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Recycling of aluminum dross for producing calcinated alumina by microwave plasma



Wen-Chang Lin¹, Cheng-Hsien Tsai², Da-Nian Zhang¹, Sheng-Syong Syu¹ and Yi-Ming Kuo^{2*}

Abstract

Due to the excellent engineering property, aluminum has become an important material for processing industries. As the demand of aluminum increased, a large amount of waste aluminum dross has been generated during the aluminum smelting process. The aluminum dross contained *aluminum nitride* and would cause odor while being disposed in landfill, making the aluminum dross disposal a tough issue. Therefore, the aluminum dross was mostly stored in the original plants. The objective of this study is to develop an economically-feasible and environmentally-friendly technology to recover aluminum dross.

In this study, the original aluminum dross was collected from the secondary smelting aluminum dross factories with 33.6% Al. The aluminum dross was dissolved with 3 M NaOH at 50 °C for 60 min to form NaAl(OH)₄ solution. The NaAl(OH)₄ was then transformed to aluminum hydroxide by adding H_2SO_4 . Then, the aluminum hydroxide was filtered, washed, and dried. The thermogravimetric analysis and X-ray powder diffraction analysis result show that the main crystal phase of aluminum hydroxide (intermediate product) is boehmite. The aluminum hydroxide powder was calcined at 700 °C for 5 min by an atmospheric-pressure microwave plasma to produce Al_2O_3 . The result show that this process can reduce environmental pollution and recycle aluminum as recoverable form.

Keywords: Atmospheric pressure microwave plasma, Aluminum dross, Aluminum trihydrate, Alumina, Desilication

1 Introduction

Aluminum, characterized by its lightweight, conductivity, corrosion-resistant metal, and strong affinity for oxygen, has been extensively used in different industries [1]. The global output of aluminum dross has been increasing due to the high aluminum demand. In 2020, the annual global output of metallic aluminum was 65.3 Mt with an average daily production of 183.7 t [2, 3]. At present, the two main sources of aluminum material are primary aluminum smeltery, which uses bauxite as raw material, and secondary aluminum smeltery, which uses the scrap aluminum and recycled aluminum cans as raw material [4, 5]. During the smelting process, the aluminum

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² Department of Environmental and Safety Engineering, Chung Hwa University of Medical Technology, Tainan 717, Taiwan Full list of author information is available at the end of the article is melted to 700-750 °C and some molten salt mixtures (e.g., sodium chloride, potassium chloride, sodium fluoride) will be added. A protection layer is formed on the metal surface to separate the molten aluminum from the ambient air. At this point, the dross is formed on the surface of molten aluminum, known as aluminum dross. The primary dross still has a very high aluminum content, so it is remolten by blending until the aluminum content is reduced to 30-50% before it is discarded. The aluminum dross is an inorganic waste that contains oxygen as an impurity [6]. Its properties vary with the source, dross forming time, dross removal method, the amount of additive, and reprocessing frequency [7]. On average, 1000 kg of molten aluminum can produce 15 to 25 kg of aluminum dross [8]. There are two kinds of aluminum dross, namely primary aluminum dross (PAD) and secondary aluminum dross (SAD). The SAD has a low aluminum content, which is 5-10wt%, but high oxide and



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salt contents. The PAD has a high aluminum content, which is about 80 wt% and a small amount of oxide and salt [8, 9]. Previous studies analyzed the composition of aluminum dross, including aluminum, aluminum carbide, aluminum nitride, aluminum oxide, Fe(III) oxide, aluminum hydroxide, cryolite, diaoyudaoite, and magnesium aluminate [1, 10]. Salts, such as sodium chloride and potassium chloride, and small amounts of metals, such as copper, titanium, iron, manganese, and calcium and silicon dioxide, were used for dross removals [11].

At present, the world produces approximately 4 Mt of PAD and more than 1 Mt of SAD annually. About 95% of the SAD is temporarily stored in the original factories [6]. When the aluminum nitride in aluminum dross reacts with water vapor in rain or the air, ammonia odor is generated and emitted, thereby causing air pollution [12, 13]. Flammable gases, such as hydrogen and methane, are also released [14]. Moreover, when the aluminum dross contains hazardous heavy metals, such as chromium, copper, lead, cadmium, mercury, barium, arsenic, and selenium, rainfall could wash these hazardous materials present in the aluminum dross into the soil, which leads to soil or water pollution. Skin irritation and pulmonary disease could also be induced or aggravated [14]. Inhaling the SAD particles suspended in the air may induce serious Alzheimer's disease, silicosis, and bronchitis [8]. Consequently, communities in nearby landfills often oppose against the disposal of aluminum dross, and at present, landfills hardly dispose aluminum dross. However, the mass stacking and illegal disposal of aluminum dross have become a serious issue. Environmental legislations have compelled European and American secondary aluminum smelting industry to adopt recovery techniques to reduce waste [15].

