

A method of forming aluminium trihydrateTechnical Field

The present invention relates to a method of forming aluminium trihydrate.

5 Background

Aluminium dross is a by-product from aluminium smelting and may contain metallic aluminium, aluminium oxide and other metallic oxides. Generally, after the recovery of aluminium from aluminium dross, the dross is discarded via landfills, which can lead to leaching of toxic metal ions into groundwater and cause water pollution problems and
10 loss of raw material. Further, when aluminum dross comes into contact with water, ammonia, hydrogen gas and other combustible gases may be generated, which not only pollutes the air but can be a source of fire and explosion when stored improperly.

There are several methods of recovering aluminium from aluminium dross. For example, 85-90% of the aluminum oxide in dross may be recovered and purified using
15 an acid dissolution method and sodium hydroxide high temperature fusion method. Such methods can recover more than 90% of aluminum in aluminum dross. However, both methods are energy intensive and are therefore not cost or energy effective.

Aluminium trihydrate (ATH) may be converted to alumina and subsequently converted to aluminium. ATH is also widely used in fire retarded polymers for use in electronics
20 and automotive industries. However, these applications are a small percentage compared to the volume that is converted to alumina for aluminium production.

Thus, there is a need for an improved method of recovering as much metallic and chemical forms of aluminium from aluminium dross.

Summary of the invention

25 The present invention seeks to address these problems, and/or to provide an improved method for preparing aluminium trihydrate.

According to a first aspect, the present invention provides a method of preparing aluminium trihydrate (ATH), the method comprising:

- mixing aluminium dross with sodium hydroxide at a first pre-determined
30 temperature to form a mixture, wherein the aluminium dross has an

aluminium oxide content of $\geq 30\%$ based on the total weight of the aluminium dross;

- filtering the mixture to obtain a first filtrate and a first residue;
- diluting the first filtrate with water; and
- 5 - mixing the first filtrate with carbon dioxide at a second pre-determined temperature to obtain ATH residue and a second filtrate.

The aluminium dross may be any suitable aluminium dross. In particular, the aluminium dross may have an aluminium oxide content of 60-90% based on the total weight of the
10 aluminium dross.

According to another particular aspect, the aluminium dross may be powdered aluminium dross. In particular, the aluminium dross may have an average particle size of 0.002-10.0 mm.

The mixture may comprise any suitable amount of aluminium dross and sodium
15 hydroxide. For example, the mixture may comprise aluminium dross and sodium hydroxide in a ratio of 1:0.2-1:8.

The first pre-determined temperature may be any suitable temperature. For example, the first pre-determined temperature may be 50-100°C.

The diluting may comprise diluting the filtrate with any suitable amount of water. In
20 particular, the diluting may comprise diluting the first filtrate by a dilution factor of 1.5-4.

According to a particular aspect, the mixing the first filtrate with carbon dioxide may comprise flowing carbon dioxide into the first filtrate at a flowrate of 9-20 kg/min. The second pre-determined temperature at which the first filtrate is mixed with carbon dioxide may be at a suitable temperature. For example, the second pre-determined
25 temperature may be 40-100°C.

The mixing the first filtrate with carbon dioxide may comprise flowing carbon dioxide into the first filtrate for a suitable period of time. For example, the mixing may be for 60-180 minutes.

The method may be carried out under any suitable conditions. In particular, the method
30 may be carried out at atmospheric pressure.

According to a particular aspect, the method may further comprise evaporating the second filtrate to form sodium bicarbonate. The evaporating may be any suitable form of evaporation. In particular, the evaporating may comprise vacuum evaporation.

According to a particular aspect, the method may further comprising heating the sodium bicarbonate to form sodium carbonate.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows weight of the aluminium dross used and weight of wet and dry reaction oxide residue (ROR) recovered;

Figure 2 shows weight of the aluminium dross used and weight of wet and dry white precipitate product (WPP) recovered;

Figure 3 shows percentage purity of aluminium trihydrate (ATH) recovered;

Figure 4 shows oil absorption (g/100g) of aluminium trihydrate (ATH) recovered;

Figure 5 shows whiteness of aluminium trihydrate (ATH) recovered; and

Figure 6 shows moisture content (% weight) of aluminium trihydrate (ATH) recovered.

