Leaching process investigation of secondary aluminum dross: the effect of CO_2 on leaching process of salt cake and AlN hydrolysis behavior

Peng Li[1), 2)]*, Min Guo*[1)]*, Mei Zhang*[1)]*, Lidong Teng*[2)]*and Seshadri Seetharaman*[2)]

1) *State key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing,Beijing 100083, PR China*
2) *Department of Materials Science and Engineering, Royal Institute of Technology,*

SE-10044 Stockholm, Sweden

Abstract: For the recycling/disposal of dross/salt cake from secondary aluminum melting, aqueous leaching process offers an interesting economic process route. One of the major obstacles is the reaction between AlN present in the dross and the aqueous phase which can lead to the emission of NH_3 gas, as this would pose a serious environmental problem. In the present work, the AlN hydrolysis behavior in NaCl solution was investigated by immersing pure AlN powder in deionized water, 0.3mol/l NaCl aq, 0.6mol/l NaCl aq and NaCl solution with CO_2 bubbling at 291K, respectively. Leaching process of salt cake using CO_2-saturated water is attempted with a view to absorb the ammonia formed *in situ*. The results showed that AlN powder underwent enhanced hydrolysis in NaCl aq than that in deionized water, while, the introduction of CO_2 was found to hinder the hydrolysis even in the presence of NaCl. Aqueous leaching of salt cake was attempted by CO_2-saturated water with a view to absorb the ammonia gas formed in situ. With continuously CO_2 bubbling, mass of producing and escaping NH_3 decreased irrespective of different conditions, indicating effective hindrance and absorption by carbonized water. The plausible mechanisms for the observed phenomenon are discussed. The retainment of AlN and leaching out of salt open up a promising route towards further processing of dross, viz. development of a process to synthesize AlON from the leaching residues.

Keywords: CO_2, leaching, hydrolysis, absorption, AlN.

1. Introduction

During the remelting of aluminium scrap, the rest product formed is the aluminium dross /salt cake. This contains the salt mixture added during melting to prevent the oxidation of aluminium along with products of reaction between liquid aluminium and air, *viz.*Al_2O_3 and AlN. Very small amounts of Al_4C_3 and AlP are also found in the salt cake. The composition of salt cake from secondary aluminum remelting varies depending upon the production practice. In addition to the compounds mentioned above, the dross may contain even lesser amounts of SiO_2 and MgO, apart from entrapped elemental aluminium. [1, 2] One of the important process steps in the treatment of this waste material is the recovery of metallic aluminium by leaching the salts out and separating Al metal. Wastes generated from treatment of the salt cake (non-metallic products including some chlorides) are usually land-filled or disposed without treatment, causing a load on the environment [3].

The first submitted method for salt cake processing was patented in 70s by Papafingos and Lance [4]. This patent features the equipment for cooling and disaggregating aluminum dross with water in order to dissolve the salts.

However, during the leaching process, AlN, Al_4C_3,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)–(3):

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 \downarrow + 3CH_4 \uparrow \tag{1}$$

$$AlN + 3H_2O \rightarrow Al(OH)_3 \downarrow + NH_3 \uparrow \quad \text{[5]} \tag{2}$$

$$AlP + 3H_2O \rightarrow Al(OH)_3 \downarrow + PH_3 \uparrow \tag{3}$$

The amount of ammonia escaping from the processs is significant. NH_3 is also readily soluble in water, increasing simultaneously its pH value up to 9 or higher causing the hydrolysis of the entrapped metallic aluminium. The use of carbonic acid would be of interest as it is a weak acid and have a moderate effect on pH. Further advantage is to utilize the environmentally harmful CO_2 [6]; and the fixation of the same as ammonium carbonate as shown in eqns. (4-6), which can be utilized as a fertilizer.

$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \tag{4}$$

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \tag{5}$$

$$NH_4^+ + HCO_3^- \rightleftarrows NH_4HCO_3 \tag{6}$$

The present work deals with the leaching of carbonated water with a view to optimize the conditions for minimizing the hydrolysis of AlN. Corresponding reference experiments were conducted with pure synthetic AlN and the results were used to compare those obtained with salt cake leaching. The effect of salinated water and CO_2-saturated water on the hydrolysis of AlN was investigated systemically.