The main challenges in waste treatment technology are to meet the decontamination effect and reduce operating costs at the same time. If high-value products are produced from waste materials using low-energy-consuming processes, this study falls within the framework of sustainable management of resources by recycling waste and limiting energy consumption during calcination process. Waste recycling could thus become a novel approach for enhancing circular economy [16]. The common processing technique for aluminum black slag in aluminum smelting is grinding and sieving the dross to recover metallic aluminum, and immersing the residual aluminum dross in water at a high temperature to hydrolyze the salts [17, 18]. The salts are recovered by filtering and evaporation techniques. The residual aluminum dross contains alumina and other alloying elements, and can be used in different industries (i.e., cement, ceramic, and building industries) after washing or calcination [19, 20].

The methods of extracting aluminum and aluminum compounds from aluminum dross include pyrometallurgy and hydrometallurgy. The former requires a reducing agent and consumes a great deal of energy for combustion. The latter uses a solvent to react with aluminum dross and extracts some constituents from the aluminum dross. Hydrometallurgy is more commonly adopted due to its low disposal cost [21]. The recycling technique is to mix aluminum dross as raw material with complexing agents of different and mixed proportions, to produce simple ceramic bricks. Homogeneous powder can be prepared by adding aqueous carboxymethyl cellulose solution in aluminum dross, and calcining at high temperature to produce a refractory material, aluminum trihydrate Aluminum trihydrate and aluminum sulfate products have recycling value, but most processes fail to completely treat the odor emitted by aluminum nitride in the aluminum dross. Also, the disposal cost is high and the disposal of aluminum dross is restricted.

The main hydrolysis product of aluminum compound is aluminum trihydrate, such as aluminum hydroxide and aluminum oxyhydroxide. There are several forms according to the structure, lattice, and crystal water content. Gibbsite, which is the aluminum trihydrate crystalline phase prepared in the Bayer process, has been extensively used for making smelter-grade alumina [22]. Boehmite has also been used for preparing catalytic grade alumina [23]. The aluminum trihydrate can be dehydrated by calcination at high temperatures and changed into alumina. The alumina has multiple crystalline phase forms according to different calcination temperatures including α , β , γ , δ , and θ crystalline phases [24]. When the temperature rises, the water of hydration content in the alumina decreases and the structural stability increases. In the α phase, which is known as corundum, its structure has the oxygen atom layer of hexagonal closest packing. It appears in columnar, granular, or plate-like shapes with the highest chemical stability, heat resistance, hardness, and density. In the y phase, which is known as alumina, it appears in scale-like shape at a low temperature. When the temperature reaches above 1200°C, it changes into the α -phase [25]. The reaction between aluminum dross and alkali liquor can facilitate the dissolution of the aluminum constituent, as the dissolution of metal oxides in the alkali liquor is influenced by physical property, concentration, temperature, and pressure. For example, when the magnesium oxide or magnesium hydroxide reacts with alkali liquor, a higher temperature contributes to dissolution [26]. The ferriferous oxide is hardly soluble in alkali solution, while the metallic sodium and aluminum form a compound, such as cryolite [7]. The metallic impurity can be separated and purified by adjusting pH. At pH10-11, mixed oxide precipitates can be generated; at pH8-9, magnesium hydroxide precipitates can be generated; at pH7, aluminum trihydrate precipitates



can be generated [27]. The main silicon compound in the aluminum dross is silicon dioxide. The solubility in alkali solution is influenced by its concentration, temperature, and chemical structure. The dissolved silicon compound and the alkali liquor form silicate (e.g., $Na_2(H_2SiO_4)$) adhere to the inner wall of metal, so that the thermal conductivity is reduced [28]. The desiliconization is very important for reducing equipment maintenance and increasing the recovery rate and purity of products. The traditional desiliconization method uses a small amount of calcium oxide or calcium hydroxide in the reaction, which performs desilication with the solution, thereby forming

insoluble calcium silicate precipitates [29]. As for other desilication methods, for example, the Friedel's salt $(3CaO \cdot A1_2O_3 \cdot CaCl_2 \cdot 10H_2O)$ can be added in sodium aluminate solution to exchange anions with silicon. The effect of desilication is influenced by the temperature, silicon concentration, and sodium hydroxide/aluminum oxide concentration ratio of the solution up to 95% [30].

