Review on Oxide Formation and Aluminum Recovery Mechanism during Secondary Smelting

Lawrence Opeyemi Osoba¹, Oluwasegun Biodun Owolabi²*, Segun Isaac Talabi³, Samson Oluropo Adeosun⁴

¹University of Lagos, Department of Metallurgical and Materials Engineering, University Road, Akoka-Yaba, Lagos, Nigeria
²National Engineering Design Development Institute, Department of Research and Development, Emma Bia, 1–3, Okpuno-Egbu Umudim, Nnewi, P.M.B 5082, Anambra, Nigeria
³University of Ilorin, Department of Materials and Metallurgical Engineering, P.M.B. 1515, Ilorin, 24003, Kwara, Nigeria
⁴e-mail: segsodje@yahoo.com

Received: 5 May 2018/Accepted: 26 June 2018/Published online: 25 July 2018
This article is published with open access at AGH University of Science and Technology Press

Abstract

The remelting, refining, and casting process of aluminum alloys often generate aluminum dross containing primarily oxides and nitrides of aluminum and entrapped metallic aluminum at the surface of the molten metal as a result of reactions within the furnace atmosphere at elevated temperatures. The handling of dross is an expensive but necessary activity during aluminum smelting. Furthermore, the amorphous Al₂O₃ oxide film formed on the pure molten aluminum surface due to the liquid metal randomly distributed atoms is impermeable to the diffusion of aluminum metal and oxygen. In amorphous materials, there is a low mobility of the charge carriers and an absence of preferred diffusion paths. This film can transform to crystalline Al₂O₃ by nucleation and grows with time and opportunity. This review discusses the mechanism of oxide formation and the aluminum metal recovery processes.

Keywords:
Al dross, Al recovery, hydrometallurgy, oxidation, oxide film

1. INTRODUCTION

Aluminum scrap recycling is a secondary production process. This metal and its alloys are 100% recyclable without property loss and can be melted and recast over and over again. Hence, aluminum is a renewable resource that has endless opportunities for generations to come.

The primary aluminum production generates more than 40 kg of Al dross per ton and about 200 kg of Al dross per ton in secondary aluminum smelting [1]. The energy required for the secondary smelting of aluminum is often estimated to be 5% of that required for primary aluminum production and yields similar quality aluminum of that obtained in the primary smelting operation [2–4]. The secondary smelting of aluminum leads to raw material saving, as the used product can be recycled instead of dumped in a landfill. Also, it helps to reduce pollutant emission to the atmosphere (~17%), with about 5- to 9-times-less solid waste and 35-times-less water consumption than the primary aluminum process [5]. Thus, recycling aluminum is beneficial and sustainable compared to primary aluminum production.

The continuous film on the liquid Al surface (known as dross) is a mixture of gases, nitrides, carbides, and other substances [6, 7]. The amount of dross formed/skinned per cycle depends on factors such as type and quality of the input material (primary aluminum and aluminum scrap), operating conditions, type of technology, and the used melting furnace [8]. About 1% of aluminum is oxidized each minute that the uncooled dross remains exposed to the air during production [9]. Aluminum dross is divided into three types; namely, white dross (wet dross), black dross (dry dross), and salt cake. The dross obtained from primary melting operations is known as white dross and is often a compact material in large clotted lumps consisting mainly of aluminum oxide (with some oxides of other alloying elements such as magnesium and silicon) and ~15–70% recoverable metallic aluminum. The dross from secondary smelting operations is known as black dross; it is granular in sizes with high metal content in the coarse fraction and chiefly oxides and salt in the fines. Lazzaro et al. [10] gave the composition of black dross from a secondary smelting as a mixture of aluminum/alloy oxides and slag, with recoverable aluminum contents ranging from 12–18%. Salt cake is a nonmetallic by-product residue from secondary smelting operations with 3–5% of metallic aluminum [11]. In the past, salt slag was used for landfilling [12]. However, the possibility of treatment has led to the minimization of its use for that purpose. This practice is the present order in Europe, the US, and Canada. Both aluminum and salt are recovered during the salt slag treatment [13].
The dross formed during aluminum smelting operations constitutes a loss and a source of inclusion in cast products. Researchers have associated Al metal loss to the furnace atmosphere as well as variations in temperature and pressure during smelting [14–16]. Consequently, the reduction in dross formation is an attractive venture that can lead to cost reduction and improved yield.