2. Experimental

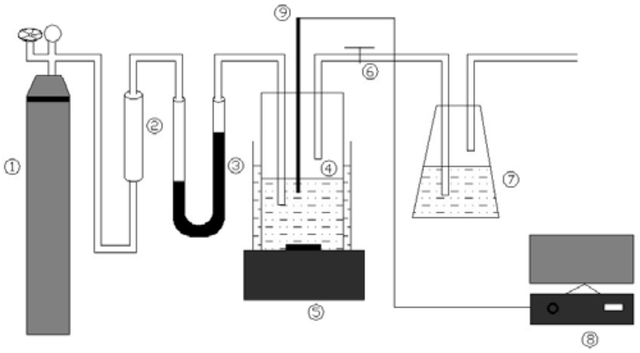

Fig.1 Experimental apparatus

1-carbon dioxide, 2- gas buffer, 3-manometer, 4-reaction bottle, 5-thermostatic magnetic stirrer, 6-gas valve, 7-absorption bottle, 8-computer, 9-pH measurement

2.1 The hydrolysis tests of AlN

Experimental apparatus used in the present investigation is presented in Fig. 1. Commercial AlN powder used in the present work was supplied by XiLong Chemical Company, China and the maximum impurity content was less than 2wt%. The particle size of the powder was less than 1 micron. The hydrolysis tests were carried out in dilute suspensions containing 0.25 mass % of AlN in 0.3mol/l and 0.6mol/l NaCl solutions with and without CO_2 bubbling, for various time intervals, *viz.* 48, 96, 144h. Taking into consideration the possibility that a small amount of ammonia gas may escape from the reaction bottle, a scrubber bottle with 2 mol/l boric acid solution was provided downstream (Fig. 1(7)). In the tests, 400 ml of aqueous solution was kept under constant stirring (300 rotations per min) at a temperature of 291K using a water bath provided with a thermostat (Fig. 1(9)). The pH was monitored as a function of time using a combined glass electrode/ Pt 512 thermometer pH meter (SanXing Company, Shanghai, China).

2.2 The leaching experiments with salt cake from Al remelting

Salt cake leaching experiments similar to those with were carried out with pure AlN. The aluminum salt cake used in the present work was supplied by Stena Aluminum AB, Sweden. The samples consisted of rounded lumps up to about 10 mm in size and some smaller metallic fragments. The sample had a slight smell of ammonia. The salt cake sample was crushed using a pulverizer and sieved through a 100 um aperture screen. The leaching tests were conducted by treatment with both pure water as well as the CO_2-saturated water for 1 h, 3h at different solid to liquid mass ratios, *viz.* 1:5, 1:10, 1:20, respectively. The experimental procedure adopted was the same as in the case of hydrolysis experiments.

In the case of leaching with CO_2-saturated water, the CO_2 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 CO_2 pressure were maintained at 40ml/min, 1.05 MPa during the entire leaching process.

2.3 Analytical methods

Deposits were taken out from the suspensions, filtered, and washed with 2-propanol to remove the adherent water. The residues were dried at 60℃ for 8 h and then stored in plastic, airtight containers, before conducting the characterization tests.

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 residue after leaching process and hydrolysis products of AlN were determined by RINT 2500HF+-based 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 solution (mass ration = 1:1) at 473 K for 4 h using a polyethylene reactor. This duration of the acid treatment was considered essential in order 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 Water quality--Determination of ammonium--Distillation and Titration method (WDDT) [7-8]. 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 ICP-OES technique. As shown in eqn. (2), during the leaching and hydrolysis of AlN in the salt cake, NH_4^+ ion 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 in order to monitor the AlN hydrolysis. The analysis method adopted was the same as mentioned above, WDDT.