In comparison to traditional high-temperature furnace heating, preparation of alumina by using plasma to calcined aluminum compound has advantages of quick reaction, high conversion rate, and good efficiency. At present, the plasma types include microwave plasma, radio frequency plasma, direct current transferred arc plasma, and

direct current pulsed wire discharge. The argon admitted into the system not only increases the plasma concentration, but also removes the impurities from the target material's surface. In addition, the diatomic gases (e.g., oxygen, hydrogen, air) can increase the enthalpy and heat transfer rate in the plasma. Power is controlled to make the gas molecules rub against the free particles to raise the temperature in a short time. Higher power can better raise the temperature and change the alumina to a stable form. The carbon and hydrogen in the target material can be removed by blending oxygen, and the effect is better than blending hydrogen [31]. According to literature, the conversion of an aluminum compound into alumina is mainly influenced by temperature. When the aluminum product is gasified at high temperatures, the metal gas molecules diffuse to the regions at lower temperatures, react with the input gas to generate the precursor of alumina, and gather to be arranged as alumina [32].

This study used SAD as raw material to make highvalue and environmentally-friendly alumina products. The proposed reduction recovery technique can avoid the negative influence of aluminum dross burial on the environment, and provide a waste disposal method with an economic benefit. Most aluminum manufacturers adopt Bayer technology, which is a very energy-consuming and polluting. On the other hand, the proposed technique can reduce the energy consumption and pollution problems of aluminum smelters. This study used SAD and sodium hydroxide solution to perform an alkali dissolution reaction at atmospheric pressure to prepare sodium aluminate solution. The influence of reaction temperature, reaction time, and sodium hydroxide solution concentration on the dissolution rate of aluminum in the aluminum dross was also discussed to identify the optimum operating parameters.

The pH13.3 of the NaAl(OH)₄ solution derived from optimum parameters was reduced by H₂SO₄ to 11 to remove siliceous impurity. To obtain relatively pure aluminum trihydrate by sedimentation, the pH was reduced to 7 by H₂SO₄. Calcination by a high-temperature furnace and atmospheric pressure microwave plasma was performed to prepare the end product (alumina). The results show that the aluminum content in the aluminum dross is 33.6%. The aluminum dissolution rate of aluminum dross of alkali dissolution with sodium hydroxide solution in optimal conditions (T = 50 °C, t = 60 min, sodium hydroxide concentration = 3M) is 46.3%. The overall aluminum element recovery is 44%. The pH is reduced by H_2SO_4 to remove siliceous impurity and obtain the aluminum trihydrate precipitates. The thermogravimetric analysis and crystalline phase analysis indicate that the main crystalline phase of aluminum trihydrate is boehmite. Finally, it was calcined by atmospheric pressure microwave plasma (800–900 W, 700 °C) in an argon-oxygen environment for 5 min to obtain high purity aluminum oxide, which is equivalent to the crystalline phase of alumina obtained by thermal calcination above 1200°C in a high-temperature furnace.



2 Experiments

2.1 Experimental material

The SAD used in this study was slightly gray powder, and collected from the secondary smelting aluminum dross factories. This mean particle size of the SAD was $18.4 \mu m$ (measured using a laser particle size analyzer). The Al content accounted for about 30% (via an acid digestion and ICP-MS analysis).

2.2 Experimental process and parameter setting

Figure 1 show the experimental procedure to produce alumina, including: water washing, alkali dissolution reaction, acid-base titration, and calcination at atmospheric pressure. First, the SAD was washed with water to remove soluble salts. The washed SAD was dissolved using NaOH solution with different concentrations at different temperature to generate NaAl(OH)₄ solution. The NaOH addition amount was according to the mass ratio of Al and NaOH in the reaction equation of SAD and NaOH. The pH13.3 of NaAl(OH)₄ solution was added with concentrated H₂SO₄ acid to adjust three pH values (12, 11.5, and 11). The solutions were filtrated to remove yellow precipitates. Then, filtrated solution was added with concentrated H_2SO_4 acid to pH=7, and white aluminum trihydrate was precipitated. This precipitate was washed with deionized water and dehydrated using 99.8% isopropanol. The washed aluminum trihydrate powder was calcined by a tubular high-temperature furnace and atmospheric pressure microwave plasma to prepare high purity alumina. The advantages and disadvantages of the two methods for producing alumina were also discussed.

