,^[7] the pH value in the digester must be maintained below 8 and preferably

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between 5 and 8 to prevent these undesirable reactions, namely, Eqs. [1] through [4]. One possible method suggested is to add magnesium chloride into the solution. This salt would suppress the reactions that increase pH of the leaching liquid because it reacts with the hydroxyl ions in alkali solutions to form nondissociated $\text{Mg}(\text{OH})_2$ and HCl .

HCl would decrease the pH and consequently slow down the reaction of AlN and metallic aluminum with water. However, the accumulation of strong acid HCl would cause the difficulty in the recovery of salts. The current work presents a modification of the preceding process using CO_2 -saturated water for leaching the salt cake.

II. PRINCIPLE

The use of carbonic acid would be of interest as it is a weak acid and has a moderate effect on pH. Furthermore, this would enable the fixation of carbon from CO_2 in the form of the carbonate/bicarbonate of ammonia.

In the present work, the salt cake which is reacted with moisture thereby releasing small amounts of NH_3 is leached with water saturated with CO_2 , neutralizing the alkalinity. As the solubility of CO_2 in water is limited (the saturated solution of CO_2 in water obeys Henry's law),^[8] a continuous stream of the gas was bubbled through the aqueous medium during leaching. The leaching process of aluminum dross involves a series of complicated reactions. The absorbed CO_2 would form ionized carbonic acid, which in turn would react with ammonia formed as a result of Reaction [2] to form bicarbonate (HCO_3^-) and carbonate, (CO_3^{2-}) ions as shown in Eq. [6].

A stability diagram illustrating the species formed in aqueous medium is shown in Figure 1, where in the CO_2/NH_3 ratio is plotted as a function of temperature.

It is shown that, at room temperature, in CO_2 -saturated solution, at the beginning of hydrolysis, the stable species in solution would be NH_4HCO_3 when the ratio (CO_2/NH_3) is high (>0.53). With the increase of the concentration of dissolved ammonia, the species $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$ would be formed. The solubility of the carbonates NH_4HCO_3 and $(\text{NH}_4)_2\text{CO}_3$ in water at 293 K (20 °C) are 21.7 g and 100 g per liter of the solution. Thus, ammonia gas is likely to be retained in the aqueous solution.

Furthermore, it is reasonable to expect that the acidic solution formed, with a low pH, would lead to a decrease on the hydroxyl ion concentration. Figure 2 presents the mol fractions of various dissolved species formed during the hydrolysis of aluminum hydroxide in

Fig. 1—Stability diagram showing stable components in aqueous solution at different CO_2/NH_3 ratios and temperature.^[9]

Fig. 2—Molar fractions of dissolved hydrolysis products of mononuclear aluminum hydroxides in equilibrium with amorphous hydroxides.^[10]

equilibrium with various amorphous hydroxyl ions in solution.

Preliminary experiments (Section IV-C) carried out as part of the current work showed that CO_2 -saturated water had a pH value of approximately 3.9. From Figure 2, it is observed that at this pH value, the most stable species in solution are Al^{3+} and $\text{Al}(\text{OH})^{2+}$. Because $\text{Al}(\text{OH})_3$ is relatively less stable, it would be expected that Reaction [2] may be hindered when AlN comes into contact with carbonated water. Thus, the use of CO_2 -saturated water would have two functions:

- Hinder significantly the ammonia forming reaction, *viz.* the hydrolysis of AlN .
- The small amount of NH_3 produced can be effectively absorbed by the formation of NH_4HCO_3 species in aqueous solution.

Based on the preceding reasoning, it is expected that leaching with CO_2 -saturated water would dissolve most of the chlorides and part of the iron present in the salt cake. The residue after leaching would contain Al_2O_3 and lesser amounts of SiO_2 , MgO , and AlN , along with metallic Al .

This is likely to form an ideal precursor for the synthesis of high-performance oxynitride ceramics.^[11]

Experimental work is needed to optimize the conditions for minimizing the hydrolysis of AlN. Another advantage is to utilize the anthropogenic CO₂^[12]; the fixation of the same as ammonium carbonate can be utilized as a fertilizer.

Corresponding reference experiments were conducted with pure synthetic AlN, and the results were compared with those obtained with salt cake leaching. Previous experiments^[13] showed an acceleration effect of saline water on the hydrolysis of AlN. In the current work, the leaching of AlN was carried out with both deionized and saline water.

