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# Review Aluminium salt slag characterization and utilization – A review

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### ABSTRACT

Aluminium salt slag (also known as aluminium salt cake), which is produced by the secondary aluminium industry, is formed during aluminium scrap/dross melting and contains 15–30% aluminium oxide, 30–55% sodium chloride, 15–30% potassium chloride, 5–7% metallic aluminium and impurities (carbides, nitrides, sulphides and phosphides). Depending on the raw mix the amount of salt slag produced per tonne of secondary aluminium ranges from 200 to 500 kg. As salt slag has been classified as toxic and hazardous waste, it should be managed in compliance with the current legislation. Its landfill disposal is forbidden in most of the European countries and it should be recycled and processed in a proper way by taking the environmental impact into consideration. This paper presents a review of the aluminium salt slag chemical and mineralogical characteristics, as well as various processes for metal recovery, recycling of sodium and potassium chlorides content back to the smelting process and preparation of value added products from the final non metallic residue.

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#### 1. Introduction

Aluminium is the most abundant metal and the third most abundant element in the earth's crust, after oxygen and silicon. It makes up about 8% by weight of the earth's solid surface and it never occurs as a free element in nature [1]. It is a light, conductive, corrosion resistant metal with a strong affinity for oxygen. This combination of properties has made it a widely used material, with applications in the aerospace, architectural construction and marine industries, as well as many domestic uses. Today aluminium is produced via two different routes: primary aluminium production from bauxite ore and recycling aluminium from process scrap and used aluminium products.

#### 1.1. Primary aluminium production

The production of primary aluminium consists of three steps: bauxite mining, alumina production and electrolysis. There are four different processes identified in alumina production. The



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Bayer process and three alternatives: the Sinter process, the combined/parallel Bayer-Sinter process and the Nepheline-based process. The alternative processes mainly aim at accommodating different raw materials and improving the recovery rate of alumina and in total, they produce 17% of the world's alumina. One of the most important wastes generated during the production of primary aluminium is the red mud, whose production ion varies from 1.0 to 1.6 tonnes per tonne of alumina and it is estimated that over 120 million tonnes of this waste are produced annually in the world [2]. Primary aluminium is produced entirely through the Hall-Heroult process, which involves the electrolysis of alumina dissolved in a bath of molten cryolite (Na<sub>3</sub>AlF<sub>6</sub>) at 960 °C. A significant environmental concern of the primary aluminium production is the generation of GHGs including two perfluorocarbons (PFCs), CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, which are formed as a result of the anode effects during electrolysis. Both PFCs have a global warming potential much higher than CO<sub>2</sub>. Furthermore, primary aluminium production is electricity intensive, therefore CO<sub>2</sub> emissions of the industry highly depend on the primary fuel for electricity generation [3].

#### 1.2. Secondary aluminium production

Secondary aluminium is also known as recycling aluminium. All aluminium products can be recycled after use. Recycling of aluminium is extremely important due to several economic and environmental reasons. Compared with the production of primary aluminium, recycling of aluminium products needs as little as 5% of the energy and emits only 5% of the greenhouse gas. Furthermore, it saves raw materials, whereas the waste product can be recycled instead of being sent to landfill [4,5].

In 1990 total aluminium production was around 28 million tonnes (with over 8 million tonnes recycled from scrap) and in 2010 the total was close to 56 million tonnes (with close to 18 million tonnes recycled from scrap). By 2020 metal demand is projected to have increased to around 97 million tonnes (with around 31 million tonnes recycled from scrap). Today, around 50% of the scrap is old scrap (i.e. scrap from end of life products) [5]. In Europe (European Union-25) more than half of all the aluminium currently produced originates from recycled raw materials and that trend is on the increase. Primary aluminium production currently amounts to just 3 million tonnes, whereas 4.5 million tonnes of ingots for aluminium castings, wrought aluminium (rolling ingots and extrusion billets) and deoxidation aluminium from aluminium scrap are produced [6].