2.3 Experimental equipment and analytic instruments

The water washed and oven-dried aluminum dross was put into an alkali dissolution device. Excessive NaOH solution was calculated according to chemical dose. An alkali dissolution reaction was performed at a constant temperature of 50 °C and the BAR (weight ratio of base solution and aluminum dross) was 20. Al and Al- compounds were dissolved into NaAl(OH)₄ solution. The influence of reaction time and NaOH concentration on dissolution was discussed. In the process of using H_2SO_4 for acid-base decontamination and neutralization of sodium aluminate solution to obtain aluminum trihydrate, the variance in solution pH was measured via a pH meter (EUTECH, pH510). To make alumina, the aluminum trihydrate precipitate after briquetting $(0.3 \text{ g ingot}^{-1})$ was calcined by a tubular high-temperature furnace (Tender, RH245). The air was admitted into the tubular high-temperature furnace. The temperature rose from 400 to 1200°C (heating rate = 10° C min⁻¹). This temperature was maintained for 2h for calcination to generate alumina product. Figure 2 shows the calcining equipment of the atmospheric pressure microwave plasma. The aluminum trihydrate powder was pressed into round ingots $(0.3 \text{ g ingot}^{-1})$ and held on a sample stage in a quartz tube. Argon-oxygen mixed gas was spirally induced into the quartz tube and heated using the atmospheric pressure microwave plasma. The calcination temperature was controlled at three temperatures (500, 600, and 700 $^{\circ}$ C) by the power supply for 5 min to generate alumina product.

To promote the melting process, the fluxing agent (99% LiBO₂, 99% Li₂B₄O₇) was mixed with a sample at mass of flux agent: sample = 10 in a crucible and the specimens





were held in a heating furnace. The specimens were heated to 1100 °C with a heating rate of 10 °C min⁻¹, and held isothermally for 2 h.

To measure the composition of the SAD, alkali dissolution residue, and the powder of intermediate product, these specimens were digested using 10N hydrochloric acid and heated to 200 °C using a microwave heater (MARS Xpress, CEM). The metal concentration in the digests were measured by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) to obtain the metal content of solid specimens.

The operating conditions of ICP-MS included Agilent (ICP-MS 7500), nebulizer (PEEK), sample uptake rate of $0.7 \,\mathrm{mL\,min^{-1}}$ (injection rate for liquid samples), spray chamber made of glass, radio frequency power of 1500 W, total analysis time of 4 min, and carrier gas (Ar) of $0.94 \,\mathrm{L\,min^{-1}}$. The water content in the intermediate product aluminum trihydrate was analyzed by the thermogravimetric analyzer (TGA N-1500). The operating conditions were: sample weight of 6–7 mg, airflow rate of 10 sccm, heated to 1300°C with heating rate of $5 \,^{\circ}\mathrm{C\,min^{-1}}$. The surface morphology of the specimens was observed using a field emission scanning electron microscope (SEM). Energy Dispersive Spectroscopy (EDS) is a standard procedure for identifying and quantifying elemental composition of sample areas of a micron or less. In this study, the composition elements of the intermediate product aluminum hydroxide was analyzed by SEM/EDS. The characteristic X-rays are produced when the sample is bombarded with electrons from the SEM. Detection of these X-rays can be accomplished by an energy dispersive spectrometer, which is a solid state device that discriminates among X-ray energies.

To improve the electrical conductivity of the sample, the sample surface was coated with gold film before the scanning process. To evaluate the quality of Al_2O_3 , the specific surface area was measured by a specific surface area analyzer (Micromeritics, ASAP2010). The nitrogen was used for physical adsorption at 77 K. Relative pressure and absorbance in the isothermal adsorption curve were derived from the absorbance of nitrogen. The specific surface area of the sample was calculated by the Brunauer–Emmett–Teller equation.

