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Review

Recovery of valuable products from hazardous aluminum dross: A review

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ABSTRACT

Aluminum dross is a toxic industrial waste generated in large quantities in aluminum smelter plants. The presence of leachable salts like NaCl and KCl in aluminum dross aggravates the environmental crisis, whereas the metallic aluminum entrapped in the matrix of alumina can be used as raw material for metal extraction. Pyrometallurgical methods, like rotary salt furnaces and salt-free technologies, are industrially applied for recovery of aluminum. Many hydrometallurgical technologies have been patented that consume aluminum dross to produce aluminum alum and other industrially applicable products. Newer applications of aluminum dross include its direct utilization in the production of zeolites, ion exchangers, refractories, composites, cement and concrete products and generation of gases like hydrogen, ammonia, methane. This review paper discusses the generation of aluminum dross, its environmental impacts, the industrial methods for recovery of metal from it and recent developments in its utilization.

1. Introduction to aluminum dross

The world production of metallic aluminum in 2016 was 58,890 thousand metric tons with a daily average of 160.9 tons (International Aluminum Institute, 2017). The rise of secondary aluminum production has been evident as the utilization of waste products and scraps have increased in recent years. The overall production of secondary aluminum reached nearly 60% of primary aluminum production in 2003 in European continent (Blomberg and Söderholm, 2009; Grimaud et al., 2017) with an annual increase of 2.4%, whereas it was reported by Nakajima et al. (Nakajima et al., 2007) that secondary aluminum ingot production in Japan reached 1257.7×10^3 tons. Nearly 413 million tons of secondary aluminum reserves were available globally in the year 2010 (Maung et al., 2017), a major proportion of which amassed in the landfill sites. Although newer technologies like severe plastic deformation (SPD) and powder metallurgy (P/M) have been designed to utilize aluminum scraps (Wan et al., 2017), primary and secondary aluminum smelting are still the eminent processes for the recycling of bulk aluminum scrap wastes.

Such rise in the secondary aluminum production implies higher production of aluminum dross, both in primary and secondary smelters. The primary and secondary smelters generate 1.5–2.5% and 8–15% of white and black dross per ton of molten metal produced, respectively (Mankhand, 2012). According to Gil et al. (Gil and Korili, 2016), nearly 200,000 tons of salt cakes and white dross is produced in the UK whereas the cost of waste disposal amounted to nearly 80 million Euros. Dai et al. (Dai and Apelian, 2016) reported that nearly 5 million tons of dross is generated annually. Owing to the large annual production of dross and its economic impacts, proper recycling and utilization of aluminum dross become mandatory.

The recycling of aluminum consists of sorting, salt fluxing and remelting of various products of aluminum like ingots, beverage cans, utensils, scraps, wastes etc. During the process of remelting, which is performed in a smelter plant, molten aluminum comes in contact with the atmosphere. Therefore surface oxidation takes place, forming a semisolid skim over the molten metal. After tapping the molten metal, this skim is removed (Schlesinger, 2007). This mixture, called aluminum dross, essentially consists of aluminum oxide, metallic aluminum, magnesium spinel ($MgAlO_4$), periclase (MgO), quartz (SiO_2) and salt fluxes with small traces of aluminum carbides and nitrides (Jafari et al., 2014; Mankhand, 2012; Schlesinger, 2007). Carbides and nitrides are formed due to the reactions that take place after the removal of aluminum dross from the remelting furnace (Manfredi et al., 1997; Schlesinger, 2007).

The types and composition of aluminum dross produced are described in Table 1 (Manfredi et al., 1997; Mankhand, 2012). Primary smelters usually produce white dross with higher percentages of metallic content (15–80%) because the raw material for smelting is chiefly aluminum ingot, whereas the secondary smelters produce black dross because aluminum wastes, scraps are used as raw materials. The remelting process requires fluxing of salt, which reduces the metallic content (7–50%) in the black dross. The salt cakes generated post remelting is weakly concentrated in aluminum content (3–10%) (Manfredi et al., 1997; Mankhand, 2012).

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Table 1
Types and composition of aluminum dross (Manfredi et al., 1997; Mankhand, 2012).

Type of dross	% Metallic aluminum	% Aluminum Oxide	% Salt Flux
White dross	15–80	20 − 85	< 5
Black dross	7 − 50	30 − 50	30 − 50
Salt cake	3 − 10	20 − 60	20 − 80

Due to variation in operation schemes, a variation of composition in terms of the metallic content of aluminum is found in aluminum dross samples from primary and secondary smelters. Sorting of raw material feed for production of secondary aluminum is one of the key steps in smelting process (Brommer, 2013). Operation parameters such as speed of dross removal and depth of dross removal alter the chemical composition in the dross removed. The higher speed of dross collection results in the breaking of the continuous film of oxide over the surface. This leads to the removal of aluminum along with the dross, decreasing the efficiency of the process gradually. Similarly, greater depths for collection would result in the loss of metal and fall in efficiency (Maropoulos et al., 2015). Dispinar et al. (2011) have shown that recycling of coated aluminum sheets leads to larger loss of metal to aluminum dross, as compared to uncoated metal sheets. Hence metal loss can be prevented by controlling the operation parameters.

