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알루미늄 폐드로스를 再活用한 Alum과 Poly Aluminum Chloride 製造 研究†

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Preparation of Alum and Poly Aluminum Chloride Using Waste Aluminum Dross†

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요 약

알루미늄 지금 및 스크랩 용해시 발생되는 알루미늄 폐드로스를 사용하여 황산알루미늄(Alum)과 폴리염화알루미늄(Poly Aluminium Chloride: PAC)을 제조하였다. 알루미늄 폐드로스를 황산과 반응시켜 폐드로스 중에 잔류하는 금속알루미늄을 용액 중으로 침출시켜 황산알루미늄 용액으로 제조하였으며, 알루미늄 폐드로스를 염산과 반응시켜 PAC 용액으로 제조하여 수처리응집제로 재활용하고자 하였다. 이와 같이 알루미늄 폐드로스를 재활용함으로써 수산화알루미늄을 원료로 사용하여 황산알루미늄과 PAC를 제조하는 종래의 방법에 비해 제품의 원료비를 줄일 수 있고, 매립 등으로 폐기시켜야 할 폐드로스의 양을 줄이는 효과가 있었다.

주제어 : 알루미늄 폐드로스, 재활용, 황산알루미늄, 폴리염화알루미늄, 수처리응집제

Abstract

Waste aluminum dross was processed to prepare alum with sulfuric acid, and poly aluminum chloride(PAC) with hydrochloric acid. Metallic aluminum remained in the waste dross was dissolved into the sulfuric acid solution, and the solution could be used as alum for water treatment chemicals after adjusting the required alumina concentration and pH of the solution. Also, it was dissolved into the hydrochloric acid solution and processed to make PAC solution. Compared with the conventional method for preparation of alum and PAC using aluminum hydroxide, material cost could be saved in this method. Also, there is an additional merit in view of recycling of the waste aluminum dross by reducing the amount of waste disposed to landfill.

Key words : waste aluminum dross, recycling, alum, PAC, water treatment chemicals

1. Introduction

Aluminum dross is formed on molten aluminum due to its great affinity for oxygen. The types and the amount of dross would be widely varied with fluxing techniques in the melting and production practices of the aluminum industries. Skimming of dross from the molten bath invariably results in loss of the underlying metal, and dross is a major waste in the production of aluminum.

It is assumed that about sixty thousand tons of dross have been generated annually in Korean aluminum industries. Aluminum dross is processed to recover the remained aluminum metal by means of physical separation and remelting. After extracting the remained aluminum from the dross the waste residue was generates. It is called the waste aluminum dross. Although waste aluminum dross could be reused in some case such as castable refractory materials or ceramic raw

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materials[1,2], most of them have been generally landfilled. However, in recent years, land-filling cost in waste management increases, and it becomes more difficult to dispose of dross in landfills due to the reinforcement of local environmental regulations. Therefore, recycling of the waste dross has become an important issue in the secondary aluminum industries.

Major components of the waste aluminum dross are aluminum oxide and remained metallic aluminum, and the content of the metallic aluminum in the waste dross is usually in the range of 10-35%.

In this study, the waste aluminum dross was processed to recycle it as an aluminum sulfate(Alum: $Al_2(SO_4)_3$) by reaction of the remained metallic aluminum with sulfuric acid and a poly aluminum chloride(PAC) by reaction with hydrochloric acid which could be used as water treatment chemicals. Conventionally industrial alum is produced by use of aluminum hydroxide($Al(OH)_3$) with sulfuric acid, and PAC is with hydrochloric acid. Here, waste aluminum dross was used instead of aluminum hydroxide in producing those chemicals to save the material cost and to reduce the amount of the waste residue to discard.

2. Experiments

2.1. Raw Material

The waste dross used as raw material was a kind of black dross generated in the domestic secondary aluminum smelter. The waste dross was previously processed in the smelter to recover the remaining aluminum, and was about to be discarded by landfilling. The chemical composition of the sample dross was shown in Table 1. Magnesium, calcium, iron, zinc, sodium and potassium were contained as impurities. Also, metallic aluminum in the sample dross was about 30% by weight. The used sulfuric acid and hydrochloric acid were commercial grade chemicals, and were diluted with water to adjust the concentrations.

Table 1. Chemical composition of the waste dross sample

Component	Mg	Mn	Fe	Zn	Ca	K	Na	Al
Wt %	3.85	0.15	1.54	0.82	1.86	0.47	0.80	res.