The X-ray diffractometer (BRUKER, model: D8 Advance, Germany) was used for the identification and quantitative analysis of crystalline phase in the SAD, washed salt, alkali dissolution residue, intermediate product (aluminum trihydrate), and final product (Al_2O_3). The operating parameters of the X-ray diffractometer were voltage of 40 kV, current of 40 mA, scanning rate of 3° min⁻¹, and scanning range (20) of 15–85°. The crystalline phases of specimens were identified by comparison with the Joint Committee on Powder Diffraction Standard (JCPDS) software.





3 Results and discussion

3.1 Composition, and crystalline phase of aluminum dross The Al content in the SAD was up to $336.1 \, g \, kg^{-1}$. The levels of Mg, Fe, Na, and Cr were 45.2, 42.4, 16.9 and $12.3 \, g \, kg^{-1}$, respectively. The contents of Ca, Cu, Ni, Si, As, Ba, Pb, Cd, and Se were 6830, 4620, 4230, 4030, 2830, 279, 206, 25.6 and 9.5 mg kg⁻¹ respectively. solid in the leach ate was mainly NaCl, KCl, and ${\rm NaSiO}_3$ (verified by the XRD analysis).

3.2 Influence of temperature and time on Al dissolution

To obtain the optimal parameters of Al dissolution, the 3 M NaOH was used for the alkali dissolution of Al at different temperatures (25, 50, and, 80 °C) with the result shown in Fig. 4. The dissolution of SAD included several equations as follows.

$$Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow NaAl(OH)_{4(aq)} \triangle H^{o} \left(kcal \ mol^{-1} \right) = -4.8$$
(1)

Aluminum nitride+NaOH_(aq)+3H₂O_(l)
$$\rightarrow$$
 NaAl(OH)_{4(aq)}+NH_{3(g)} \triangle H^o(kcal mol⁻¹) = -52.0 (2)

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2NaAl(OH)_{4(aq)} \triangle H^o\left(kcal \ mol^{-1}\right) = -3.1$$
(3)

Figure 3 shows the XRD analysis results of SAD. The crystalline phases in the SAD were aluminum trihydrate (Al(OH)₃ and β -Al(OH)₃), alumina (α -Al₂O₃, δ -Al₂O₃), aluminum nitride, spinel (MgAl₂O₄ and NiAl₂O₄), and Ca₂Al₂SiO₇. Among them, aluminum trihydrate had the highest crystalline phase intensity.

After being water washed for using 60min at room temperature and normal atmospheric pressure, about 1.9% of SAD mass was leached out and the dissolved

$$2AI + 2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2 \uparrow (4)$$

The Al dissolution rate increased with the reaction temperature and time. For the reaction temperature of 25 °C, the maximum dissolution ratio was only about 30%. When the reaction temperature increased to 50 and 80 °C, the Al dissolution ratios were increased to 46 and 50% which were roughly the same. In addition, for 50 °C,



the Al dissolution ratios were also roughly the same at 60 and 120 min. Therefore, the temperature and time for the reaction were set at $50 \,^{\circ}$ C and $60 \,^{\circ}$ min for further experiments for the purpose of energy-saving.

To investigate the Al dissolution behaviors, the crystalline phases of alkali dissolution residue from different reaction temperatures were analyzed and the XRD analysis results are shown in Fig. 5.

The peak intensity of Al(OH)₃, β -Al(OH)₃ and δ -Al₂O₃ in the alkali dissolution residue decreased gradually as the reaction temperature increased. These three crystals were the major Al sources of NaAl(OH)₄ solution. The intensity

Table 1 Element content of undissolved residue ($ppm = mg kg^{-1}$ aluminum dross)

Element	Content (ppm)	The element of SAD weight ratio (%)
Al	342,600	55.0
Si	1210	15.8
Fe	22,900	29.2
Mg	65,800	78.6
Ca	9800	77.5
Cu	6600	77.1
Na	10,000	32
Ni	513	6.5
Cr	9610	42.2
Pb	261	68.4
Cd	65.4	138
Hg	N.D.	0.0
Ва	426	82.5
As	2390	45.6
Se	20.9	118.8

Element	Content (ppm)	The element of SAD weight ratio (%)
Al	327,350	40.9
Si	560	5.8
Fe	287.5	0.3
Mg	83	0.1
Ca	665	4.1
Cu	19.4	0.2
Na	505	1.3
Ni	5.5	0.1
Cr	4515	15.4
Pb	5.5	1.1
Cd	N.D.	0
Hg	N.D.	0
Ва	4	0.6
As	449	6.7
Se	7	30.9