The nitride change, ΔN, which stands for the degree of nitride hydrolyzed from AlN by the reaction with the aqueous phase, was expressed as:

$$\Delta N = \frac{C_{Nt}}{C_{No}} \times 100\% \qquad (7)$$

Where C_{Nt} is the total content of ammonia in the reaction bottle (Fig.1 (4)) and absorption bottle (Fig.1 (7)) at time t, and C_{No} is the theoretical content of ammonia after the hydrolysis reaction has been completed.

In the case of the hydrolysis of AlN, the morphology of the micro powders was studied by high resolution transmission electron microscope (HRTEM, Philips, Tecnai F20).

3. Results and Discussions

3.1 Hydrolysis of pure AlN

3.1.1 pH and ΔN variation of hydrolysis

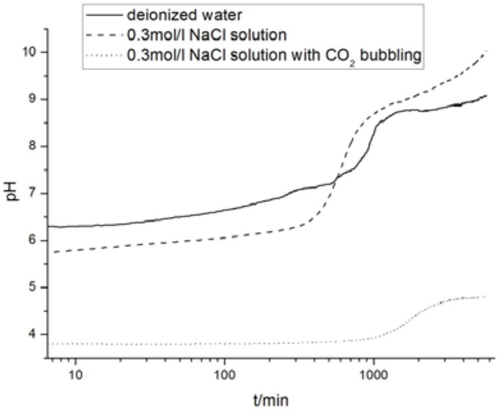

Fig.2 PH vs. time for a 0.25 wt% AlN powder at 291K in deionized water and 0.3mol/l NaCl solution and with CO_2 bubbling.

Fig. 2 shows the variation of the value of pH as a function of hydrolysis time of pure AlN. The pH value did not show much significant variation during the first 6 hours. This initial period was followed by a sudden increase of the pH value. After one day, the slope of curve showing the pH change with time in deionized water became less at about pH=9. This might indicate that the hydrolysis was retarded due to the formation of a product layer around AlN particle. Introduction of NaCl into water resulted in a decrease in time for the initial slow reaction stage. In this case, the hydrolysis reaction was still strong, even after one day immersion, in contrast to the reaction in deionized water. On the other hand, after the introduction of CO_2, the pH curve had a slight rise around pH =4.0, and became nearly horizontal.

Table 1 N change in the solution after immersion for 2, 4 and 6 days (√: with CO_2 bubbling)

No.	Condition		△N		
	NaCl solution	CO_2 bubbling	2days	4days	6 days

1			2.79	3.45	54.47
2	0.3mol/l		6.94	15.17	69.98
3	0.6 mol/l		10.3	46.62	92
4	0.3 mol/l	√	0.64	0.87	1.41
5	0.6 mol/l	√	0.64	0.86	1.40

The total content of ammonia in the reaction bottle (4) and absorption bottle (7) was measured by WDDT method, which was represented as the degree of AlN hydrolysis. The nitride change △N was calculated based on eqn. (7). The results are shown in Table 1, it is seen that the hydrolysis in NaCl solution could accelerate the hydrolysis of AlN and higher content of NaCl would benefit the reaction. The hydrolysis with CO_2-saturated water is significantly less in comparison with non-carbonated water.

3.1.2 Hydrolysis product of pure AlN

The extent of the hydrolysis reaction during the first 1-10 hours is very little as shown in Fig. 2. Some earlier researchers observed a similar slow-reaction stage prior to the fast hydrolysis reaction [9]. This was attributed to a thin layer of aluminum hydroxide compound, formed on the surface of the AlN particles while contact with moisture, acting as a barrier layer, which have to be dissolved or penetrated by water molecules. [10-11] At different pH region, as shown in Fig.2, the slow-reaction stage of the hydrolysis case in CO_2-saturated solution is much longer than the case without CO_2 bubbling, which strongly indicates that the solubility of aluminum hydroxide compound is depend on the pH of the solution.