2. ALUMINUM DROSS FORMATION

One or a combination of several activities causes dross formation. Such processes include melt surface oxidation, oxide skin crushing by bath movement, oxide particles sinking and floating, oxide particle conglomeration, metallic aluminum filling up interspace, dispersed aluminum oxidation, dross skimming, and the follow-up oxidation of solids during dross cooling [17]. Antrekowitsch [17] and Freti et al. [18] recommended that cascading molten aluminum during the transfer from one process stage (e.g., melting) to another (holding in the furnace) should be eliminated by counter-tilting the furnace. The method will enable the molten aluminum to flow under an existing oxide layer without mechanical cleaning in the melting furnace afterwards. However, their study focused on a typical smelter cast house operation whose analyses apply to re-melt and casting operations.

A significant increase in the oxidation rate can result in breakaway oxidation, which is characterized by the formation of an abnormally thick oxide layer. This observation was first identified in industrial melting furnaces. An early reference to this phenomenon by Thiele [19] shows that oxidation proceeds rapidly from the beginning with alloys containing 10 and 20% Mg, while those with a 5% Mg alloy showed the phenomenon of breakup oxidation most clearly. Table 1 shows that oxidation occurred steadily for ~40 hours before the rate of weight change increased suddenly.

Table 1
Effect of Mg concentration on the percentage of formed dross [19]

<table>
<thead>
<tr>
<th>Time, hr</th>
<th>3% Mg</th>
<th>5% Mg</th>
<th>10% Mg</th>
<th>20% Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.10</td>
<td>1.0</td>
<td>1.9</td>
<td>4.25</td>
</tr>
<tr>
<td>20</td>
<td>0.10</td>
<td>1.5</td>
<td>3.9</td>
<td>8.0</td>
</tr>
<tr>
<td>30</td>
<td>0.15</td>
<td>2.25</td>
<td>4.25</td>
<td>9.25</td>
</tr>
<tr>
<td>40</td>
<td>0.20</td>
<td>3.0</td>
<td>5.00</td>
<td>12.0</td>
</tr>
<tr>
<td>50</td>
<td>0.25</td>
<td>4.0</td>
<td>4.0</td>
<td>12.25</td>
</tr>
<tr>
<td>60</td>
<td>0.25</td>
<td>5.25</td>
<td>5.25</td>
<td>12.25</td>
</tr>
</tbody>
</table>

Cochran et al. [20] investigated the oxidation phenomenon of the Al-Mg alloy observed by Thiele [19]. The researcher measured the oxidation rates of relatively small samples continuously with precise measurement techniques and presented the results in a general oxidation curve (Fig. 1). The profile summarized all of the oxidation inhibition or accelerating effects and provides a clear explanation of the formation of breakaway oxidation.

It can be seen from Figure 1 that the time interval between A and B decreases if the temperature of the metal surface increases. If the Mg concentration in the melt increased, the melted surface is “seeded” with crystalline MgO or MgAl₂O₄ and the melting is carried out more slowly. An increase will occur if a Be or Na addition is in the melt or if the melt surface was doped with boron and rapid melting and homogenization of the solid charge occur just before reaching the melt temperature.

Impey et al. [21] also investigated the effect of Mg additions to molten aluminum and obtained a 15% yield reduction in aluminum metal due to metallic aluminum entrapment within the formed dross. Silva and Talbot [22] suggested that MgO rather than MgAl₂O₄ (spinel) is responsible for the onset of breakaway oxidation and that the process starts immediately (without an incubation period) if the melt is within the zone between the liquidus and solidus temperatures. At intermediate magnesium levels between 0.005 and 2 wt.%, a mixed oxide MgOAl₂O₄ (known as spinel) is formed [22]. The oxidation mechanism was considered to start with the formation of amorphous MgO, MgAl₂O₄ or Al₂O₃ which transforms to a crystalline MgO, or MgAl₂O₄ or γ-Al₂O₃ film. The oxide films change from magnesia to spinel and finally to alumina with the progressive depletion of magnesium at the oxide melt interface.

Stewart et al. [23] studied alloy composition, scrap thickness, and the effect of organic coatings on melt loss. The result of the study showed that increasing the melting time from 40 to 105 minutes increased dross formation to between 3 and 8% of the melt. The authors recommend the removal of all coatings, and that light-gauge and finely divided scrap should be submerged in a molten bath. In another study, Stewart and McCubbin [24] investigated the effect of sheet gauge thickness, magnesium content, and coating effects on melt loss in a 22-kg gas-fired furnace. The results showed that decreasing the gauge thickness had an extreme effect on melt loss, as it increased exponentially. As the metal sheet begins to heat and melt, a tightly adhering oxide film forms when the aluminum inside the film melts drains away due to gravity effect.