III. EXPERIMENT

A. Sample Preparation

The aluminum dross used in the current work was supplied by Stena Aluminum AB (Älmhult, Sweden). The samples consisted of rounded lumps up to approximately 10 mm in size (as well as some smaller metallic fragments) and had a slight smell of ammonia. The samples were crushed using a pulverizer and sieved through a 100- μ m aperture screen. A sample before and after crushing is shown in Figure 3. The dry solids were sampled and used for X-ray diffraction, chemical analysis, and subsequent leaching tests. In the case of the leaching treatment, deposits were taken out from the suspensions, filtered, and washed with 2-propanol to remove the adherent water. The residues were dried at 333 K (60 °C) for 8 hours and then stored in plastic, airtight containers before conducting the characterization tests. The leach liquids from each test were also subjected to a chemical analysis. Corresponding experiments were also performed on pure, synthetic AlN samples to understand the impact of CO₂ on the hydrolysis behavior.

B. The Leaching Experiments with Salt Cake from Al Remelting

The experimental apparatus used in the current investigation is shown in Figure 4. The leaching tests were conducted by treatment with both pure water as well as the CO₂-saturated water for 1 hour and 3 hours

at different solid-to-liquid mass ratios 1:5, 1:10, and 1:20, respectively. In the tests, 400 mL aqueous solution was kept under constant stirring (300 rotations per minute) at a temperature of 291 K (18 °C) using a water bath provided with a thermostat. The pH was monitored as a function of time using a combined glass electrode/Pt 512 thermometer pH meter (SanXing Company, Shanghai, China). Taking into consideration of the possibility that a small amount of ammonia gas might escape from the reaction bottle, a scrubber bottle with 2 mol/L boric acid solution was provided downstream.

In the case of leaching with CO₂-saturated water, the CO₂ gas was kept bubbling into the deionized water for about half an hour prior to the experiment, which ensured the stabilization of the pH value, before the leaching was started. The flow rate and CO₂ pressure were maintained at 40 mL/min and 1.05 MPa during the entire leaching process.

C. The Hydrolysis Tests of AlN

As mentioned, reference leaching experiments similar to those with the salt cake were carried out with pure AlN. Commercial AlN powder used in the current work was supplied by Xiong Chemical Company (Guangzhou, China), and the maximum impurity content was less than 2 wt pct. The particle size of the powder was less than 1 μ m. The hydrolysis tests were carried out in the dilute suspensions containing 0.25 mass pct of AlN in 0.3 mol/L and 0.6 mol/L NaCl solutions, for various time intervals, viz. 48 hours, 96 hours, and 144 hours. The experimental procedure adopted was the same as in the case of salt cake experiments.

D. Analytical Methods

The chemical analysis of the elements of raw aluminum dross was carried out by the Central Iron & Steel Research Institute (Beijing, China). The compounds of the as-received salt cake as well as the residue after the leaching process were determined by RINT 2500HF+-based (Rigaku Corporation, Tokyo, Japan) X-ray diffraction and X-ray fluorescence (XRF) methods.

Nitrogen in the solid dross was determined by digesting a suitable amount of the sample in HCl

Fig. 3—The aluminum dross before and after grinding.

Fig. 4—Experimental apparatus: 1—carbon dioxide, 2—gas buffer, 3—manometer, 4—reaction bottle, 5—thermostatic magnetic stirrer, 6—gas valve, 7—absorption bottle, 8—computer, and 9—pH measurement.

Table I. The Chemical Analysis of Raw Aluminum Dross

Composition	Al ₂ O ₃	AlN	MgO	Fe ₂ O ₃	KCl	NaCl	SiO ₂	CaO
Mass pct	44.71	7	4.21	2.67	10.69	22.28	6.64	1.8

solution (mass ratio = 1:1) at 473 K (200 °C) for 4 hours using a polyethylene reactor. This duration of the acid treatment was considered essential to ensure that the AlN had reacted completely with HCl. The pulp was filtered and the amount of ammonia dissolved in the aqueous solution, present as NH_4^+ ions, was determined by the water quality—determination of ammonium—distillation and titration method (WDDT).^[14,15] Nitrogen measurements were used to quantify the amount of aluminum nitride (AlN) in the sample.