Table 3 Total element analysis of the product (mg kg⁻¹ product)

Table 2 pH drop of Na_2SO_4 solution and element analysis of the intermediate product

Element	Content (ppm)	The element of SAD weight ratio (%)
AI	327,350	40.9
Si	560	5.8
Fe	287.5	0.3
Mg	83	0.1
Ca	665	4.1
Cu	19.4	0.2
Na	505	1.3
Ni	5.5	0.1
Cr	4515	15.4
Pb	5.5	1.1
Cd	N.D.	0
Hg	N.D.	0
Ва	4	0.6
As	449	6.7
Se	7	30.9

of α -Al₂O₃ and spinel (MgAl₂O₄, Na₂Al₂O₄) was not changed significantly, indicating that they were inert to the alkali dissolution. The dissolution ratio (50%) at 80°C was higher than that (46%) at 50°C by 4%. The XRD analysis shows that the intensity of β -Al(OH)₃ and δ -Al₂O₃ was slightly reduced at 80°C, indicating that these two crystals accounted for the increased Al dissolution ratio.

In addition, the intensity of CaSiO₄ decreased as the reaction temperature increased, possibly because it was

partially dissolved into impurities in the $\mathrm{NaAl(OH)}_4$ solution.

3.3 Influence of NaOH concentration on Al dissolution

To obtain the optimal NaOH concentration of Al dissolution, the temperature and time and BAR for the reaction was set at 50 °C, 60 min, and 20 for the alkali dissolution of Al at different NaOH concentration (1.55, 2, 3, and 6M) with the result shown in Fig. 6. The Al dissolution ratio increased from 32% (at 1.55 M) to 48% (at 6M) and 3M is the optimal NaOH concentration from the economic point of view.

To investigate the Al dissolution behaviors, the crystalline phases of alkali dissolution residue from different NaOH concentrations were analyzed with the XRD analysis results shown in Fig. 7.

The intensity of $Al(OH)_3$ and β - $Al(OH)_3$ for the reaction time of 60 min at 50 °C decreased as the NaOH concentration increased. The reaction rate of NaOH for $Al(OH)_3$ was higher than that for β - $Al(OH)_3$ because the $Al(OH)_3$ structurally has more acid sites which would be easily dissolved [33]. In addition, the relative intensity of CaSiO₄ increased as the NaOH concentration increased. This explained why the Al dissolution ratio increased with the increase of NaOH concentration. Therefore, the NaAl(OH)_4 solution would contain more impurity (CaSiO_4) with higher NaOH concentration. The element content of undissolved residue is shown in Tables 1 and 2. The Al content was up to 342.6 g kg^{-1} and the Al dissolution ratio of SAD was 46%.





3.4 Influence of adjusting pH by H₂SO₄ for removing impurity

The original pH of the NaAl(OH)₄ solution was about 13.3, and H_2SO_4 was used to adjust the pH (12, 11.5,

and 11) to precipitate the Si-based impurity from the NaAl(OH)₄ solution. The solution was filtrated to remove impurity and the pH was adjusted to 7 to obtain the Al(OH)₃. The EDS results of the impurity removed at



different pH and the accordingly obtained products are shown in Table 3. The Si/Al atomic ratios of the Si-based impurity were 0.71, 0.67, and 0.32, respectively, pH = 12, 11.5, and 11. It indicated that the Si/Al atomic ratios of precipitate decreases with the pH of sodium aluminate solution (pH₀ \cong 13.3). As the sulphuric acid can neutralize the excessive sodium hydroxide in the solution, the alkalinity is reduced, contributing to the formation of sodium silica slag. From the products obtained at pH=7, it shows that high purity of Al-precipitation is obtained while the Si- impurity is removed at pH=11 with the Al level 34.9%. The equation is expressed as follows:

intermediate product obtained at pH=7 as a white colloid. The white colloid was washed with deionized water, dried, and calcinated at 350 °C for 2h. Then the crystalline phase and morphology of specimens before and after the calcination were analyzed by the XRD (Fig. 8) and SEM respectively.