The secondary industry is dependent on sources of scrap aluminium as the feedstock. Typical sources of aluminium scrap are process scrap, used beverage cans (UBCs), foils, extrusions, commercial scraps, turnings, and old rolled or cast metal. In addition to this aluminium is recovered from skimmings and dross/salt slags [7]. The scrap feed, which is a complex combination of all types of aluminium scraps collected, is loaded into melting furnaces. In secondary aluminium industry, reverberatory furnaces and rotary melting furnaces are widely used.

#### 1.3. Reverberatory furnaces

In the secondary production of aluminium, scrap can be melted in gas or oil-fired reverberatory furnaces of 13,000 to over 45,000 kg capacity. The name reverberatory derives from the consideration that heat reverberates (radiates) from the roof and walls of the furnace onto the molten metal bath [8]. The primary mode of heat transfer is through radiation from the refractory brick walls to the aluminium, but convective heat transfer also provides additional heating from the burner to the aluminium. It is a common practice to charge the scrap to the furnace metal pool through this side bay. The bay often contains a salt flux layer to help protect the molten aluminium pool from oxidation and to improve the metal recovery of the scrap. The flux usually consists of sodium chloride (NaCl) and potassium chloride (KCl) with the possible addition of a fluoride salt compound. The flux-containing dross resulting from this melting operation is called "black dross" because of its characteristic dark colour [9]. The formed dross material is skimmed periodically from the surface of the bath and can contain 20–70% aluminium. Typical aluminium reverberatory furnaces present energy efficiencies (ratio of the amount of heat absorbed by the raw material to the amount of heat from the total fuel consumed) of 15–39%, which can be increased (15%) by recuperation. The main advantages provided by reverberatory aluminium melters is the high volume processing rate, and low operating and maintenance costs. Their disadvantages are the high metal oxidation rates, low efficiencies, and large space requirements.

#### 1.4. Rotary melting furnace

Rotary melting furnaces are used to melt down the aluminium scrap and the materials containing aluminium. Their melting capacity varies from 0.5 to 0.7 tonnes per hour. The melt process is carried out under a layer of salt, which absorbs the oxides and contaminants from the scrap and protects the aluminium melt from oxidation loss (burn-off). The salt layer consists mainly of NaCl and KCl and some additional cryolite or CaF<sub>2</sub> [10]. Typical melting temperatures are around 700-750 °C. The waste gases have temperatures of typically 1000 °C for a normal operation. The advantage of the rotary furnace is that even highly contaminated scrap can be handled. The disadvantages are the high energy demand, because in addition to the metal the salt has to be melted, and the costs for the processing of the salt slag. Depending on the kind of rotary furnace used and the type of scrap being melted, anything up to 500 kg of salt slag can be generated in the production of one tonne of aluminium metal [6,11].

#### 2. Salt slag formation

Residues with more than 45% Al are called "skimming" and materials containing less than 45% Al are called "dross". Dross may also be separated into "white dross" from primary smelters without salt cover and "black dross" from secondary smelter. The white dross may contain from 20% to 45% recoverable metallic aluminium and it comprises a fine powder from skimming the molten aluminium. Typically, black dross contains aluminium metal (10–20%), a salt-flux mixture (40–55%), and aluminium oxide (20–50%). The non-metallic residues generated from scarp/dross smelting operations is often termed "salt cake" or "salt slag" and contains 5–7% residual metallic aluminium, 15–30% aluminium oxide, 30–55% sodium chloride, and 15–30% potassium chloride and, depending on the scrap type may contain, carbides, nitrides, sulphides and phosphides [12,13].

In the rotary salt furnace process, an oil or gas fired furnace is charged with the scrap/dross and a salt flux (up to 50% of the feed) is added. The metal when comes in contact with air forms oxide of aluminium at the outer surface of the melt. The salt protects the metal from the reactive atmosphere and facilitates agglomeration and separation of the metal, thereby increasing metal recovery [14]. It also enhances the heat transfer to the metal, it prevents the oxidation of the metal and takes up contaminants, such as oxides, nitrides, carbides and others contained in the scrap or produced by reactions during the melting process [15]. After melting, aluminium metal and salt slag are tapped from the furnace. The non metallic components from raw mix are completely absorbed by the liquid flux and forms after tapping and cooling the so-called salt slag or salt cake [16].

