



## Review

## Management and valorization of aluminum saline slags: Current status and future trends



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## HIGHLIGHTS

- Management of aluminum saline slags using wet and dry processes.
- Direct application of the NMPs as construction components.
- Valorization of the aluminum from NMPs as high-value-added products.

## ARTICLE INFO

## Article history:

Received 23 October 2015

Received in revised form 18 December 2015

Accepted 19 December 2015

Available online 25 December 2015

## Keywords:

Aluminum saline slag

Industrial waste valorization

Nonmetallic products

High-value-added product

## ABSTRACT

The current situation as regards the management and valorization of aluminum saline slags, also known as aluminum salt cake or salt slag, is reviewed in this work. Aluminum saline slags are produced by the secondary aluminum industry and formed during the aluminum scrap/dross melting processes. The amount of saline slag generated in these operations can vary between 30% and 60% of the metal produced, that is, between 300 and 600 kg per ton of aluminum produced. This waste contains about 3–9 wt.% metallic aluminum, 20–50 wt.% oxides, such as aluminum oxide (also referred to as nonmetallic products), 20–75 wt.% flux brines, and other components in smaller proportions. Due to their composition and possible reaction with water, saline slags are classified as hazardous waste and are included in the European List of Wastes, which means that they must be deposited in landfills or in secure deposits. Similarly, salt cake is a by-product which could be recovered provided the process is economically viable. Direct applications such as inert filling for construction, road paving, mortar components, aluminum salts, inert filler in polymer composites, adsorbents, mineral wool, have been reported. Aluminum, by chemical dissolution from the nonmetallic fraction, can also be recovered as a high-value-added product and used to synthesize materials such as pure alumina, salts, and hydroxides. This work reviews current methods for treating saline slags, with a primary focus on the synthesis of products from the nonmetallic fraction.

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## 1. Introduction

The economic and environmental benefits of aluminum recycling are obvious and significant. The most important aspect is that aluminum can be recycled almost completely, without loss of product quality. Thus, if the energy needed to produce aluminum, *primary aluminum*, and that expended during the recycling of aluminum, *secondary aluminum*, is compared, this latter process consumes only between 5% and 20% of the energy needed to produce aluminum from natural aluminum oxide, bauxite [1]. The amount and nature of the waste and effluent generated during the aluminum recycling process also means that this process has a lower environmental impact than the production of primary aluminum [2]. Despite all these advantages, the global demand for aluminum means that primary aluminum production remains the main source for obtaining this metal.

In recent years, the advisability of treating the waste generated during aluminum recycling, and how this treatment is performed, has generated a great deal of debate in the scientific and industrial communities. Various types of waste, including saline slags, are generated during the recycling process [2]. These slags form when salts are used to cover the melt scrap or dross, which mainly comprises low-quality aluminum and aluminum-rich slag. Molten salts reduce the melting temperature; protect the aluminum against oxidation; dissolve, absorb, and allow the metal oxides and other impurities to easily be separated from the aluminum metal; and promote coalescence of molten aluminum droplets into larger pools [3]. The average composition of saline slags can be summarized as follows: metallic aluminum (3–9 wt.%); oxides (20–50 wt.%), including  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ , also referred to as *non-metallic products*; flux brines (50–75 wt.%), normally  $\text{NaCl}$  and  $\text{KCl}$ ; and other components, including  $\text{NaI}$ ,  $\text{Al}_4\text{C}_3$ ,  $\text{Al}_2\text{S}_3$ ,  $\text{Si}_3\text{P}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}$ , and cryolite in smaller proportions [4]. As some of these components result from the reaction with air and moisture, their formation can be minimized by applying good process controls. The amount of saline slag generated in these operations can vary between 30% and 60% of the metal produced, that is, between 300 and 600 kg per ton of aluminum produced. Both the quantity of slag produced and the composition thereof can vary widely depending on the feed-stocks, the type of furnace used and the mode of operation thereof, and the composition of the fluxes used, among others [4–12]. Due to its composition and possible reaction with water, saline slag from aluminum recycling processes is classified as a hazardous waste in the European List of Wastes (ELW) 100308 [13], and as such must be deposited in landfills or in secure deposits. Salt cake is an additional by-product that could be recovered provided that the process is economically viable.