Figure 8A shows the XRD pattern before the calcination of the precipitate and after the impurity was removed, with the filtrate adjusting to pH=7. Group (a), (b), (c) in Fig. 8A show the XRD patterns of precipitates of $pH12 \rightarrow 7$, $pH11.5 \rightarrow 7$ and $pH11 \rightarrow 7$. According to JCPDS verification, the main crystalline

$$Na_2(H_2SiO_4) + 2NaAl(OH)_4 \rightarrow Na_2OAl_2O_34SiO_2nH_2O \downarrow + 2NaOH$$

(5)

When H_2SO_4 was added in the NaAl(OH)₄ solution, NaOH was neutralized and Si-based impurities started to precipitate. When the Si- based impurities in the solution was fully precipitated, excessive H_2SO_4 reacted with NaAl(OH)₄ to precipitate Al(OH)₃. The equation is expressed as follows:

$$2\text{NaAl(OH)}_4 + \text{H}_2\text{SO}_4 \rightarrow 2\text{Al(OH)}_{3(s)} \downarrow + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$$
(6)

3.5 Composition and crystalline phase of intermediate product

After the pH of NaAl(OH)₄ solution was reduced by $H_2SO_{4^{j}}$ the Si-based impurity precipitate appeared as a milky white, relatively yellow powder. After the impurity was removed (at pH=11, pH=11.5, and pH=12), the

phase of three groups of precipitate is boehmite. The result indicates that the boehmite of group (a) contains more siliceous impurity, leading to worse crystalline phase intensity, group (b) and (c) have apparent crystalline phase, but the peaks are still wider. There are two main causes. First, the Al(OH)₃ precipitate just changed into a colloid, and there was not enough time for nucleation; hence, the Al(OH)₃ crystals had inside defects. Second, the adsorbed water in the double layers of octahedra of boehmite led to poor crystallinity and relatively loose arrangement of structure. This phenomenon can be observed in the SEM images of Al(OH)₃ precipitate, as shown in Fig. 9a. The morphology before the calcination was agglomerated grains, and the particle size distribution was nonuniform.



After the calcination, crystalline intensity was promoted. The changes in the crystalline phase are shown in Fig. 8B. The results show that after calcination, their full width at half maximum peaks in the XRD pattern has been narrowed, indicating that the impurities in the crystalline phase was reduced. The adsorbed water included in the double layers of octahedra of boehmite was removed, and the crystalline formed after calcination became steadier. The morphology, as shown in Fig. 9b, indicates scale-like surface.

The differential thermal analysis was used for the TGA of the Al(OH)₃ of precipitate $pH11 \rightarrow 7$ and the thermogravimetric curve is shown in Fig. 10. Theoretically, when AlOOH was sintered at high temperature, the weight loss due to water vaporization was about 15% [33]. However, Fig. 10 shows that the total weight loss was 41%. The difference of 26% could be explained by that the vaporization of the adsorbed water and the moisture which were embedded in the double layers of octahedra γ-AlOOH. The results of XRD results (Fig. 8), TGA (Fig. 10), and elemental analysis (Table 3) found that the aluminum hydroxides contained 26% water of hydration and 74% aluminum hydroxide. The theoretical ratios of Al contained in anhydrous boehmite and anhydrous bayerite were Al/AlOOH=27/60=0.45 and Al/ $Al(OH)_3 = 27/78 = 0.35$, respectively. The ratio of Al contained in the precipitation product was 0.327/0.74=0.44 which is roughly equal to that of anhydrous boehmite. The results show that the anhydrous boehmite was in high purity (98%) which also matched the finding of the XRD analysis results.

3.6 Prepare end product alumina by calcination

Different forms of Al_2O_3 can be obtained by calcining aluminum trihydrate at different temperatures. The water content decreased as the calcination temperature and time increased. The aluminum trihydrate prepared in this experiment was calcined by a tubular heating furnace and atmospheric pressure microwave plasma.

The pressed aluminum trihydrate (0.3 g ingot⁻¹) was held in the tubular heating furnace, heated to 400, 600, 800, 1000, and 1200 °C at a heating rate of 10 °C min⁻¹ and stayed isothermally for 2 h. The XRD analysis results are shown in Fig. 11. Before the calcination, the crystalline phase of aluminum trihydrate was boehmite. While it was calcinated, the crystalline phase started to be transformed into γ -Al₂O₃ (2 θ =46°) at 400 °C and fully converted into γ -Al₂O₃ at 600 °C. Then the crystalline phase started to be transformed into θ -Al₂O₃ (2 θ =61°), and fully converted into θ -Al₂O₃ at 1000 °C. When the calcination temperature reached 1200 °C, the crystalline phase partially transformed into α -Al₂O₃.