The corrosion rate of AlN began to increase after slow-reaction stage. The exposed aluminum atoms at the surface react readily with water molecules, forming as H-Al-OH structure [12-13]. In Fig. 3(a), even after 6 days immersion in CO_2-saturated solution, very thin amorphous flaky shell is at the surface of AlN particle, which is very similar with the morphology of boehmite (AlOOH) [14]. It indicates that the corrosion product would remain on the surface of AlN when its solubility is at a minimum and acts as a barrier layer. While, after the same time immersion in deionized water, the Fig. 3(b) shows the big typical wedge-shaped particles, which correspond to bayerite as shown in Fig. 3(d) accompanied with poor crystallized boehmite. This becomes predominant rod-like shape in Fig. 3(c).It is suggested that the presence of NaCl can enhance the growth of side faces and reinforce the cohesion among the layers, indicating that unit layers attach themselves at a greater rate to the edges of crystallites than to the top and bottom surfaces.

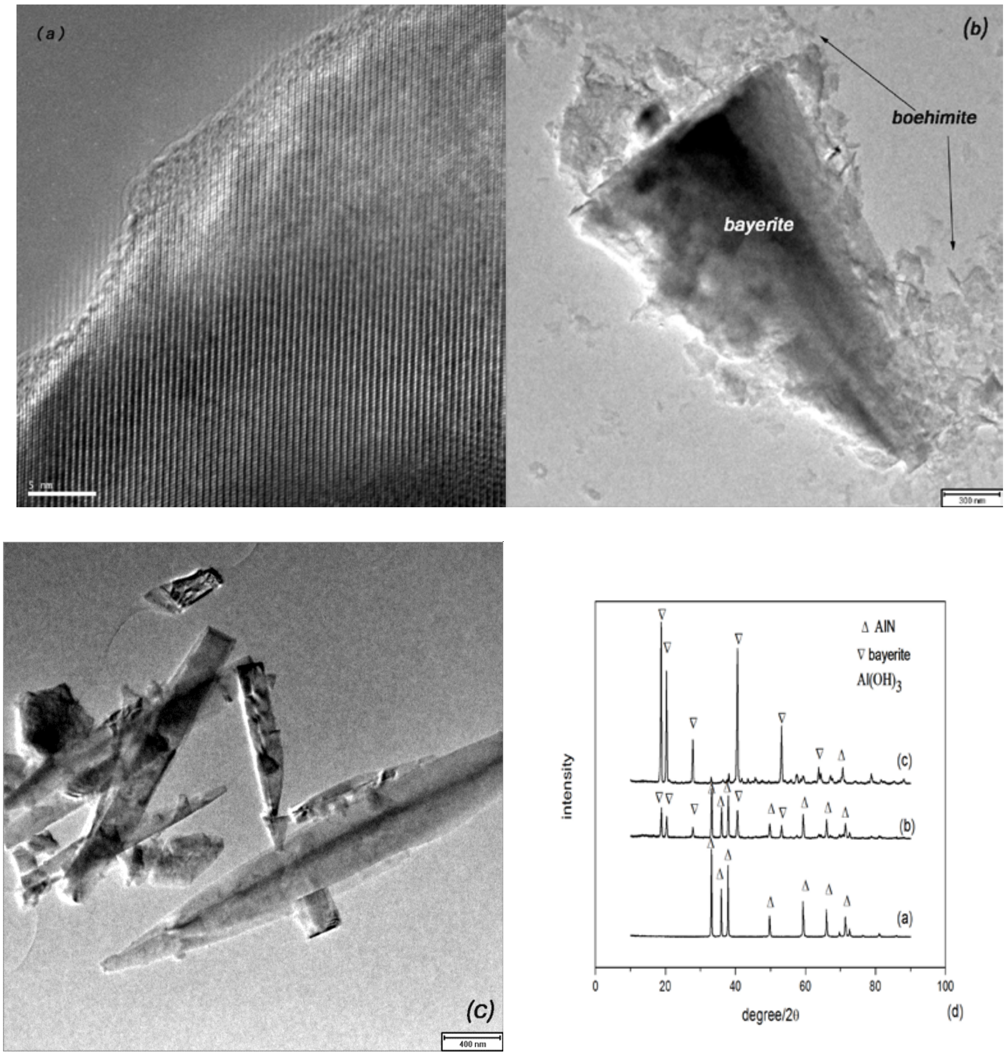

Fig.3 TEM images of products with stirring after 6 days immersion in (a) 0.6mol/l NaCl solution with continuously CO_2 bubbling (b) deionized water (c) 0.6 mol/l NaCl solution (d) and corresponding XRD patterns