Detailed Description

As explained above, there is a need for an improved method of recovering aluminium from aluminium dross.

In general terms, the present invention provides an improved method of preparing aluminium trihydrate (ATH). The ATH may subsequently be converted to aluminium. In this way, effective recovery of aluminium may be achieved from aluminium dross in an environmentally friendly manner. Further, the method of the present invention utilises carbon dioxide, thereby helping to reduce carbon emissions. By-products of the method may also have further use, thereby making the method advantageous in minimising waste and reducing loss of resources to landfill.

According to a first aspect, the present invention provides a method of preparing aluminium trihydrate (ATH), the method comprising:

- mixing aluminium dross with sodium hydroxide at a first pre-determined temperature to form a mixture, wherein the aluminium dross has an aluminium oxide content of $\geq 30\%$ based on the total weight of the aluminium dross;
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- filtering the mixture to obtain a first filtrate and a first residue;
- diluting the first filtrate with water; and
- mixing the first filtrate with carbon dioxide at a second pre-determined temperature to obtain ATH residue and a second filtrate.
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The aluminium dross may be any suitable aluminium dross. For example, the aluminium dross may have an aluminium oxide content of 30-95%, 35-90%, 40-85%, 45-80%, 50-75%, 55-70%, 60-65% based on the total weight of the aluminium dross. In particular, the aluminium dross may have an aluminium oxide content of 60-90% based on the total weight of the aluminium dross.
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The aluminium dross may comprise salts. The salts may comprise, but not limited to, silicates, chlorides, fluorides, nitrates. For example, the aluminium dross may comprise sodium chloride.

The aluminium dross may be in any suitable form. For example, the aluminium dross may be in powdered form. The aluminium dross may be formed into a powder by any suitable method known in the art. For example, the aluminium dross may be processed with a hammer, jaw crusher, or by physical crushing methods using pulverisers to grind the aluminium dross. According to a particular aspect, the aluminium dross may be in a block form, in which case the aluminium dross may be further processed as explained above to convert it into a form more suitable for the purposes of the method of the present invention.
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The aluminium dross may be in any suitable size. For example, the aluminium dross may have an average particle size of 0.002-10.0 mm. For the purposes of the present invention, average particle size may refer to the average dimension of the height of the aluminium dross particle or the average width of the aluminium dross particle. In particular, the aluminium dross may have an average particle size of 0.01-9.0 mm,
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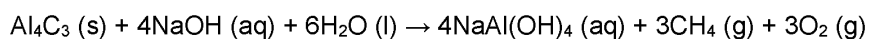
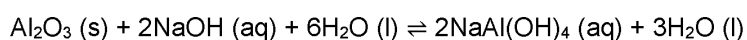
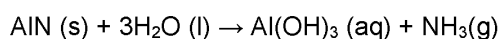
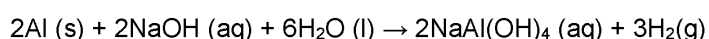
0.05-8.0 mm, 0.1-7.0 mm, 0.5-6.0 mm, 1.0-5.0 mm, 2.0-4.0 mm, 2.5-3.0 mm. Even more in particular, the aluminium dross may have an average particle size of 0.002-3.0 mm.

The mixing may comprise mixing a suitable amount of aluminium dross and sodium hydroxide to form a mixture. According to a particular aspect, the mixing may comprise mixing aluminium dross and sodium hydroxide in a weight ratio of 1:0.2-1:8. For example, the ratio may be 1:0.5-1:7, 1:0.7-1:6, 1:1-1:5, 1:1.3-1:4, 1:1.5-1:3, 1:2-1:2.5. In particular, the ratio may be 1:0.7-1:1.3. Even more in particular, the ratio may be 1:0.7.