Moreover, the experimental results showed that, for heavy gauge sheet (greater than 15 mm), increasing levels of magnesium content had little effect on melt loss. However, on thinner gauge sheet (0.5 mm), increasing the magnesium

https://journals.agh.edu.pl/jcme
content from 0–2.5% Mg resulted in an increased melt loss of between 4 and 8%. This observation was attributed to the thicker oxide film on the aluminum-containing magnesium alloy [24].

Wenz [25] carried out a complementary study using a sophisticated pilot scale laboratory furnace. Table 2 shows the effect of gauge thickness on the quantity of the dross formed on melting aluminum. The 0.34 mm gauge thickness shows that increasing the melt rate reduces the percentage skim from 26% (with the lowest power input) to 21% when the power input rate was increased to 117 kW. Furthermore, the effects of paints and lacquer coatings on melt loss were also investigated. In each case where coatings were present, melt losses to dross increased. The release of volatile compounds from the submerged scrap caused dross formation on the surface of the melt. The findings from their work provided much of the justification for the development of the Alcan UBC decoating process, which was based on the possibility of melt loss reduction from >15% to <5% by removing the coatings before melting.

### Table 2

<table>
<thead>
<tr>
<th>Power, kW</th>
<th>Skim weight % of charge</th>
<th>Gauge length, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>2.5</td>
</tr>
<tr>
<td>33</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>60</td>
<td>3.0</td>
<td>6.0</td>
</tr>
<tr>
<td>65</td>
<td>2.5</td>
<td>5.5</td>
</tr>
<tr>
<td>90</td>
<td>30.0</td>
<td>5.0</td>
</tr>
<tr>
<td>117</td>
<td>3.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

#### Mechanism of aluminum oxide formation

The oxidation of liquid aluminum starts with amorphous alumina layer formation due to the randomly distributed atoms of the liquid metal. This phase will transform to the crystalline form by nucleation and growth at a higher temperature [18–19]. After an incubation time of 5–10 minutes at about 750°C, the amorphous film transforms to a crystalline form of γ-Al₂O₃ or η-Al₂O₃. The transformation occurs rapidly at the melt/oxide surface. However, once the crystalline alumina has formed, ion diffusion is hindered, resulting in a low oxidation rate. After an incubation period that can last several hours based on many factors such as temperature, alloy type and environment, the structure converts to α-Al₂O₃ crystal (corundum) [20].

The amorphous oxide film is impermeable to the diffusion of aluminum metal and oxygen because of the lower mobility of charge carriers in this material and the absence of preferred diffusion paths such as the grain boundaries. The amorphous film is typically very thin, with estimated thicknesses of between 20–45 Å (10⁻¹⁰ m) [26] and about 100 Å; however, this may be up to 2–3 nm [27] and form a protective layer over the molten aluminum [20]. This film is unstable compared to the crystalline alumina [22]. During the oxidation process, cracks can form within the oxide layer and combine with the aluminum ions (with high mobility), leading to a much faster oxidation rate.

Cochran, Belitslaus, and Kinosz [20] stated that the crystalline alumina grew laterally and vertically by the continuous oxidation of the metal and not by the recrystallization of the amorphous film, whereby oxygen must be supplied from the atmosphere. At temperatures around 700°C, the lattice diffusion rate in refractory oxides such as Al₂O₃ is too slow to provide enough oxygen. Therefore, open pathways between the atmosphere environment and the melt are required to maintain the reaction between the aluminum and oxygen. Jeurgens, Sloof, Tichelaar, and Mittemeijer [28] demonstrated that, below a certain critical thickness, an amorphous film could be more thermodynamically stable than the crystalline form, owing to the relative free energy of the bulk material and the free energy of the material surface. In systems with large surface areas (i.e., a thin oxide film), the total free energy is dominated by the surface energy, which is lower in the amorphous form than in the crystalline form. In thicker films where the ratio of the surface area to the volume is low, the total free energy is dominated by the bulk energy of the material, which is higher in the amorphous form as compared to the crystalline form.