Metallic elements Na and K in aqueous leach solutions after the leaching process were determined by a standard inductively coupled plasma (ICP)-optical emission spectroscopy (OES) technique. As shown in Eq. [2], during the leaching and hydrolysis of AlN in the salt cake, NH_4^+ ions would be formed by the *in situ* dissolution of NH_3 gas formed into the solution. The content of NH_4^+ in the solution was measured to monitor the AlN hydrolysis. The analysis method adopted was the same as mentioned, WDDT.

In the case of the hydrolysis of AlN, the morphology of the micropowders was studied by SUPRATM55 field emission scanning electron microscope (SEM; Carl Zeiss, Oberkochen, Germany) and high-resolution transmission electron microscope (HRTEM; Tecnai F20; Philips, Amsterdam, the Netherlands).

IV. RESULTS

The analysis of the raw salt cake was conducted for many samples, and the average analysis is reported in

Table I. The variation between the various analysis values was found to be less than ± 2 pct indicating that the sampling was reliable.

As shown in Table I, the salt cake contained nearly 32 mass pct of alkali chlorides, 7 mass pct AlN, and small amounts of iron. The amounts of Al_4C_3 and Al_3P were found to be below the detection limits.

A. Salts Removal in the Leaching Process

Figure 5 presents the pattern of the as-received dross (bottom pattern). It is observed that the material contains significant amounts of KCl and NaCl, in addition to the presence of other phases (spinel, Al_2O_3 , and AlN). The top pattern in Figure 5, corresponding to the residue after leaching treatment, shows that most of the chlorides have been removed with a consequent increase in the intensity of the AlN peaks as a result of increased concentration. From Table II, it is observed that the extraction of Na and K calculated from the ICP-OES results increased with the increase of solid:liquid ratio and leaching time. Most of the sodium present in the salt cake as halite (NaCl) and potassium as sylvite (KCl) is readily soluble in water. At solid:liquid ratio of 1:20 and after a leaching time of 3 hours, the removal of NaCl and KCl could be kept as high as 95.64 pct and 95.87 pct, respectively.

B. Ammonia Dissolution During Leaching

Figure 6 shows the change of pH with time during the leaching experiment for a 1:20 ratio of deionized water

with and without CO₂ bubbling carried out over a period of 3 hours.

It can be observed in Figure 6 that as soon as the salt cake was added to the deionized water, the value of pH rose immediately from 6.5 to 8.75. This result may be indicative of the dissolution of a moisture layer on the surface of the salt cake containing some amount of ammonia. This NH₃ is likely to have been produced by the hydrolysis of AlN in the moist air before the leaching process. After this initial rise, the pH value increased slowly to 9.0 because of the continuation of the hydrolysis reaction mainly according to Eqs. [2] and [4]. The corresponding curve for the experiment with CO₂-saturated water showed only a marginal increase of pH from the initial value of 4.5 to 5.5, which is still in the acid range. Under such circumstances, the following reactions will occur:

During the leaching experiments, the ammonia gas generated would first dissolve in the leachant in the reaction bottle (Figure 4, marked (4)), but a small amount can escape to be absorbed in the absorption bottle (Figure 4, marked (7)). It will be interesting to know the mass of ammonium ions (presented as “ammonia”) in the solution in these two bottles in order to understand the extent of the hydrolysis reaction in both cases. Figure 7 presents the mass of “ammonia” in the reaction bottle when leaching was carried out both with deionized water as well as CO₂-saturated water at different solid:liquid ratios and different leaching times.

The following was observed:

- (a) Leaching time had virtually no impact on the concentration of ammonia in solution in when leaching is carried out in carbonated water.
- (b) The amount of ammonia present in the solution when leaching was carried out using CO₂-saturated water, which was less compared with the corresponding results with deionized water.

Fig. 5—The XRD patterns of the residue after leaching process with CO₂-saturated water (top) and as-received salt cake (bottom).

Fig. 6—pH vs time for aluminum salt cake in deionized water and CO₂-saturated water at 291 K (18 °C).

Table II. The Extraction Results after Leaching Treatment with Deionized Water at 291 K (18 °C)*

Solid:Liquid Ratio	Dross (g)	Leaching Time (h)	CO ₂ Bubbling	Mass Loss pct	Na Pct Extraction	K pct Extraction
1:5	80	1	√	24.75	80.11	81.45
1:5	80	1		24.64	80.06	81.69
1:5	80	3	√	25.82	82.72	82.99
1:5	80	3		25.3	81.83	83.18
1:10	40	1	√	28.4	86.86	84.77
1:10	40	1		28.25	84.35	88.35
1:10	40	3	√	30.72	91.16	93.36
1:10	40	3		29.8	92.35	91.87
1:20	20	1	√	31.8	89.77	91.49
1:20	20	1		31.65	87.04	88.64
1:20	20	3	√	32.28	92.06	95.19
1:20	20	3		32.2	95.64	95.87

*All percentages are mass pct.
√: With CO₂ bubbling.