Several millions of tons of salt cake are produced every year, with this number increasing with the increasing use of aluminum, particularly recycled aluminum [14]. Around 95% is landfilled, at an estimated cost of 80 million euros. In the case of the UK, for example, where waste disposal-related costs are spiraling as a result of tighter regulation and landfill taxation, the industry has to dispose of around 200,000 tons of salt cake and white dross [15]. The best way of dealing with salt cake is to prevent it from being produced during the aluminum recycling process. Several salt-free melting processing options that use a plasma torch or an electrical arc as the heat source have been evaluated [16]. In both cases the furnace can be sealed and an inert gas can be used to minimize oxidation of the aluminum metal during the heating process. The advantages of these processes are that no salt flux is used and no salt cake is generated, whereas the main disadvantages are the higher cost of the electrically-generated heat source in comparison with natural gas.

Although the treatment and recovery of saline slag is important and interesting from an industrial point of view, this process must consider both environmental and economic aspects. This second aspect must take into account the energy consumed during the treatment process, the reagents and water used, and even transportation to the treatment facility or storage. Energy is also required to cool the slag to a safe temperature for transportation before it can be transported. The cooling process requires about 2–3 days. The materials that can be recovered are aluminum metal, salts and the final waste, which comprises a mixture of various metal oxides. The water used in the washing and separation processes required to recover the salts has by far the greatest impact. Economic improvements can be made to this treatment process if the amount of salt cake produced can be minimized, most of the metal present is recovered in the waste, and if less of the final *non-metallic products* fraction is obtained.

The hydrometallurgical processes involved in this waste treatment process are complex. After separation of the aluminum metal from the material by crushing and screening, the waste is treated with water to separate the soluble and insoluble fractions. This generates a new waste containing less salt and a saline solution containing the salts to be recovered. While it may seem tempting to reuse the salt in a subsequent process, recovery involves a significant energy expenditure to remove the water and obtain salts of little commercial value. In addition, this process is difficult to apply. The composition of the solid waste is very diverse and depends on the materials that have been sent for recycling treatment. This heterogeneity limits the possible applications, which is why most such waste is sent for landfill. Indeed, controlled landfill storage is currently the best alternative to saline slag management once the aluminum metal fraction has been recovered.

The treatments described would be consistent with the waste management hierarchy proposed in Directive 2008/98/EC [17]. This hierarchy is a priority for the best overall choice for the environment. However, it may be necessary to deviate from this hierarchy for specific waste streams when justified for reasons of technical feasibility, economic viability, and environmental protection, among others. The order of priority is: prevention, preparing for reuse, recycling, and disposal. As such, the first option is to try to prevent formation of the salt cake, then try to reuse, recycle and, ultimately, eliminate it, the latter process in this context being understood to be storage in landfill.

The actions that have been implemented by several companies to reduce the generation of these wastes include treatment systems for flux materials, optimization of furnace burners to control the oxidizing or reducing atmosphere, heating furnaces that avoid the combustion of organic compounds, such as electrical, plasma, and arc heating systems, and the development of new smelters (i.e., tilting rotary furnaces). Despite these improvements, it remains impossible to eliminate the generation of these materials since fluxes are necessary to maximize the recovery of aluminum.

The various options available for appropriate management of the saline cake include environmental regulations, the cost of deposit authorized landfill, and the cost of processing operations. Below we present and review the possible management options and applications of the oxides resulting from this treatment.

## 2. Saline slag treatment methods

### 2.1. Wet valorization of salt slags. Why treat the salt cake?

The reasons that justify the recovery of salt slags as first option instead of storage in landfills are twofold, namely economic benefits and as an alternative to managing hazardous waste. These

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