The oxide in the dross (in the raw mix) exhibits the form of a continuous net where aluminium stays entrapped. The molten flux breaks this framework and facilitates the coalescence of aluminium drops that sinks to the aluminium bath [17]. Organic contaminants after decomposition normally leave carbon in the salt slag. If there is insufficient salt, high concentration of oxides and other contaminants may lead to high viscosity levels in the molten salt. More viscous slag keeps the metal droplets entrapped and leads to significant metal loss in practise. Aluminium carbide Al<sub>4</sub>C<sub>3</sub> is formed when liquid aluminium is in contact with finely dispersed carbon, originated from organic contaminations of scrap like paints, plastic coatings, and hybrid-sandwich components. The dross containing AlN is fed into rotary furnaces, where the AlN is picked up by salt slag. Aluminium phosphide and sulphide are generated by the reaction of liquid aluminium with phosphates and sulphates in the feed [18]. The recovery efficiency of aluminium is range from 65% to 75% [19].

#### 3. Salt slag disposal

Due to the salt slag properties, it is classified as toxic and hazardous waste (100,308), according to the European Catalogue for Hazardous Wastes [20]. It is considered as "highly flammable" (H3-A: substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities), "irritant" (H4: non-corrosive substances or preparations which through immediate prolonged or repeated contact with the skin or mucus membrane can cause inflammation), "harmfull" (H5: substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, involve limited health risk) and "leachable" (H13: substances and preparations capable by any means, after disposal, of yielding another substance) [20,21].

The disposal of salt slag is a worldwide problem. In case of improper disposal, leaching of toxic metal ions into ground water would cause serious pollution problems [11,17]. The main problem is its leachability (H13) and its high reactivity with water or even humidity in air (H3-A), leading to the formation of toxic, harmful, explosive, poisonous and unpleasant odorous gases, such as NH<sub>3</sub>, CH<sub>4</sub>, PH<sub>3</sub>, H<sub>2</sub>, and H<sub>2</sub>S. The gaseous emissions from the salt slag that result from contact with water are of great environmental concern [10,21–27].

Ammonia gas is produced from the hydrolysis of nitrides (pH increase) present in salt slag.

 $2AIN + 3H_2O \rightarrow 2NH_3 + AI(OH)_3 \tag{1}$ 

 $2AIN + 4H_2O \rightarrow AI(OH)_3 + NH_4OH \tag{2}$ 

 $Al_5O_6N + 4H_2O \rightarrow 2Al_2O_3 + Al(OH)_3 + NH_4OH$ (3)

$$NH_3 + H_2O \rightarrow NH_4OH \tag{4}$$

Ammonia is easily soluble in water, increasing simultaneously its pH value up to 9 or higher. The odour of ammonia gas (NH<sub>3</sub>) near a problematic landfill is evidence that the environment is alkaline. High pH dissolves alumina film on un-recovered aluminium particle surface and hydrogen is generated from the hydrolysis of metallic aluminium.

$$2AI + 3H_2O \rightarrow Al_2O_3 + 3H_2(+heat)$$
(5)

$$Hot H_2 + O_2(air) + combustibles \rightarrow fire$$
(6)

Methane is generated through the reaction of  $Al_4C_3$  with water. The amount of methane evolved from salt slag is a quantitative indicator for its aluminium carbide content.

$$Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al_2O_3 \tag{7}$$

In cases of increased pressure and temperature (inside the landfills) aluminium cyanide could be also produced, because of the presence of aluminium carbides. Aluminium cyanide hydrolysis could lead to HCN generation.

$$Al_4C_3 + 6N_2 + 9C \rightarrow 4Al(CN)_3 \tag{8}$$

$$4\text{Al}(\text{CN})_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}_2\text{O}_3 + 12\,\text{HCN}$$
(9)