After 6 days immersion in deionized water some amount of AlN has transformed into bayerite, which has been transformed completely in 0.6 mol/l NaCl solution, while the peaks of the product in 0.6 mol/l NaCl solution with CO_2 bubbling did not show any other phases but AlN. The major difference of these three cases is that for those without CO_2 bubbling, the solutions were alkaline has a pH range of 9-11, but with CO_2 bubbling, the equilibrium between H^+ and HCO_3^- in carbonate solution can keep the pH range at 4-6. It suggests that the corrosion rate of AlN is at a minimum when the corrosion product is not very soluble (pH 4-6) thus hinders the hydrolysis reaction. At pH 9.0-11, where the solubility of the corrosion product increases, the corrosion of AlN increases. Svedberg et al [15] also observed that the corrosion rate was related to the pH value of solution.

3.2 Leaching process of salt cake

During the recycling of salt cake, leaching process is considered as an economical way, however, it can produce waste gas and cause environmental problem. Since the introduction of CO_2 can greatly hinder the hydrolysis of AlN even in the salts solution which has been proved above, it is consequential to bring the CO_2 into the leaching process of salt cake.

The analysis of the raw salt cake was conducted for a number of samples and the average analysis is reported in Table 2. The variation between the various analysis values was found to be less than ± 2 % indicating that the sampling was reliable.

Table 2 the chemical analysis of raw aluminum dross

Composition	Al_2O_3	AlN	MgO	Fe_2O_3	KCl	NaCl	SiO_2	CaO
Mass %	44.71	7	4.21	2.67	10.69	22.28	6.64	1.8

As shown in Table1, the salt cake contained nearly 32 mass % of alkali chlorides, 7 mass % AlN and small amounts of iron. The amounts of Al_4C_3 and Al_3P were found to be below the detection limits.

3.2.1 Ammonia dissolution during leaching process

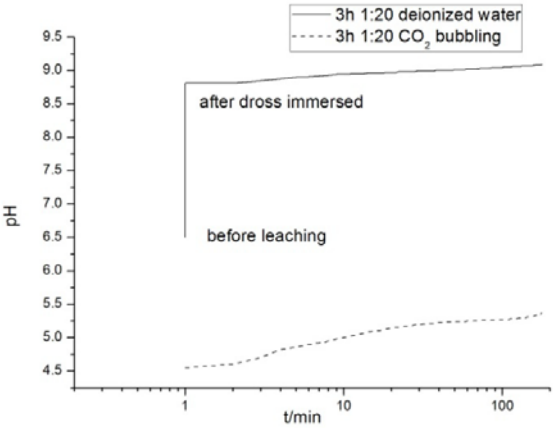

Fig.4 pH vs. time for aluminum salt cake in deionized water and CO_2-saturated water at 291K

It can been observed in Fig.4 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 may suggest that the dissolution of a moisture layer on the surface of the salt cake may contain some amount of ammonia formed 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 according to mainly eqn. (2). The corresponding curve for the experiment with CO_2-saturated water, showed only a marginal increase of pH from the initial value of 4.5 to 5.5, still in the acid range.

During the leaching experiments, the ammonia gas generated would first dissolve in the leachant in the reaction bottle (Fig. 1, marked (4)) and a small amount can escape to be absorbed in the absorption bottle (Fig. 1, 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. Table 4 presents the extent of hydrolysis using M_{NH3}/Mo (M_{NH3} is the mass of ammonia produced during the leaching, Mo is the initial mass of aluminum dross) when leaching was carried out both with deionized water as well as CO_2-saturated water at different solid-liquid ratios and different leaching times.