These results indicate that during leaching with carbonated water, the reaction stops already by the first hour of leaching. This could be attributed to the presence of carbonic ions in the leaching water.

Figure 8 presents the mass of “ammonia” that escaped from the reaction bottle (Figure 4, marked (4)) during the leaching process. Although in the case of the pure deionized water the amount of ammonia escaping from the reaction bottle was as high as 0.48 mg, the amount that escaped into the absorption bottle during leaching with CO₂-saturated water was almost negligible (<0.006 mg). This finding indicates that during leaching with CO₂-saturated water, practically no ammonia escaped into the atmosphere. This

Fig. 7—Mass of ammonia in the reaction bottle after leaching process with and without CO₂ bubbling at different solid:liquid ratios: 1:5, 1:10, and 1:20.

Fig. 8—Mass of ammonia escaped in the absorption bottle during leaching process with and without CO₂ bubbling at different solid:liquid ratios: 1:5, 1:10, and 1:20.

result is attributed to the low pH of the carbonated water, which is a strong indication that leaching with carbonated water would be extremely environmentally friendly.

It is to be noted that the contents of the residue after leaching process shown in the Table III are recalculated from the XRF results based on oxides. Most of the residue consisted of oxides, including Al₂O₃, SiO₂, and MgO, accompanied by 10 mass pct of AlN, which is suitable for the production of high-performance AlON refractory.

C. Hydrolysis of Pure AlN in Carbonated Water

Reference leaching experiments were conducted with pure AlN using CO₂-saturated water containing 0.3 mol/L (0.6 mol/L) NaCl. This would enable a comparison of the leaching results with salt cake with pure AlN and subsequent understanding of the impact of chloride impurities in the salt cake on the hydrolysis with carbonated water. Figure 9 shows the variation of the value of pH as a function of hydrolysis time in the case of the hydrolysis of AlN in 0.3 mol/L NaCl solution with CO₂ saturation.

The pH value did not show much variation during the first 6 hours, which was attributed to a thin layer of aluminum hydroxyl layer formed on the surface of the AlN particles.^[13] Dissolution of the thin film is marked by the sudden increase of the pH value after 1000 minutes. After 2 days, the curve shows a strong tendency toward being horizontal, indicating that the hydrolysis rate was extremely low.

Table IV presents the ammonia concentration in the solution at three different time intervals, viz, 2, 4, and 6

Fig. 9—pH vs time for AlN powder at 291 K (18 °C) 0.3 mol/L solution with continuous CO₂ bubbling.

Table III. The Contents of the Residue after Leaching Process at a Solid:Liquid Ratio 1:20 and 3 h Leaching Time with CO₂ Bubbling at 291 K (18 °C)

Content	Al ₂ O ₃	AlN	NaCl	KCl	MgO	SiO ₂	Fe ₂ O ₃	Fluorides	CaO
wt pct	60	10	1.4 to 1.8	1.4	6	14	1.5 to 2	1	2.5 to 3

Table IV. Ammonia Concentration in the Solution after Immersion for 2, 4, and 6 Days

Number	Condition		$C_{\text{NH}_3}/\text{mg/L}$		
	NaCl Solution	CO ₂ Bubbling	2 Days	4 Days	6 Days
1	0.3 mol/L	√	5.6	7.02	12.6
2	0.6 mol/L	√	6.0	7.9	12.5
3 ^[13]	0.3 mol/L		57.2	129.7	594.0

√: With CO₂ bubbling.

Fig. 10—(a) The SEM of raw material AlN, (b) after 4 days immersion in 0.3 mol/L NaCl solution with CO₂ bubbling, and (c) after 4 days immersion in 0.3 mol/L NaCl solution without CO₂ bubbling.

days. It is observed that the amount of ammonia produced by hydrolysis with CO₂-saturated water is significantly less compared with noncarbonated water. Furthermore, it is observed that the concentration of chloride in the solution does not have any serious impact on the hydrolysis in the case of carbonated water. Previous experiments on leaching of salt cake with noncarbonated water containing NaCl in the solution^[13] could accelerate the hydrolysis of AlN, and a high content of NaCl would lead to more reaction. With CO₂-containing water, however, the level of hydrolysis was observed to be almost the same in both 0.3 mol/L and 0.6 mol/L NaCl solution.