The mixing may be at any suitable temperature. For example, the mixing may be at a first pre-determined temperature of 50-100°C. In particular, the mixing may be at a temperature of 55-95°C, 60-90°C, 65-85°C, 70-80°C, 75-78°C. Even more in particular, the temperature may be 80-100°C.

The mixing may be carried out for a suitable period of time. For example, the mixing may be for 1-4 hours. In particular, the mixing may be carried out for 1.5-3.5 hours, 1.75-3.0 hours, 2.0-2.5 hours. Even more in particular, the mixing may be for 2 hours.

The mixing may comprise the following reactions:

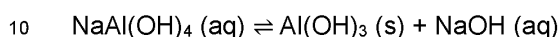
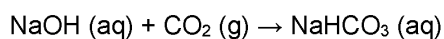


Following the mixing, the mixture may be filtered. The filtering may be by any suitable method. The filtering may be to separate a first residue from a first filtrate. The first residue may be collected and stored for further use and/or processing.

The first filtrate may comprise sodium aluminate liquor. The first filtrate may be diluted with water to obtain a diluted filtrate. For example, the diluting the first filtrate may

comprise diluting the first filtrate with a suitable amount of water. In particular, the diluting may comprise diluting the filtrate by a dilution factor of 1.5-4. Even more in particular, the dilution factor may be 2.

Once the first filtrate is diluted, the method may comprise mixing the first filtrate with
5 carbon dioxide. The mixing may comprise mixing the first filtrate with carbon dioxide may comprise flowing carbon dioxide into the first filtrate. In particular, the mixing may comprise bubbling carbon dioxide into the first filtrate. The mixing the first filtrate with carbon dioxide may comprise the following reactions:



The mixing the first filtrate with carbon dioxide results in the carbon dioxide forming carbonic acid and reacting with the sodium hydroxide in the first filtrate to form NaHCO₃. Accordingly, the pH of the first filtrate reduces. The depletion of NaOH causes the solution to seek equilibrium, which results in the sodium aluminate splitting
15 into NaOH and Al(OH)₃, with the latter precipitating as a second residue. In particular, the reaction may be considered to reach equilibrium when the pH of the first filtrate is about 7.0-8.6, preferably a pH of about 8.3-8.6.

Following the mixing, any silica comprised in the aluminium dross may become inert and may no longer be reactive to produce ammonia or hydrogen.

20 The carbon dioxide may be mixed with the first filtrate at any suitable flow rate. For example, the flowrate may be 9-20 kg/min. In particular, the flowrate may be 9-18.5 kg/min, 10-18 kg/min, 12-16 kg/min, 13-15 kg/min, 13.5-14 kg/min. Even more in particular, the flowrate may be 9-10 kg/min.

The mixing the first filtrate with carbon dioxide may be carried out under suitable
25 conditions. For example, the mixing the first filtrate with carbon dioxide may be carried out for a suitable period of time. The mixing may be carried out for a pre-determined period of time. According to a particular aspect, the pre-determined period of time may be any suitable time for enabling the pH of the first filtrate to reduce to about 7.0-8.6. For example, the pre-determined period of time may be 60-180 minutes. In particular,
30 the pre-determined period of time may be 70-160 minutes, 75-150 minutes, 90-120

minutes, 100-110 minutes. Even more in particular, the pre-determined period of time may be 120-135 minutes.

The mixing the first filtrate with carbon dioxide may be carried out at a suitable temperature. For example, the mixing may be carried out at a second pre-determined temperature. According to a particular aspect, the second pre-determined temperature may be 40-100°C. In particular, the second pre-determined temperature may be 45-95°C, 50-90°C, 65-85°C, 70-80°C, 75-78°C. Even more in particular, the second pre-determined temperature may be 55-70°C.

The mixing the first filtrate with carbon dioxide results in the formation of ATH as a residue in a second filtrate. In particular, ATH of high purity may be obtained from the method. According to a particular aspect, the purity of the ATH may be $\geq 70\%$. In particular, the purity may be 70-90%.