Table 4 The extent of hydrolysis in the reaction bottle after leaching process with and without CO_2 bubbling at different solid-liquid ratio: 1:5, 1:10, 1:20. (√: with CO_2 bubbling).

Leaching time /h	CO_2 bubbling	M_{NH3}/Mo ($\times 10^{-4}$)		
		1:5	1:10	1:20
1	√	3.8	3.84	3.64
1		6.31	5.34	4.5
3	√	3.81	3.88	3.68
3		8.74	6.67	5.46

It is seen that the M_{NH3}/Mo present in the solution water was less in CO_2-saturated solution compared to the corresponding results with deionized water, it can also be noticed that leaching time had virtually no impact, and reaction almost stops already at the first hour of leaching. Further the value of M_{NH3}/Mo present in the solution without CO_2 bubbling is increasing with dross amount. These results indicate that, the increasing amount of dross in the solution will bring more aggressive environment, *viz*. higher concentration of salts, thus enhancing the hydrolysis.

Table 5 Escaped ammonia in the absorption bottle during leaching process with and without CO_2 bubbling at different solid liquid ratio: 1:5, 1:10, 1:20 (√: with CO_2 bubbling).

Leaching time /h	CO_2 bubbling	M_{NH3}/Mo ($\times 10^{-6}$)		
		1:5	1:10	1:20
1	√	<0.006	<0.006	<0.006
1		12.75	7.19	3.91
3	√	<0.006	<0.006	<0.006
3		17.85	10.2	5.96

The data in Table 5 shows the same trend as Table 4 in the case of the pure de-ionized water, with the more amount of dross, more amount of ammonia will escape. Meanwhile, the amount escaped into the absorption bottle during leaching with CO_2-saturated water was almost negligible. This indicates that, during leaching with CO_2-saturated water, there is practically no ammonia escaping into the atmosphere. This is a strong indication that leaching with carbonated water would be extremely environment-friendly.

3.2.1 Residue phase analysis

Table 6 the contents of the residue after leaching process at solid liquid ratio 1:20, leaching time 3h with CO_2 bubbling at 291K.

content	Al_2O_3	AlN	NaCl	KCl	MgO	SiO_2	Fe_2O_3	Fluorides	CaO
wt%	60	10	1.4-1.8	1.4	6	14	1.5-2	1	2.5-3

It is to be noted that the contents of the residue after leaching process shown in the Table 6 are recalculated from the XRF results based on oxides. Most of the residue consisted of oxides, including Al_2O_3, SiO_2 and MgO, accompanied by 10 mass% of AlN, which is suitable for the production of high-performance AlON refractory. During the leaching, part of the ferromagnetic solid residue was found to get adsorb onto the magnetic stirrer. Fig.5 shows the XRD results of the ferromagnetic residue, which contains the peaks of AlN, Fe_3O_4 and Al_2O_3. The mosaic distribution of iron oxides poses the problem of the removal of iron oxides from the dross.

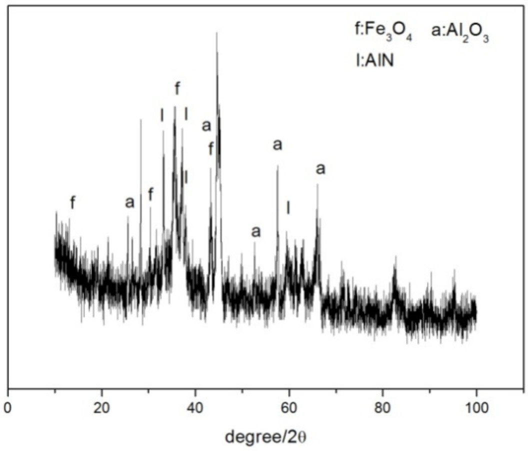

Fig.5 The XRD patterns of dross adsorbed on the magnetic stirrer during the leaching process.