Wilson and McConnell [29] suggested that the transformation from γ-Al₂O₃ to α-Al₂O₃ is challenging to obtain in practice since the total conversion occurs on heating above 1200°C for more than one hour. However, α-Al₂O₃ crystallization has been reported by Impey et al. [30] to occur at 750°C after an incubation time of about five hours in an industrial grade 319 alloy (Al-6Si-3Cu alloy). Traces of α-Al₂O₃ were identified even at the early stages of melting. The transformation resulted in a 24% reduction in oxide volume, which causes film rupture and further exposes the liquid metal beneath to oxidation. The melt will react with oxygen to form alumina on the initially formed Al₂O₃ film [21]. Hence, the development and growth of oxide films on liquid Al alloys result from the local penetration of the film.

It has been proposed by Agema and Fray [31] that oxidation occurred through oxygen transportation in continuous pathways that penetrated the oxide film. The pathways in the oxide films at the surface of the melt could be cracks, pores, or zones of loose structure inherent in the films or formed by the volume change associated with the conversion of metal to oxide. Although Sleepy [32] had earlier proposed that oxidation caused aluminum ion diffusion through the oxide film, the difficulty of this model was the oxide was almost impermeable to both metal and oxygen diffusion. Another suggestion was that the arrival of the metal at the surface of the film was not by diffusion but by melt flow along the capillary channels, which is much faster [33].

Oxide films exhibit a variety of appearances, owing to the differences in the chemical compositions, thickness, strength, and interaction with the melts. The morphology of aluminum oxides has been categorized [32] into ‘old oxides’ (thick) and ‘young oxides’ (thin). Old oxides develop from
the thickening of the oxide that initially exists on the ingot’s surface during the melting process and during the transport of the liquid from the furnace to a crucible. Old oxides form under longer exposure times to an oxidizing atmosphere. An earlier study by Thiele [19] on the thickening of the oxide film indicated that, after five seconds at 700°C, the measured oxide film thickness on the surface of a melt was 24 nm and increased to 900 nm after being held for one hour at the same temperature.

Dignam [34] used a high purity (99.996%) aluminum foil that was oxidized at temperatures from 454–530°C. The amorphous oxide can be present up to the incubation time and then decreases with increasing temperatures. After the incubation period, transmission electron microscopy and electron diffraction showed the presence of crystalline oxide particles, which were presumed to be γ-Al₂O₃, and observed to nucleate at the metal/oxide interface [35–38].

Table 3 Composition of raw and calcined dross [wt.%] [44]

<table>
<thead>
<tr>
<th>Oxide/element</th>
<th>Raw Dross</th>
<th>Calcined Dross</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>48</td>
<td>84</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AI</td>
<td>28</td>
<td>MgO</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>7</td>
<td>SiO</td>
</tr>
<tr>
<td>NO₃-Al₂O₃</td>
<td>6</td>
<td>CaO</td>
</tr>
<tr>
<td>NaAlO₂</td>
<td>6</td>
<td>Na₂O</td>
</tr>
<tr>
<td>CaF₂</td>
<td>3</td>
<td>K₂O</td>
</tr>
<tr>
<td>Al</td>
<td>2</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>TiO₂</td>
</tr>
</tbody>
</table>

The chemical composition of aluminum dross particles before and after the purification procedure, which involved boiling the dross in water followed by stirring, cooling, milling, and vacuum filtration, was analyzed as shown in Table 4. After purification, the main constituent in the final product is found to be aluminum oxide. The aluminum in the dross is oxidized at temperatures from 4150°C for an hour, which resulted in the oxidation of phases such as aluminum nitride (AlN), Al₂O₃, calcium fluoride (CaF₂), corundum, and spinel phases, with small amounts of beta β-Al₂O₃.

Table 4 Composition comparison of a aluminum dross [45]

<table>
<thead>
<tr>
<th>Oxide/element</th>
<th>As-received, wt.%</th>
<th>After purification, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>78.24</td>
<td>94.74</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.46</td>
<td>1.56</td>
</tr>
<tr>
<td>Na₂O</td>
<td>6.28</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.47</td>
<td>0.13</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.97</td>
<td>0.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.47</td>
<td>0.53</td>
</tr>
<tr>
<td>Zn</td>
<td>0.05</td>
<td>0.53</td>
</tr>
<tr>
<td>Cu</td>
<td>0.51</td>
<td>0.55</td>
</tr>
<tr>
<td>Al</td>
<td>1.16</td>
<td>1.24</td>
</tr>
<tr>
<td>Mn</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The methods for aluminum recovery from aluminum dross [46–52] include reducing metal loss during cooling, physical separation of metal from the dross, and the remelting of the metallic fraction. Groteke [53–56] developed a method to stir hot dross for the easy separation of molten aluminum from the dross. This method combines agitation and chemical reactions, which can lead to a recovery of up to 90% of the Al in the dross. The agitation by the rable stirrer promoted Al droplet coalescence.