1.1. Environmental impacts of aluminum dross

Environmental impacts of aluminum dross are detrimental. When dross comes in contact with water, hazardous gases are released including ammonia, which pollutes the atmosphere (Peng et al., 2013). Aluminum nitride finds its application in ceramic industry, as it is used as high thermal conductive refractories (Saito et al., 1994), but when dross containing aluminum nitride comes in contact with water, nitride gets decomposed and ammonia gas is released. The effluents produced in the tertiary aluminum treatment industries that recycle aluminum dross contain chemical species like Na^+, Ca^{2+}, Mg^{2+}, K^+, and N-NH_3 (Shinzato and Hypolito, 2016). Heavy metal precipitation results when these effluents are disposed into aquatic bodies. Moreover, ammonia oxidation declines in the reducing conditions at the bottom of water bodies, leading to unionized accumulation of ammonia (NH_3), which is highly toxic to aquatic organisms. The contamination of soil and groundwater is also evident in the proximity of these tertiary aluminum treatment plants (Shinzato and Hypolito, 2016). The pH of the groundwater drops down to 4 due to the action of bacteria that break down ammonia, which is highly unfavorable and the disposal of non-metallic products (NMP) in the soil increases the percentage of aluminum in the form of $Al(OH)_3$.

Toxic chemical compounds such as polychlorinated dibenzo-p-dioxins and furans (PCDD/DF) and Polybrominated dibenzo-p-dioxins and furans (PBDD/DF) exist around the secondary aluminum smelter plants. The largest quantity of these toxic chemicals is detected in the fusion feeding stage of processing aluminum waste products. At this stage, the raw materials are fed to the furnace and fusion takes place. Alloying elements, as required, are added and fusion of these materials is achieved (Wang et al., 2016). Due to incomplete combustion of compounds in this stage, these toxic chemicals are released. It has been mentioned that pretreated aluminum scrap decreases the amount of PBDD/F and reduces the impact on the environment. These chemicals are produced due to the presence of salt fluxes used in the smelter plant processes (Wang et al., 2016). The incomplete combustion of salts and the organic compounds lead to the production of such harmful compounds. The presence of such hazardous compounds is enough to indicate the effect of aluminum dross on human health and environment. Therefore aluminum dross needs proper recycling to minimize the environmental pollution by a large margin.

According to Gil (Gil, 2007), landfilling of salt slags obtained from secondary aluminum industries leads to severe environmental pollution. The amount of toxic leachable salts is quite high in saline slags and salt cakes, which makes these wastes potential water pollutants. Due to the disturbance in water composition around the landfilling sites, flora and fauna get disturbed, further upsetting the ecological balance (Gil, 2007). Landfilling of aluminum waste products can be done only when leaching of waste is avoided by sealing the waste products properly (Calder and Stark, 2010). Therefore proper measures are necessary while disposing of aluminum waste materials.

1.2. Properties of aluminum dross

When the metallic aluminum present in white dross is above 53%, granular dross particles tend to form. In case of lower metallic content, the formation of oxide is predominant (Manfredi et al., 1997). Metal losses due to entrapment of liquid metal and agglomeration of oxide films are quite significant in the assessment of the physical properties of dross. The density of dross is 0.828–1.118 tons/m^3 for granular particles and 2.396–2.528 tons/m^3 for compacted particles (Manfredi et al., 1997). The density of the pressed dross can be determined using Archimedes's principle as well as fully automatic gas pyknometer. Morphological changes of particles take place from porous to compact when there is a rapid rise in density with around 50–60% free metallic content in the dross (Kevorkijan, 2002). Gas evolution of about 0.25–1.17 L/kg of granular dross takes place when brought into contact with water, whereas compact dross leads to no gas evolution (Manfredi et al., 1997).

In order to determine the free aluminum content in white aluminum dross, dissolution of weighed aluminum dross samples into 6 N HCl is carried out. After 2 h of dissolution and vacuum filtration, the weight of the residue is collected and weighed. The difference gives the total metallic content in the dross (Kevorkijan, 2002). On the other hand, according to a theoretical model, the proportion of metallic aluminum is taken as a function of the density of pressed skull, the density of non-metallic phase and volume fraction of closed pores (Kevorkijan et al., 2013). The macrostructural and microstructural investigations using SEM justify the presence of metallic content in varying degrees.

Physical properties like volume shrinkage, bulk density, cold-crush strength and permeability of aluminum dross can be evaluated by producing bricks of aluminum dross and using them for experiments. Brick samples using 50–90% of white aluminum dross, 10–50% bentonite with a proportional amount of water are dried and sintered at varying temperatures from 303 K to 723 K for varying duration of time (8–24 h). Bricks with particle size nearly 105 μm depict highest volume shrinkage of approximately 15% with a peak bulk density is 1.9 g/cm^3 which is fair enough to serve as refractory bricks. The cold crushing strength of the bricks reaches around 940 kn/m^2, advocating the applicability of bricks, replacing the medium fireclay refractories. Permeability indicates the extent of resistance towards slag, melt or gas attack and penetration in-service period. Lower permeability implies higher resistance to slag attack (Berger, 2010). The permeability varied from 85% of 105 μm to 70% of 185 μm, which normally indicates that permeability increases with a decrease in the particle size (Adeosun et al., 2014).

The prime objective of this review paper is to study the preprocessing, treatment and utilization of aluminum dross. Many routes of processing dross have been successfully applied industrially while newer alternatives have been designed recently. For instance, utilization of white aluminum dross for generation of value-added products, such as hydrogen, presents itself as a new horizon of research. This review paper shall cover various aspects of utilizing aluminum dross to convert it into more eco-friendly products like refractories, composites, ion-exchangers.