In Figure 10, the SEM pictures of raw AlN as well as those after 4 days immersion with and without CO₂ bubbling in 0.3 mol/L NaCl solution are presented. A comparison of Figure 10(a) with Figure 10(b) reveals that after 4 days immersed in 0.3 mol/L NaCl solution with CO₂, the morphology did not show any significant

change compared with the raw material AlN. The residue still exhibits a regular shape. In contrast, Figure 10(c) shows great differences in morphology. The edge of the particles became irregular and fell apart, forming columnar agglomerates in depth, which would enhance the hydrolysis reaction.

V. DISCUSSION

The current results show that, during the leaching process of aluminum salt cake, the extraction of key elements (Cl, Na, and K) and dissolution reactions were complete in less than 3 h at 291 K (18 °C). The introduction of CO₂ would have a dual function in hindering the hydrolysis of AlN, as follows:

- (a) By absorbing the ammonia formed to form ammonium bicarbonate.

(b) Effectively stifling the hydrolysis reaction as fewer hydroxyl ions would be available for hydrolysis.

Although the presence of chlorides has an accelerating effect on the hydrolysis reaction in the absence of CO₂ dissolved in the aqueous phase, as shown in our previous experiments,^[13] this seems to be more than offset by the CO₂ saturation in the leachant solution.

To discuss a possible mechanism of the effect of CO₂ in hindering the hydrolysis, it is necessary to understand the behavior of various ions in water-salt-CO₂ solution. A hydrated aluminum ion with a six coordination of H₂O molecules, *viz.* (Al(H₂O)₆)³⁺, because of the polarization of the OH bonds, would behave as an acid in terms of Brønsted-Lowry acid-base theory.^[16,17] The weakening of the O-H bond of an attached water molecule would benefit to liberate a hydrogen ion easily.

Figure 2 shows the molar fractions of various hydroxyl species present in the system at different pH values. These species were expected to be formed by the hydrolysis of AlN is given by the reaction Eq. [9]; this aspect has been discussed in detail in Appendix A.

Appendix A shows that the concentration of hydrogen ions produced from the hydration of Al would be insufficient to form NH₄⁺ by AlN hydrolysis. The dissociation of the carbonic acid in aqueous solution would release some protons (to be more precise, hydronium ions, H₃O⁺) as shown in Eq. [10]. An attempt is made to simulate the increase in the NH₃ concentration in the leachant, and the same change of pH with CO₂ bubbling was observed.

$$\begin{aligned} K_{a12} &= \frac{[\text{H}_i^+][\text{HCO}_{3i}^-]}{[\text{CO}_{2(\text{aq})}][\text{H}_2\text{O}]} \\ &= \frac{[\text{H}_i^+ - \Delta\text{H}_N^+ + \Delta\text{H}^+][\text{HCO}_{3i}^- + \Delta\text{HCO}_{3\text{CO}_2}^-]}{[\text{H}_2\text{O}][\text{CO}_{2(\text{aq})}]} \end{aligned} \quad [11]$$

[H₂O] is the initial concentration of water that has constant value of 55.55 mol/L, [CO_{2(aq)}] is the concentration of 3.36 × 10⁻² mol/L when the pH value was stable after 30 minutes of bubbling.^[18] [H_i⁺] is the initial concentration once the pH value was stable after 30 minutes of bubbling of 1.58 × 10⁻⁴ mol/L. ΔH_N⁺ is the concentration of protons for NH₄⁺.

Thus, Eq. [11] would become

$$[\text{H}_i^+]^2 = [\text{H}_i^+ - \Delta\text{H}_N^+ + \Delta\text{H}^+][\text{H}_i^+ + \Delta\text{H}^+] \quad [12]$$

Substituting Eq. [12] into Eq. [11] would yield

$$[10^{(-\text{pH}_i)}]^2 = 10^{(-\text{pH}_c)} \times [10^{(-\text{pH}_i)} + \Delta\text{H}^+] \quad [13]$$

where pH_i is the initial pH value 3.8 and pH_c is the pH value after a certain amount of NH₃ produced during the hydrolysis.