the thickening of the oxide that initially exists on the ingot’s surface during the melting process and during the transport of the liquid from the furnace to a crucible. Old oxides form under longer exposure times to an oxidizing atmosphere. An earlier study by Thiele [19] on the thickening of the oxide film indicated that, after five seconds at 700°C, the measured oxide film thickness on the surface of a melt was 24 nm and increased to 900 nm after being held for one hour at the same temperature.

Dignam [34] used a high purity (99.996%) aluminum foil that was oxidized at temperatures from 454–530°C. The amorphous oxide can be present up to the incubation time and then decreases with increasing temperatures. After the incubation period, transmission electron microscopy and electron diffraction showed the presence of crystalline oxide particles, which were presumed to be γ-Al₂O₃, and observed to nucleate at the metal/oxide interface [35–38]. There have been issues raised as to whether the amorphous oxide transforms into a crystalline oxide or the crystalline oxide nucleates separately. It has been observed that the oxide film growth and the solid aluminum substrate observed an orientation relationship [35]. However, with a transmission electron microscope (TEM) and electron diffraction techniques, the oxide present was identified as γ-alumina. Impey, Stephenson, and Nicholls [21] observed α-alumina in oxide films formed on molten aluminum using TEM to study the morphology of oxide films at the initial stages of oxidation. Samples were taken from the melt using a copper-loop, and the sampled material was dissolved in a 3% bromine-methanol solution to dissolve the aluminum from the oxide. The α-Al₂O₃ crystals that nucleated first were observed to be from the γ-Al₂O₃ film. Moreover, Drouzy and Mascré [39] had earlier noted that, at longer times, α-alumina is observed to form. Thus, it is accepted that this α-alumina forms from the transformation of γ-alumina.

The furnace choice may also facilitate oxide growth, and air convection may bring inclusions such as ceramic particles from furnace linings and large dust particles onto the aluminum surface [33]. If these inclusions are sufficiently heavy, they break through the oxide into the melt. These inclusions attach to the oxide layers and may become incorporated into the melt as part of a bifilm defect [33].

3. ALUMINUM RECOVERY FROM DROSS DURING SECONDARY SMELTING

Recycling aluminum dross is a challenging task in secondary smelting processes due to the difficulty in separating the oxides from the metallic aluminum even at a high temperature. Several activities described by its life cycle assessment (LCA) influence aluminum product market cost. In 2010, aluminum LCA showed that ~50% of the total ingots produced in Spain were from the secondary aluminum industry and ~20% from imported secondary aluminum [40]. At elevated temperatures in a recovery furnace, the dross will melt, and the free metallic aluminum becomes susceptible to oxidation and tends to ignite or burn in the air, emitting toxic gases [41]. This aluminum burning has been reported to significantly decrease the amount of recovered aluminum [42, 43].

Aluminum dross contains metallic aluminum as well as nitrides, carbides, and sulfides of aluminum along with some other compounds. The typical chemical composition of raw aluminum dross and calcined dross is shown in Table 3 based on the study by Yoshimura et al. [44]. The analyzed dross was calcined at 1450°C for an hour; which resulted in the oxidation of phases such as aluminum nitride (AlN), Al₂O₃, calcium fluoride (CaF₂), corundum, and spinel phases, with small amounts of beta β-Al₂O₃.

Table 3 Composition of raw and calcined dross [wt.%] [44]

<table>
<thead>
<tr>
<th>Oxide/element</th>
<th>Raw Dross</th>
<th>Calcined Dross</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>48</td>
<td>84</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AI</td>
<td>28</td>
<td>MgO</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>7</td>
<td>SiO</td>
</tr>
<tr>
<td>NO₃-Al₂O₃</td>
<td>6</td>
<td>CaO</td>
</tr>
<tr>
<td>NaAlO₂</td>
<td>6</td>
<td>Na₂O</td>
</tr>
<tr>
<td>CaF₂</td>
<td>3</td>
<td>K₂O</td>
</tr>
<tr>
<td>Al</td>
<td>2</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>TiO₂</td>
</tr>
</tbody>
</table>

The chemical composition of aluminum dross particles before and after the purification procedure, which involved boiling the dross in water followed by stirring, cooling, milling, and vacuum filtration, was analyzed as shown in Table 4. After purification, the main constituent in the final product is found to be aluminum oxide. The aluminum in the dross is oxidized to Al₂O₃ during the water treatment.