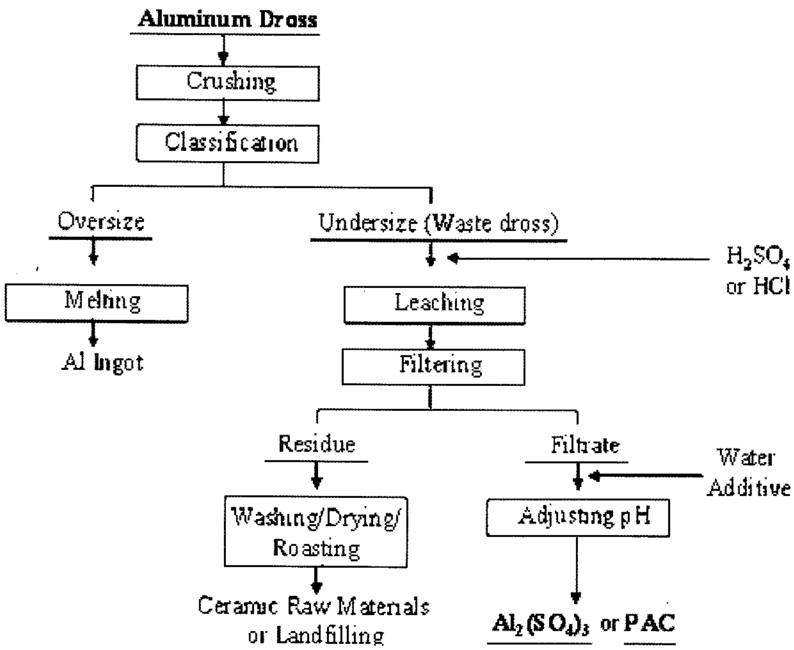

Fig. 1. Schematic process flowsheet for Alum or PAC from aluminum dross.

2.2. Procedures for aluminum sulfate

Fig. 1 schematically shows the process flow sheet carried out in this study. The main idea of this process is that it could be more effective on recovery of the remaining aluminum from the dross to separate small size dross from large size ones before melting. It is better in consideration of melting efficiency because there is much larger amount of metallic aluminum in the large size dross than the small size. If dross is crushed, size of oxide phase in the dross becomes smaller and metallic phase becomes larger. The critical size in the classification was 1mm in this study. The dross over this size could be directly remelted to recover aluminum in a secondary aluminum smelter, and the smaller one(the undersize at the classification step in Fig. 1) was treated as a waste dross and processed.

The metallic aluminum remained in the waste dross was leached with 98 % sulfuric acid(specific gravity 1.84) in the reaction tank, and reaction occurred in the solution as the following equation (1).

$$2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3\ H_2\uparrow \qquad (1)$$

The aluminum sulfate(alum) solution was obtained through filtration. The filtered solution was diluted with water to adjust the required alumina content and pH of the solution. The residue in the leaching step was processed through washing, drying, and roasting to reuse it as raw materials for alumina castable refractories. Also, the hydrogen gas generated in this reaction could be collected.

2.3. Procedures for aluminum chloride

The process to make aluminum chloride was also shown in Fig. 1. In the case of aluminum chloride, 30 % hydrochloric acid solution(specific gravity 1.15) was used instead of sulfuric acid in the leaching of the waste dross, and other procedures were similar to those of aluminum sulfate. The remained metallic aluminum in the waste dross reacted with hydrochloric acid as the following equation (2). This aluminum chloride is a kind of aluminum complex whose molecular structure is similar to polymer. So, it is called poly aluminum chloride(PAC).

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2\uparrow \qquad (2)$$

The PAC solution was obtained through filtration. The filtered solution was diluted with water and small addition of sodium aluminate or sodium silicate solution to adjust pH and alumina content and basicity which were required by Korean Standard(KS) for a water treatment product. Here, the basicity is defined as the ratio of mole number of OH ion to that of aluminum ion as the equation (3), and indicates the degree of polymerization of the PAC.

$$\text{Basicity}=\{(\text{mole of OH})/(\text{mole of Al}\times 3)\}\times 100 \qquad (3)$$

3. Results and Discussion

3.1. Preparation of alum

The waste aluminum dross and the sulfuric acid were charged into a reaction tank, and reacted at 80 °C for 3 hours with agitation. Through the experiments 18 kg of waste aluminum dross were charged at one batch. In this case the remained aluminum was about 5.4 kg because the content of metallic aluminum in the waste dross sample was about 30%.

Stoichiometric equivalence of the 98% sulfuric acid was calculated according to the equation (1), and expressed as following equation (4). Here, W_{H2SO4} is amount of 98% sulfuric acid to be charged, W_{Al} is amount of metallic aluminum, and M denotes the molecular weight. So, one equivalent amount of the sulfuric acid to the one batch of the waste dross was 30 kg.

$$W_{H2SO4} = \{W_{Al} \times (3M_{H2SO4}/2M_{Al})\}/0.98 \qquad (4)$$

The requirements of alum for a water treatment product in the Korean Standard(KS) are above 8 % of Al_2O_3 content, above pH 3.0 and above 1.3 for specific gravity [3]. So, sulfuric acid was charged in the range of 0.6-1.1 equivalence to the one equivalent of metallic aluminum, and the water was charged to adjust pH and specific gravity with consideration of balancing the same pulp density of the reacting solution. The experimental conditions were listed in the Table 2 with the analytic results of the prepared samples. The content of alumina was analyzed according to the instruction No. 2004-95 by Korean Ministry of Environment.