The dissociation of CO₂ has been finished in seconds,^[19] which can keep pace with the hydrolysis reaction of AlN. Thus, it can be written as follows:

$$\Delta[\text{HCO}_2^+] + \Delta[\text{H}_{\text{Al}}^+] = \Delta[\text{H}_N^+] = \frac{4}{17} \Delta_m \text{NH}_3 \quad [14]$$

Δ[HCO₂⁺] and Δ[H_{Al}⁺] are the concentration of hydrogen ion generated by the dissociation of H₂CO₃. The ionization of Al, as mentioned in Appendix A, Δ[H_{Al}⁺] can be ignored. Combining Eqs. [14], [13], and [12] gives

$$\begin{aligned} \Delta[\text{HCO}_2^+] = \Delta[\text{H}_N^+] &= \frac{4}{17} \Delta_m \text{NH}_3 = [\text{H}_i^+] + \frac{[10^{(-\text{pH}_i)}]^2}{10^{(-\text{pH}_c)}} \\ &\quad - 10^{(-\text{pH}_i)} - 10^{(-\text{pH}_c)} \end{aligned} \quad [15]$$

In the deionized water or completely dissociated acid, if the effect of anions can be ignored, then Eq. [15] becomes

$$10^{(-\text{pH}_b)} = [10^{(-\text{pH}_i)}] - \frac{4}{17} \Delta_m \text{NH}_3 \quad [16]$$

where pH_b is the pH value after a certain amount of NH₃ produced during the hydrolysis under deionized water or completely dissociated acid.

In Figure 11(a), the concentrations of produced NH₃ after 2 days and 4 days agree with the calculated data for Δ_mNH₃ based on the hypothesis, which is that during the immersion, CO₂ would continuously dissociate into HCO₃⁻ and H⁺ to satisfy the hydrolysis of AlN. Thus, the calculated Δ_mNH₃ can be used as a reference to evaluate the pH fluctuation that is brought on by the same hydrolysis level in completely dissociated acid or deionized water without considering the influence of anions. A simulation based on Δ_mNH₃ in Eqs. [15] and [16] (the dotted line) was made to compare the experimental pH changing as shown in Figure 11(b). It can be observed that the pH is continuously increased in a completely dissociated acid; however, after CO₂ bubbling, the pH value has been prolonged because of the deprotonation based on the equilibrium between H⁺ and HCO₃⁻.

The solubility of the corrosion product is a critical factor when evaluating the extent of AlN corrosion. Svedberg *et al.*^[20] observed that the corrosion rate was related to the pH value of solution. In Figure 12(a), an approximately 2-nm-thin layer at the edge of the raw AlN particle can be considered as the preservative for the first 6 hours of the nonreaction stage as shown in Figure 9. After 4 days of immersion, an amorphous flaky shell is formed, as indicated by a diffused ring at the surface of the AlN particle in Figure 12(b), which is very similar with the morphology of boehmite (AlOOH).^[13] This observation would indicate that the corrosion product would remain on the surface of AlN when its solubility is at a minimum and acts as a barrier layer.^[20]

Fig. 11—The comparison between calculated data based on Eqs. [15] and [16] and experimental value.

Fig. 12—(a) HRTEM images of raw AlN powder. (b) HRTEM images of AlN particles after 4 days with stirring immersed in 0.3 mol/L NaCl solution with CO_2 bubbling.

Another possible reason can be taken into consideration. Krnel and Kosmac^[21] found that the hydrolysis of AlN has been hindered in incompletely dissociated diprotic acids (H_2SO_4 and H_2CO_3), including HSO_4^- and HCO_3^- , which are not completely dissociated. Because of the high electrostatic attraction, these species can be adsorbed on the powder surface by forming hydrogen bonds with Al-OH groups, thus hindering the dissolution of aluminum hydroxyl precipitates.

VI. CONCLUSIONS

The effect of CO_2 saturation in water on the leaching process of salt cake produced in secondary aluminum melting was investigated in the present work. The solid to liquid ratio as well as the leaching time were varied.

The results were also compared with that of CO_2 -less leaching. The results show that an extraction level of Na and K to 95.64 wt pct and 95.87 wt pct, respectively, could be reached under a solid-to-liquid ratio of 1:20 and a leaching time of 3 hours. The mass of escaping NH_3 decreased from 0.25 mg in pure water down to <0.006 mg in CO_2 -saturated water. This finding indicates that NH_3 evolution from hydrolysis is reduced considerably by CO_2 bubbling in the leaching water, which makes the hydrolysis process environmentally friendly.