Table 4 Composition comparison of a aluminum dross [45]

<table>
<thead>
<tr>
<th>Oxide/element</th>
<th>As-received, wt.%</th>
<th>After purification, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>78.24</td>
<td>94.74</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.46</td>
<td>1.56</td>
</tr>
<tr>
<td>Na₂O</td>
<td>6.28</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.47</td>
<td>0.13</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.97</td>
<td>0.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.47</td>
<td>0.53</td>
</tr>
<tr>
<td>Zn</td>
<td>0.05</td>
<td>0.53</td>
</tr>
<tr>
<td>Cu</td>
<td>0.51</td>
<td>0.55</td>
</tr>
<tr>
<td>Al</td>
<td>1.16</td>
<td>1.24</td>
</tr>
<tr>
<td>Mn</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The methods for aluminum recovery from aluminum dross [46–52] include reducing metal loss during cooling, physical separation of metal from the dross, and the remelting of the metallic fraction. Groteke [53–56] developed a method to stir hot dross for the easy separation of molten aluminum from the dross. This method combines agitation and chemical reactions, which can lead to a recovery of up to 90% of the Al in the dross. The agitation by the rable stirrer promoted Al droplet coalescence.

https://journals.agh.edu.pl/jcme
Black dross (obtained from the secondary smelting of Al) can be managed by hydrometallurgical (the selective dissolution of metals from their waste) and pyro-metallurgical processes (the use of heat to separate metals). Pyrometallurgical processes involve high energy consumption that also requires some reducing agents and relatively high temperatures [57–59]. The hydrometallurgical leaching process is carried out either by acid or leaching. Pure aluminum sulfate, known as ‘paper-makers’ alum or filter alun \((\text{Al}_2\text{(SO}_4\text{)}_3\_12\text{H}_2\text{O})\) used in water treatment, cellulose insulation, dying, and fire-proofing fabrics was produced from aluminum black dross by the acid leaching process [60–63]. Other similar processes targeted at the recovery of pure aluminum hydroxide by the neutralization of sulfuric leach liquor and recovery of pure alumina by heat treatment of the produced aluminum hydroxide [64]. The alkaline leaching process was based on Al and Al\(_2\text{O}_3\) dissolution in a strong sodium hydroxide solution at atmospheric or high-pressure conditions. Aluminum is recovered as aluminum hydroxide by crystallization/precipitation. High-grades of metallurgical alunina will then be produced by calcination at a high temperature (1100°C) [2].

Miskufova et al. [65] examined the leaching propensity of Al from dross fines after mechanical pre-treatment in alkaline solution under atmospheric conditions. The result showed 98% of leachable Al from the dross was achieved by leaching with a 10% NaOH solution at 96°C for 120 minutes. Lucheva et al. [43] also investigated the possibility of alkaline leaching of black dross. The leach liquor consists of a 10% volume-to-volume ratio (v/v) – NaOH, with a molar ratio (alkaline module) \(\text{Na}_2\text{O}/\text{Al}_2\text{O}_3\) equal to 2. The results yield ~42% of Al and other minor elements.

Tsakiridis et al. [66] investigated the possibility of aluminum recovery from aluminum black dross by alkaline pressure leaching. The dross was crushed in a jaw crusher and ground in a ball mill to ~100 µm. Firstly, soluble salts were recovered by atmospheric pressure via water leaching, and aluminum was then recovered by pressure leaching at 200°C with sodium hydroxide. The result showed that ~57.5% of aluminum by weight was recovered using this technique.