The method of the present invention may be carried out at any suitable pressure. In particular, the method may be carried out at atmospheric pressure. In this way, the method is a safe method and contributes to keeping the method economical.

The method may further comprise evaporating the second filtrate to form sodium bicarbonate. The evaporating may be any suitable form of evaporation. In particular, the evaporating may comprise vacuum evaporation.

According to a particular aspect, the method may further comprising heating the sodium bicarbonate to form sodium carbonate. The heating may be at a suitable temperature. For example, the temperature may be 150-200°C.

Overall, the method of the present invention forms ATH, as well as sodium bicarbonate and/or sodium carbonate. The sodium bicarbonate and/or sodium carbonate may be formed as by-products of the method, which may, in turn, be used for other purposes. Accordingly, the method of the present invention not only enables effective recycling of waste aluminium dross to obtain ATH for use in extracting metallic aluminium, but also enables production of other useful by-products.

Having now generally described the invention, the same will be more readily understood through reference to the following embodiment which is provided by way of illustration, and is not intended to be limiting.

Example

- 5 Aluminium dross was obtained and oxide layers were ground from the aluminium dross. The oxide layers were in powdered form and collected. The dross powder was chemically analysed using XRF scanning (LaFarge Aluminates Laboratory). The results of the analysis are shown in Table 1.

Component (%)	Composition (%)
Al ₂ O ₃	82.00
CaO	1.62
BaO	0.39
Fe ₂ O ₃	1.53
TiO ₂	1.39
K ₂ O	0.13
NiO	0.11
Cr ₂ O ₃	0.10
ZnO	0.07
SrO	0.03
CuO	0.05
ZrO ₂	0.07
SiO ₂	4.49
MgO	6.41
SO ₃	0.56
MnO	0.04
Na ₂ O	0.94
V ₂ O ₅	0.07

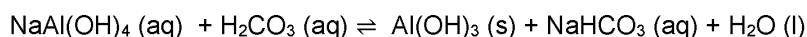
Table 1: Chemical composition of aluminium dross powder

- 10 About 100 g dross powder was then added to sodium hydroxide solution in a ratio of about 3:2 and was constantly stirred. The mixture was maintained at 100°C for 2 hours.

After two hours, sodium aluminate liquor is obtained. The liquor is filtered out from the reaction oxide residue (ROR) cake. The sodium aluminate liquor had a concentration of about 68% to remain soluble in water.

- 15 Carbon dioxide gas was then pumped into the filtered sodium aluminate liquor to form carbonic acid and H₂CO₃. Due to the high alkalinity of the liquor, the carbonic acid neutralized the NaOH that kept the sodium aluminate soluble. Therefore, the sodium

aluminate dissociated back to NaOH and aluminum trihydrate. As there was insufficient NaOH to keep the aluminum trihydrate soluble, the aluminum trihydrate precipitated out as a runny white precipitate product (WPP). The general reaction is shown below:



- 5 In order to find the effect of varying different conditions on the overall reaction, five different combination of conditions were carried out as shown in Table 2.

Sample No	Sample neutralization technique	Method description	pH endpoint achieved
1	CO ₂ at 0.38L/min for 2h	300ml of 20% NaOH + 140ml H ₂ O, 2h reaction time at 100°C, Filter, top up to 2L, CO ₂ gas used to neutralize at 300rpm (Filtered solution was cooled overnight to room temperature before neutralization)	7.95
2	CO ₂ at 0.38L/min for 2h	300ml of 20% NaOH + 140ml H ₂ O, 2h reaction time at 100°C, Filter, top up to 2L, CO ₂ gas used to neutralize at 300rpm (Filtered solution was cooled 50-60°C before neutralization)	8.12
3	CO ₂ at 0.38L/min for 2h	300ml of 20% NaOH + 140ml H ₂ O, 2h reaction time at 100°C, Filter, top up to 2L, CO ₂ gas used to neutralize at 300rpm (Filtered Solution was immediately neutralized after filtration, cooling was minimal)	8.32
4	CO ₂ at 0.38L/min for 2h	300ml of 20% NaOH + 140ml H ₂ O, 2h reaction time at 100°C, Filter, Top up to 2L, Neutralization done at 300rpm (Filtered solution was cooled to 50-60°C before neutralization)	8.5
5	CO ₂ at 0.38L/min for 2h	Same conditions as Run 4 (to test for consistency)	8.46