The grade of the samples through the experiments 3 and 4, whose equivalent ratios of sulfuric acid to aluminum were 0.8 and 0.9 respectively, satisfied the

Table 2. Experimental conditions and results of the prepared alum samples

Test No.	Charge of Al dross, kg	Equivalent of H_2SO_4/Al	Charge of 98% H_2SO_4, kg	Charge of water, kg	Grade of the samples		
					Al_2O_3 (%)	pH	s.g.
1	18	0.6	18	91	7.8	3.9	1.286
2	18	0.7	21	88	8.03	3.5	1.292
3	18	0.8	24	85	8.06	3.3	1.304
4	18	0.9	27	82	8.07	3.1	1.306
5	18	1.0	30	79	8.07	2.8	1.312
6	18	1.1	33	76	8.08	2.3	1.318

Table 3. Experimental conditions and results of the prepared PAC samples

Test No.	Charge of Al dross, kg	Equivalent of HCl/Al	Charge of 30%HCl, kg	Charge of water, kg	Grade of the samples		
					Al_2O_3 (%)	Basicity	pH
1	18	0.5	36.5	38	9.7	58	4.6
2	18	0.6	43.7	31	10.2	57	4.2
3	18	0.7	51.0	24	10.8	55	3.9
4	18	0.8	58.3	17	11.2	53	3.3

KS requirements. The sample No. 1, whose equivalent ratio of sulfuric acid to aluminum was 0.6, was lower in alumina content and specific gravity, and No.2 was lower in specific gravity. The samples No. 5 and 6, whose equivalent ratios of sulfuric acid to aluminum were higher than 0.9, were unsatisfied with pH requirement. From the test results, it was considered that the optimum ratio of sulfuric acid to aluminum was 0.8-0.9 in processing the waste aluminum dross with sulfuric acid to make alum.

3.2. Preparation of PAC

The waste aluminum dross and the hydrochloric acid solution were charged into a reaction tank, and reacted at room temperature for 3 hours with agitation. In this case also 18 kg of same waste aluminum dross were charged at one batch.

Stoichiometric equivalence of the 30 % hydrochloric acid was calculated according to the equation (2) and the following equation (5). Here, W_{HCl} is amount of 30 % hydrochloric acid to be charged, W_{Al} is amount of metallic aluminum, and M denotes the molecular weight. So, one equivalent amount of the 30% hydrochloric acid in a test batch was 73 kg.

$$W_{HCl} = \{W_{Al} \times (3M_{HCl}/2M_{Al})\}/0.3 \qquad (5)$$

The requirements of PAC for a water treatment product in the Korean Standard (KS) are 10-11% of Al_2O_3 content, pH range 3.5-5.0 and 45-60 for the basicity of the solution[4]. So, hydrochloric acid was charged in the range of 0.5-0.8 equivalence to the one equivalent of metallic aluminum, and the water was charged to adjust pH with consideration of balancing the same pulp density of the reacting solution. Also, sodium aluminate($NaAlO_2$) solution with alumina content 15% was added to the filtered PAC solution to adjust the basisity, whose charged amount was about 3 vol% of the PAC.

The experimental conditions were listed in the Table 3 with the analytic results of the prepared samples. The grade of the samples through the test No. 2 and 3, whose equivalent ratios of hydrochloric acid to aluminum were 0.6 and 0.7 respectively, satisfied the KS requirements. The others were unsatisfied with the alumina content. The sample No. 1, whose equivalent ratio of hydrochloric acid to aluminum was 0.5, was lower in alumina content, and the No.4, whose equivalent ratio was 0.8, was a little higher than the required value. From the test results, it was considered that the optimum ratio of hydrochloric acid to aluminum was 0.55-0.75 in processing the waste aluminum dross with hydrochloric acid to make PAC.

4. Conclusions

In this study it was tried to recycle the waste aluminum dross for making an alum and a PAC which could be used as water treatment chemicals. Through the experiments alum could be prepared by leaching the waste aluminum dross with sulfuric acid, and PAC by leaching it with hydrochloric acid. In each case the equivalent ratio of sulfuric acid to the remained aluminum or the equivalent ratio of hydrochloric acid is an important factor for the processing. It was considered that the prepared alum and PAC samples could be used for water treatment chemicals, and this process could be an effective method for recycling of waste aluminum dross in consideration of saving the material cost for making those chemicals and reducing the amount of the waste dross to discard.

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