The non-metallic byproduct residue from dross smelting operations known as “salt cake” contains 3–5% residual metallic aluminum. It is classified as toxic and hazardous waste [67], and this material is considered to be a highly flammable, irritating, and harmful but leachable substance [68, 69]. The gaseous emissions from the salt slag that result from contact with water are of great environmental concern [70–73]. Ammonia gas is produced by the hydrolysis of nitrides (pH increase) present in salt slag as described by Equations (1)–(4).

\[
\begin{align*}
\text{AIN} + 3\text{H}_2\text{O} & \rightarrow \text{NH}_3 + \text{Al(OH)}_3 \quad (1) \\
\text{AIN} + 4\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + \text{NH}_4\text{OH} \quad (2) \\
\text{Al}_2\text{O}_3\text{N} + 4\text{H}_2\text{O} & \rightarrow 2\text{AlO}_2\text{OH} + \text{Al(OH)}_3 + \text{NH}_4\text{OH} \quad (3) \\
\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4\text{OH} \quad (4)
\end{align*}
\]

Ammonia is easily soluble in water, simultaneously increasing its pH to 9 or higher. The odor of ammonia gas (\(\text{NH}_3\)) near a problematic landfill is evidence that the environment is alkaline. The high pH of the soil environment dissolves the alumina film on the unrecovered aluminum particle surface, and hydrogen is generated from the hydrolysis of metallic aluminum (Eqs. (5) and (6)) [66].

\[
\begin{align*}
2\text{Al} + 3\text{H}_2\text{O} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2 + \text{heat} \quad (5) \\
\text{Hot} \ \text{H}_2 + \text{O}_2(\text{air}) + \text{combustible} & \rightarrow \text{fire} \quad (6)
\end{align*}
\]

Methane is generated through the reaction of Al\(_2\text{C}_3\) with water (Eq. (7)). The amount of methane evolved from the salt slag is a quantitative indicator of its aluminum carbide content.

\[
\text{Al}_2\text{C}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{CH}_4 + 2\text{Al}_2\text{O}_3
\]

In the cases of increased pressures and temperatures within landfills [66], aluminum cyanide could be produced because of the presence of aluminum carbides (Eq. (8)). Aluminum cyanide hydrolysis could lead to HCN generation (Eq. (9)).

\[
\begin{align*}
\text{Al}_2\text{C}_3 + 6\text{N}_2 + 9\text{C} & \rightarrow 4\text{Al(CN)}_3 \quad (8) \\
4\text{Al(CN)}_3 + 6\text{H}_2\text{O} & \rightarrow 2\text{Al}_2\text{O}_3 + 12\text{HCN} \quad (9)
\end{align*}
\]

Finally, except for aluminum carbide and nitride, aluminum phosphide and sulfide can rapidly react with water, even with moisture of the air (Eqs. (10) and (11)).

\[
\begin{align*}
\text{AlP} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + \text{PH}_3 \quad (10) \\
\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} & \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2\text{S} \quad (11)
\end{align*}
\]

As a result, the improper disposal of aluminum slag at landfills can lead to the contamination of groundwater (e.g., F\(^{−}\), Cl\(^{−}\), NH\(_4\)\(^{+}\), CN\(^{−}\), high pH) and the ambient air (e.g., CH\(_4\), H\(_2\), NH\(_3\)) [74]. However, because of increasing local environmental and institutional barriers to the development of new landfills, the disposal of salt cake residue is anticipated to be rare and expensive [74, 75].

Nevertheless, aluminum can be recovered from this material (salt cake). This was accomplished by Tsakiridis et al. [66] via a rotary salt furnace process that involved a charge of scrap/dross and salt flux. The mechanism leading to the recovery has also been discussed in the literature [34, 66, 74]. The metal in contact with the air formed aluminum oxide at the outer surface of the melt. The “salt” shields the metal from the reactive atmosphere, which facilitates agglomeration and metal separation while enhancing metal recovery [34, 66]. The process also improves the heat transfer to the metal, inhibits oxidation, and takes up unwanted compounds such as oxides, nitrides, carbides, and others contained in the scrap or produced by reactions during the melting process. After melting, aluminum metal and salt slag were tapped from the furnace. The non-metallic components from the
raw mix were completely absorbed by the flux and formed the dross after tapping and cooling the salt slag or salt cake from the molten metal surface [76].

4. CONCLUSION

This review discussed the Al oxidation mechanism during melting and its recovery from dross. Techniques to separate Al metal from its dross such as stirring hot dross, crushing and screening cold dross, bubble flotation and leaching processes were discussed, including the oxidation formation mechanism and the causes of aluminium metal loss into the dross. The amount of dross formed/skimmed cycle depends on factors such as the type and quality of the input material (primary aluminium and/or aluminium scrap), operating conditions, type of technology, and choice of heating furnace.

REFERENCES


[68] Chemicals Decree 675/1993; amendments up to 555/2001 included, Section 3.