On the other hand, the pressed aluminum trihydrate $(0.3 \text{ g ingot}^{-1})$ was held the atmospheric pressure microwave plasma reactor. The argon-oxygen mixed gas was induced into the reactor and calcined at different temperatures (500, 600, and 700 °C) for 5 min. The XRD analysis results are shown in Fig. 12. In general, the transformation of the aluminum trihydrate into θ -Al₂O₃ requires at least 1000 °C. However, the crystals were partially transformed into θ -Al₂O₃ at 500 °C. At 600 °C, partial θ -Al₂O₃ was changed into α -Al₂O₃. When the temperature reached 700 °C, the crystals was fully transformed into high purity α -Al₂O₃. When the Ar and O₂ were induced into the reactor, these atoms were excited by high energy electrons, ionized in the plasma reactor, and then transformed into active species of excited state or atomic state

(Ar, O_2 , and O_2^*). They reacted with aluminum trihydrate to accelerate the moisture vaporization and crystalline phase transformation of α -Al₂O₃.

Aluminum trihydrate have several forms. Among them, boehmite has a relatively large specific surface area and is usually used for making catalytic grade γ -Al₂O₃. When the aluminum trihydrate is heated, the internal water is evaporated, the surface cracks or forms a pore structure, and, thus, the specific surface area increases.

For heating to 600 °C in the tubular heating furnace, the γ -Al₂O₃ had a relatively large specific surface area (380 m²g⁻¹). The appearance is shown in Fig. 13a with the structure needle-like. For the calcination at 1200 °C, the specific surface area of α -Al₂O₃ decreased to 30 m² g⁻¹ with SEM image shown in

Fig. 13b. The specific surface area of the α -Al₂O₃ calcinated by atmospheric pressure microwave plasma was only 6 m² g⁻¹ with SEM image shown in Fig.13c. The specific surface area greatly decreased because the alumina particles aggregated at high temperature, in agreement with the results in a previous study [34]. When the temperature increases, the pores and seams are closed due to the agglomeration of alumina particles, which makes the specific surface area decrease. This agglomeration phenomenon is shown in Fig.13b and c.The calcination using the atmospheric pressure microwave plasma needs extremely short time to obtain completely transformed α -Al₂O₃ and, thus, saves much energy. Therefore, this method is a promising technology for the sustainable development of the environment.

4 Conclusions

This study proposed an economically-feasible and environmentally-friendly aluminum dross recycling method. In this process, 46% SAD was dissolved with NaOH to form $NaAl(OH)_4$ solution and 54% stayed as residues. With the optimal operating parameters, high purity aluminum trihydrate precipitate was obtained when the solution was adjusted to pH=7. The aluminum trihydrate precipitate was calcined by the atmospheric pressure microwave plasma to obtain high purity α -Al₂O₂ which was about 25% of Al mass in SAD. The proposed method not only could reduce the aluminum dross, but also provide an economically-feasible recycling technique. The discussion about the species and variation of principal components such as aluminum trihydrate, alumina, and aluminum nitride of the aluminum dross products in various stages can provide a reference for waste acceptance criteria for developing aluminum dross recycling in the future. In addition, this study found several factors that affect the aluminum recovery rate of aluminum dross, such as reaction temperature, reaction time, metal (e.g., iron, magnesium, calcium, copper, chromium, and lead) impurities interfere with the reaction, the diffusion resistance of aluminum nitride hydrolysis, and the type of lye. Future studies can use these factors in the parameter design, such as increasing the reaction temperature, increasing the reaction time, removing the metal impurities, and different hydrolysis methods, to increase the hydrolysis of aluminum nitride, and find better technologies to increase the aluminum recycling rate.

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Authors' contributions

DNZ and SSS conceptualized this study; WCL and YMK conducted investigation; WCL, DNZ, and SSS performed formal analysis; YMK undertook visualization and methodology, and wrote the first draft; DNZ and SSS conducted data curation; WCL and CHT reviewed and edited the article; CHT led the project administration. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

Data is contained within the article or supplementary material.

Declarations

Competing interests

The authors declare they have no competing interests.

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