A plausible explanation to the process phenomena is presented in the presence of incompletely dissociated H_2CO_3 acids. The hydrolysis product can act as a barrier layer, thus effectively hindering the hydrolysis. Continuous deprotonation based on the equilibrium between H^+ and HCO_3^- in carbonate solution can also prolong

duration time in a certain pH region where the solubility of corrosion product is kept at a very low level.

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APPENDIX A

After the initial step in hydrolysis in which $[\text{Al}(\text{OH}_2)_6]^{3+}$ is formed, the hydrolysis reaction may proceed in the following sequence^[22]:

$$\log k_i = A + B/T + C \ln T + DT^{[24]} \quad [\text{A5}]$$

$$\log \beta_i - \log k_i = I^{0.5}\alpha_0 + I^2\alpha_1 + I\alpha_2 + I^{0.5}\alpha_3/T + I^2\alpha_4/T^{[24]} \quad [\text{A6}]$$

$$\alpha([\text{Al}(\text{OH}_2)_6]^{3+}) = 1/(1 + \beta^1/C_{\text{H}^+} + \beta^2/C_{\text{H}^+}^2 + \beta_3/C_{\text{H}^+}^3 + \beta_4/C_{\text{H}^+}^4) \quad [\text{A7}]$$

where $\alpha([\text{Al}(\text{OH}_2)_6]^{3+})$ is the fraction, β_i is the stoichiometric constant, k_i is the equilibrium constant of Eqs. [A1] through [A4], and T is the temperature. The values of the parameters A , B , C , and D in Eq. [A5] and α_0 , α_1 , α_2 , α_3 , and α_4 in Eq. [A6] are the hydrolysis constants of Al(III) in water (Benezeth *et al.*^[25] and Palmer and Wesolowski^[26,27]) fit by Millero and Woosley.^[24]

When $T = 291$ K (18 °C), substituting the values of the parameters A , B , C , and D into Eq. [A5] would yield

$$\log k_1 = -5.19 \quad [\text{A8}]$$

For 0.3 mol/L NaCl solution

$$I = \frac{1}{2} [C_{(\text{Na}^+)} \times Z_{(\text{Na}^+)}^2 + C_{(\text{Cl}^-)} \times Z_{(\text{Cl}^-)}^2] \quad [\text{A9}]$$

where C is the molar concentration of the ion, Z is the valence number of ion, and I is ionic strength 0.3 mol/L. Substituting Eq. [A9] into Eq. [A6] would yield

$$\log \beta_1 = -5.6256 \quad [\text{A10}]$$

As can be observed in Figure 9, the pH value after 4 days of immersion in 0.3 mol/L NaCl solution was approximately 4.8.

Thus

$$C_{\text{H}^+} = 10^{(-\text{pH})} = 1.58 \times 10^{-5} \text{ mol/L} \quad [\text{A11}]$$

Substituting Eqs. [A11] and [A10] into Eq. [A7] yield

$$\alpha([\text{Al}(\text{OH}_2)_6]^{3+}) = 0.87 \quad \alpha([\text{Al}(\text{OH}_2)_5\text{OH}]^{2+}) = 0.13 \quad [\text{A12}]$$

After 4 days of immersion, the disaggregation of Al-N lattice in aqueous solution has resulted in the release of ammonia. The $C_{\text{NH}_3}/\text{mg/L}$ is 7.02 mg/L; thus, $C_{\text{N}} = 4.1 \times 10^{-4}$ mol/L. The ionization of the same molar amount of atom Al in water is accompanied with the liberation of proton as shown in Eqs. [A1] through [A4]. Meanwhile, one N atom needs four protons for NH_4^+ , $\Delta[\text{H}_\text{N}^+] = 16.4 \times 10^{-4}$ mol/L.

where H_{Al}^+ is the proton from the ionization of Al

$$C([\text{Al}(\text{OH}_2)_6]^{3+}) = 3.567 \times 10^{-4} \text{ mol/L} \quad [\text{A14}]$$

$$C([\text{Al}(\text{OH}_2)_5\text{OH}]^{2+}) = 0.533 \times 10^{-4} \text{ mol/L} < \Delta[\text{H}_\text{N}^+] = 16.4 \times 10^{-4} \text{ mol/L} \quad [\text{A15}]$$