Finally, except aluminium carbide and nitride, aluminium phosphide and sulphide can rapidly react with water, even with the moisture of the air.

$$AIP + 3H_2O \rightarrow AI(OH)_3 + 2PH_3 \tag{10}$$

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S \tag{11}$$

As a result, when aluminium salt slag is disposed on hazardous waste landfills, pollution of ground water (e.g.:  $F^-$ ,  $Cl^-$ ,  $NH_4^+$ ,  $CN^-$ , high pH) and ambient air (e.g.:  $CH_4$ ,  $H_2$ ,  $NH_3$ ) can be observed. However, because of increasing local environmental and institutional barriers to the development of new landfills, the disposal of salt cake residue is expected to be forbidden or become scarce and costly.

#### 4. Chemical and mineralogical characteristics

The use of salt flux promotes the coalescence of suspended metal droplets and helps separate the clean metal from oxide contamination. At high molten-metal temperatures, the flux melts and becomes dark. Depending on the scrap mix the amount of salt slag produced per tonne of secondary aluminium ranges from 200 to 500 kg. In the past, the salt slag was land filled. Today, the salt slag treatment (minimization of land-filling problems) is generally done in Europe, US and Canada. The aluminium and the salt within the salt slag are recovered [28-30]. Its composition varies with its origins, comprising 5-7 wt% aluminium, 10-50 wt% salts, and 50-85 wt% residue-oxide, which consists primarily of aluminium oxide with minor amounts of cryolite, magnesium oxide, magnesium aluminate, and other contaminants [31]. Except oxides, contains other contaminants in lower quantities as well, like carbides and sulphides and traces of polychlorinated dibenzop-dioxins and dibenzofurans (PCDD and PCDF) [32].

Graczyk et al. reported the methods for the determination of leachable salt, total halides, aluminium metal, and elemental composition of the salt cake and salt-cake-processing intermediates [15]. Their analysis reported concentration data for up to 30 elements (wt%): Al: 25.5, Ba: 0.09, Be: <0.002, Ca: 1.23, Cd: <0.002, Cr: 0.09, Co: <0.01, Cu: 0.39, Fe: 1.58, Mg: 6.69, Mn: 0.14, Mo: <0.005, Ni: 0.02, Pb: 0.10, Si: 3.40, Sr: 0.01, Sn: 0.01, V: <0.02, K: 0.49, Na: 0.66, P: <0.10, Ti: 0.55, Zn: 0.25, Zr: <0.02, Cl: 0.59, F: 3.87, S: 0.22, C: 3.60, N: 0.54, H: 1.34. They also observed that quantities of methane were sometimes on the order of 2.5 cm<sup>3</sup> per gram of salt cake but were lower in many cases. Ethane was almost always lower than the methane by a factor of 5 or more. Regarding the amounts of CO<sub>2</sub>, it was occasionally substantial reaching levels of 15 cm<sup>3</sup> per gram of sample or, equivalently, 4 wt% carbonate in the solid.

The salt slag is basically a conglomerate of crystallized salt, solid non metallic components particles and metal beads [10]. The non metallic components particles consist mainly of aluminium oxides, oxides of alloying elements (Si, Cu, Fe, Zn, etc.), spinels, Al<sub>4</sub>C<sub>3</sub>, AlN, and AlP. Depending on the amount of salt flux used per tonne of scrap, typical salt slag contains 30–60 wt% non metallic components, with the following average contents: 7–8% Al<sub>4</sub>C<sub>3</sub>, 1% AlN, and about 0.1% AlP. AlN content could go up to 5%, if higher amounts of dross are melted together with scrap. The above phases are equated to the gas emission of 9.5–10.5 m<sup>3</sup> CH<sub>4</sub>, 1.5–13.5 m<sup>3</sup> NH<sub>3</sub>, and 0.1 m<sup>3</sup> PH<sub>3</sub> per tonne of non metallic components in salt slag [34].