4 Conclusions

The effect of CO_2 saturation in water on the hydrolysis of AlN and leaching process of salt cake produced in secondary aluminium melting was investigated in the present work. The hydrolysis of AlN powder was enhanced in NaCl (aq) than in de-ionized water as indicated. The solubility of the corrosion product is a critical factor when evaluating the extent of AlN corrosion, which increased with the increasing content of NaCl solution, decreased in the CO_2-saturated solution. The equilibrium between H^+ and HCO_3^- in carbonate solution can buffer the trend of rising pH the due to the formed ammonia, thus prolong the duration time in pH region (4-6) where the solubility of corrosion product keeps at minimum level.

The results of leaching with saturated CO_2 were compared with those obtained with CO_2-less leaching. The mass of producing and escaping NH_3 decreased in CO_2-saturated water. This 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.

Acknowledgement

The authors would also like to thank the National Science Foundation of China for the financial support (No. 51072022, 5107400，50874013), Program for Talents youth in USTB (FRF-TP-09-005B). The supply of aluminum dross by Stena Metall AB is gratefully acknowledged.

References

[1] S. Fukumoto, T. Hookabe, T. Kato, and H. Tsubakino, “Chemical Behavior of Aluminum Dross in Water,” J. Jpn. Inst. Light Met., 1996, 46 [11], pp.615–16

[2] S. Fukumoto, T. Hookabe, and H. Tsubakino, “Reaction between Aluminum and Water,” J. Jpn. Inst. Light Met.,

1998,48 [4], pp.199–203.

[3] Jirang Cui, Lifeng Zhang, Metallurgical recovery of metals from electronic waste: A review, Journal of Hazardous Materials., 2008,158, pp.228–256.

[4] Papafingos, P.N., Lance, R.T., 1978. Salt cake processing method and apparatus. United States Patent: 4,073,644.

[5] Filleti, A., 1995. Aspectos ambientais na fundição de aluḿınio. In: V Seminááno de Tecnologia da Indústria do Aluḿınio, São Paulo, SP, Brazil, 29–31 May 1995, ABAL (Associação Brasileira do Aluḿḿınio), pp. 339–533. In latin.

[6] The Science of Climate Change, ed. J. T. Houghton, L. G. Meira Filho, B. A. Callender, N. Harris, A. Kattenberg and K. Maskell, Cambridge University Press, Cambridge, UK, 1995, pp. 572.

[7] E.W. Meeker and E.C. Wagner, Ind. Eng. Chem., Anal. Ed., 1933,5, pp396.

[8] E.C. Wagner, Ind. Eng. Chem., Anal.Ed., 1940,12, pp 711.

[9] Krnel, K., Drazic, G., Kosmac, T., Degradation of AlN powder in aqueous environments, J. Mater. Res., 2004,19,pp1157–1163.

[10] Svedberg, L. M., Arndt, K. C. and Cima, M. J., Corrosion of Aluminum Nitride (AlN) in Aqueous Cleaning Solutions, J. Am. Ceram. Soc., 2000,83, pp41-46.

[11] Fukumoto, S., Hookabe T. and Tsubakino, H., Hydrolysis Behavior of Aluminum Nitride in Various Solutions, J. Mater. Sci., 2000,35, pp 2743-2748.

[12] Kurtz, H. A. and Jordan, K. D., Comment on the Electronic Structure of HAlOH and AlOH2, J. Am. Chem. Soc., 1980,102, pp1177-1178.

[13] Hauge, R. H., Kauffman, J. W. and Margrave, J. L., Infrared matrix-isolation studies of the interactions and reactions of Group 3A metal atoms with water, J. Am. Chem. Soc., 1980,102, pp 6005

[14] Kocjan, A., Dakskobler, A., Krnel, K., Kosmac, T., The course of the hydrolysis and the reaction kinetics of AlN powder in diluted aqueous suspensions, J. Eur. Ceram. Soc., 2011,31 pp 815-823.

[15] Lynne M. Svedberg, Kenneth C. Arndt, and Michael J. Cima, “Corrosion of Aluminum Nitride (AlN) in Aqueous Cleaning Solutions.” J. Am. Ceram. Soc., 2000, 83[1], pp 41-46