Table 2: Summary of different conditions used for different runs

- 10 It was observed that stirring and the stoichiometric ratio of carbon dioxide to NaOH pumped into the solution determined what compound structures were produced. With no stirring and unbalanced neutralization, the agglomerated crystal structure of Na₂O.Al₂O₃.CO₂.nH₂O was formed, which was very difficult to physically separate into individual chemically distinct components.

The obtained WPP and ROR was then subjected to various tests as follows:

- 15 *1.1 Weight analysis of WPP*

The obtained WPP was filtered out and dried in a muffle furnace at 100°C for 2-5 days before being analysed. Elemental Analysis for the dried WPP was done using XRF and TOC/TC analysis.

5 *1.2 ATH Purity, Whiteness Test, Oil Absorption Test and Moisture Measurement of Testing Run using CO₂ Neutralization Method*

Aluminum Trihydrate (ATH) purity quantification for the dried WPP was done using XRF and TOC/TC analysis. Whiteness test was done using CIE L*a*b color space. Oil absorption test is done using ASTM D281-12 and moisture measurement is done using
10 TGA analysis.

1.3 Chemical Composition Analysis of Testing Run using CO₂ Neutralization Methods

Aluminum Trihydrate purity quantification for the dried WPP was done using XRF and
15 TOC/TC analysis.

1.4 Chemical Composition Analysis of dried ROR

ROR from various runs were mixed together and a sample of 100 g was taken.
20 Analysis of the ROR was done using XRF and TGA/TC methods.
The results of the above tests are follows.

Weight Analysis of Dried Reaction Oxide Residue (ROR) and White Precipitate Product (WPP) of Testing Run

From Figure 1, it can be seen that the weight of the dried ROR from the five samples
25 are between 58.43 g and 64.59 g. There was unevenness noticed in the drying amongst all the samples even though the drying conditions were the same. From Figure 2, it can be seen that Sample 3's WPP had the lowest weight and the highest moisture loss of all the samples.

ATH Purity, Oil Absorption, Whiteness and Moisture Content of WPP of Comparison Run
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From Figures 3 to 6, it can be seen that sample 3's dried WPP has the highest ATH purity (89.84%, industrial grade) and whiteness (98.32 whiteness index), and the lowest moisture content (3.30%). Its oil absorption test level was also within range of industrial grade ATH used in paint fillers.

5 Chemical Composition Analysis of WPP from Testing Run

From Table 3, it can be seen that CO₃ contamination was common. For example, for Sample 3, the CO₃ contamination was the lowest amongst all the samples.

Chemical	Sample 1	Sample 2	Sample 3*	Sample 4	Sample 5
Al(OH) ₃	42.2309	75.6637	89.8425	77.1278	74.503
SiO ₂	0.4333	1.0180	1.1599	0.9473	0.9361
Fe ₂ O ₃	0.003	0.0364	0.0056	-	-
Na ₂ O	2.2100	3.713	1.6256	3.5587	6.5827
P ₂ O ₅	-	-	0.0054	-	-
SO ₃	0.0448	0.1224	0.0233	0.0899	0.1479
Cl	0.47	0.1238	0.6756	0.1822	0.1374
K ₂ O	0.0359	0.2019	0.0771	0.1872	0.2479
CaO	0.0329	0.0981	0.0093	0.3114	0.0919
NiO	-	-	-	0.0132	-
CuO	-	-	0.0018	-	-
ZnO	0.0069	0.1463	0.0032	0.0567	0.2057
Ga ₂ O ₃	0.0013	-	0.0035	-	-
Co ₂ O ₃	-	-	-	-	0.0167
Nb ₂ O ₅	-	-	-	0.0073	-
ZrO ₂	-	-	-	-	0.0107
Rb ₂ O	-	-	0.0007	-	-
Br	-	-	0.0010	-	-
F	-	-	-	-	-
CO ₃	54.5309	18.8764	6.5654	17.5183	17.1200
Total	99.9999	99.9999	99.9999	100.0000	100.0000