REFERENCES

1. S. Fukumoto, T. Hookabe, T. Kato, and H. Tsubakino: *J. Jpn. Inst. Light Met.*, 1996, vol. 46 (11), pp. 615–16.
2. S. Fukumoto, T. Hookabe, and H. Tsubakino: *J. Jpn. Inst. Light Met.*, 1998, vol. 48 (4), pp. 199–203.
3. C. Jirang and Z. Lifeng: *J. Hazard Mater.*, 2008, vol. 158, pp. 228–56.
4. P.N. Papafingos and R.T. Lance: U.S. Patent 4,073,644, 1978.
5. A. Filleti: *V Seminário de Tecnologia da Indústria do Alumínio*, São Paulo, SP, Brazil, 1995, Associação Brasileira do Alumínio (ABAL), pp. 339–533.
6. E.G. Araújo: Desenvolvimento de agente expansora base de escórias de alumínio para a produção de concretos celulares autoclavados ou moldados “in loco”. 2002, Relatório do Projeto Pipe/Fapesp n.01/03059-9.
7. D. Yerushalmi: U.S. Patent 5,102,453, 1992.
8. J.T. Yeh, H.W. Pennline, K.P. Resnik, and K. Rygle: *Third Annual Conference on Carbon Capture & Sequestration*, 2004, May 3–6, Alexandria, VA.
9. <http://www.phasediagram.dk/ternary/>.
10. J. Duan and J. Gregory: *Adv. Colloid Interf. Sci.*, 2003, vols. 100–102, pp. 475–502.

11. F.J. Li, T. Wakahara, J. Tatami, K. Komeya, and T. Meguro: *J. Eur. Ceram. Soc.*, 2007, vol. 27, pp. 2535–40.
12. J.T. Houghton, L.G.M. Filho, B.A. Callender, N. Harris, A. Kattenberg, and K. Maskell: *The Science of Climate Change*, Cambridge University Press, Cambridge, U.K., 1995, p. 572.
13. P. Li, L. Teng, G. Min, M. Zhang, and S. Seetharaman: Royal Institute of Technology, Sweden, unpublished research, 2011.
14. E.W. Meeker and E.C. Wagner: *Ind. Eng. Chem.*, 1933, vol. 5, p. 396.
15. E.C. Wagner: *Ind. Eng. Chem.*, 1940, vol. 12, p. 711.
16. R.H. Petrucci, W.S. Harwood, and F.G. Herring: *General Chemistry*, 8th ed., Prentice-Hall, Upper Saddle River, NJ, 2002, p. 666.
17. G.L. Miessler and D.A. Tarr: *Inorganic Chemistry*, 2nd ed., Prentice-Hall, Upper Saddle River, NJ, 1998, p. 154.
18. http://en.wikipedia.org/wiki/Carbonic_acid.
19. X. Wang, W. Conway, D. Fernandes, G. Lawrance, R. Bums, G. Puxty, and M. Maeder: *J. Phys. Chem. A.*, 2011, vol. 115, pp. 6405–12.
20. L.M. Svedberg, K.C. Arndt, and M.J. Cima: *J. Am. Ceram. Soc.*, 2000, vol. 83 (1), pp. 41–46.
21. K. Krnel and T. Kosmac: *J. Am. Ceram. Soc.*, 2000, vol. 83 (6), pp. 1375–78.
22. C.F. Baes and R.E. Mesmer: *The Hydrolysis of Cations*, Wiley, New York, NY, 1976.
23. T. Ikeda, M. Hirata, and T. Kimura: *J. Chem. Phys.*, 2006, vol. 124, pp. 074503-1–074503–7.
24. F.J. Millero and R.J. Woosley: *Environ. Sci. Technol.*, 2009, vol. 43 (6), pp. 1818–23.
25. P. Benezeth, D.A. Palmer, and D.J. Wesolowski: *Geochim. Cosmochim. Acta*, 2001, vol. 65, pp. 2097–2111.
26. D.A. Palmer and D.J. Wesolowski: *Geochim. Cosmochim. Acta*, 1992, vol. 56, pp. 1092–1111.
27. D.A. Palmer and D.J. Wesolowski: *Geochim. Cosmochim. Acta*, 1993, vol. 57, pp. 2929–38.