Table 3: Chemical composition of WPP

Chemical Composition Comparison of Aluminum Dross and ROR

Table 4 shows the percentage chemical composition of the originally used dross powder and the reaction oxide residue (ROR) after NaOH extraction. From the results,

it was observed that the amount of aluminum oxide had decreased to 25.73% after the process, and a 13.83-fold increase in CaO, 17.43-fold increase in BaO, and 3.14-fold increase in Fe₂O₃.

Compound	Amount in:	
	Aluminum Dross (%)	ROR (after reaction and drying) (%)
Al ₂ O ₃	82.00	60.90
CaO	1.62	22.40
BaO	0.39	6.80
Fe ₂ O ₃	1.53	4.80
TiO ₂	1.39	2.10
K ₂ O	0.13	0.90
NiO	0.11	0.60
Cr ₂ O ₃	0.10	0.60
ZnO	0.07	0.60
SrO	0.03	0.30
CuO	0.05	0.30
ZrO ₂	0.07	0.10
SiO ₂	4.49	Not measured
MgO	6.41	Not measured
SO ₃	0.56	Not measured
MnO	0.04	Not measured
Na ₂ O	0.94	Not measured
V ₂ O ₅	0.07	Not measured

Table 4: Comparison of chemical composition of aluminium dross powder and ROR

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Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A method of preparing aluminium trihydrate (ATH):
 - mixing aluminium dross with sodium hydroxide at a first pre-determined temperature to form a mixture, wherein the aluminium dross has an aluminium oxide content of $\geq 30\%$ based on the total weight of the aluminium dross;
 - filtering the mixture to obtain a first filtrate and a first residue;
 - diluting the first filtrate with water; and
 - mixing the first filtrate with carbon dioxide at a second pre-determined temperature to obtain ATH residue and a second filtrate.
2. The method according to claim 1, wherein the aluminium dross has an aluminium oxide content of 60-90% based on the total weight of the aluminium dross.
3. The method according to claim 1 or 2, wherein the aluminium dross is powdered aluminium dross.
4. The method according to any preceding claim, wherein the aluminium dross has an average particle size of 0.002-10.0 mm.
5. The method according to any preceding claim, wherein the mixture comprises aluminium dross and sodium hydroxide in a ratio of 1:0.2-1:8.
6. The method according to any preceding claim, wherein the first pre-determined temperature is 50-100°C.
7. The method according to any preceding claim, wherein the diluting comprises diluting the first filtrate by a dilution factor of 1.5-4.
8. The method according to any preceding claim, wherein the mixing the first filtrate with carbon dioxide comprises flowing carbon dioxide into the first filtrate at a flowrate of 9-20 kg/min.

9. The method according to any preceding claim, wherein the second pre-determined temperature is 40-100°C.

10. The method according to any preceding claim, wherein the mixing the first
5 filtrate with carbon dioxide comprises flowing carbon dioxide into the first filtrate for 60-180 minutes.

11. The method according to any preceding claim, wherein the mixing the first
filtrate with carbon dioxide reduces pH of the first filtrate to 7.0-8.6.

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12. The method according to any preceding claim, wherein the method is performed at atmospheric pressure.

13. The method according to any preceding claim, further comprising evaporating
15 the second filtrate to form sodium bicarbonate.

14. The method according to claim 13, wherein the evaporating comprises vacuum evaporation.

20 15. The method according to claim 13 and 14, further comprising heating the sodium bicarbonate to form sodium carbonate.