Bruckard and Woodcock presented the results of chemical and mineralogical analysis of two samples of salt cake obtained from two Australian aluminium smelters [35]. Characterization data showed that the salt cakes contained at least 12 major metals present in at least 19 identifiable phases. The major elements (greater than 1%) differed for each sample, but also presented some similarities. The aluminium contents were similar at about 37% Al, the fluorine contents at 5% F, and the potassium contents at 3–4% K. However, the nitrogen contents, which were present as aluminium nitrides, range from 2% to 7% N. The intermediate elements calcium and carbon were present in similar amounts, but the others (iron, magnesium, and titanium) were variable. The minor elements are very variable. These variations are difficult to interpret, but presumably result from different feed-stocks and differences in operating practices [24,36]. The phases identified in the two salt cakes by qualitative XRD were: aluminium (Al), aluminium calcium (AlCa), aluminium nitride (AlN), aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), aluminium oxide nitride (Al<sub>5</sub>O<sub>6</sub>N), bayerite Al(OH)<sub>3</sub>, corundum  $(Al_2O_3)$ , cryolite  $(Na_3AlF_6)$ , diaoyudaoite  $(NaAl_{11}O_{17})$ , elpasolite (K<sub>2</sub>NaAlF<sub>6</sub>), halite (NaCl) and sylvite (KCl).

Davies et al. also presented the results of the chemical and mineralogical characterization of an Australian salt cake [37]. Their chemical analysis showed that eight elements were present in amounts greater than 2% (wt%): Al: 37.2, Cl: 9.39, Na: 8.52, N: 7.53, F: 5.15, K: 3.18, Mg: 2.59, Si: 2.07, Fe: 0.82, Ca: 0.72, C: 0.55, Ti: 0.13, Zn: 0.089, P: 0.065, Mn: 0.057, Ba: 0.037, S: 0.020, Pb: 0.019, V: 0.013. They reported that salt cakes are very expensive to dispose of in waste dumps because they contain many toxic compounds and many water-soluble compounds. According to the salt cake mineralogical analysis, the following phases were detected: corundum (Al<sub>2</sub>O<sub>3</sub>), halite (NaCl), aluminium nitride (AlN), elpasolite (K<sub>2</sub>NaAlF<sub>6</sub>), sylvite (KCl), bayerite (Al(OH)<sub>3</sub>), diaoyudaoite (NaAl<sub>11</sub>O<sub>17</sub>), aluminium (Al), cryolite (Na<sub>3</sub>AlF<sub>6</sub>), aluminium calcium (AlCa), aluminium oxide nitride (Al<sub>5</sub>O<sub>6</sub>N), fluorite (CaF<sub>2</sub>), gibbsite Al(OH)<sub>3</sub> iron (Fe), silicon (Si), sodalite (Na<sub>6</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>] 2NaCl) and villiaumite (NaF). Most of the sodium was present as halite (NaCl) and the potassium was present as sylvite (KCl), both of which are readily soluble in water.

According to Lopez et al., the salt slag contains about 25% Al, but with only 7.25% in the form of Al metal [38]. Their chemical composition showed also: Na: 21.89, K: 7.47, Si: 3.69, Mg: 2.83, Ca: 1.07, N: 0.71, C: 0.60, Fe: 0.50 S: 0.13. Approximately 50% of salt slag was made up of water-soluble minerals. They were halite (NaCl) and sylvite (KCl) and a small content of aluminium nitride (AlN), aluminium carbide (Al<sub>4</sub>C<sub>3</sub>) and aluminium sulphide (Al<sub>2</sub>S<sub>3</sub>). The remaining part of the salt slag contained mainly non-soluble Al, Mg, Ca and Si oxides, including corundum (Al<sub>2</sub>O<sub>3</sub>), spinel (Mg0.Al<sub>2</sub>O<sub>3</sub>), quartz (SiO<sub>2</sub>) and calcium silicate (b-CaOSiO<sub>2</sub>).

Pereira et al. examined a salt slag from a Portuguese aluminiumalloy producing industry and according to their results it is composed of a heterogeneous mass, in which two main mineral groups were found [33]: (i) water-soluble compounds, mainly alkaline salts (NaCl and KCl) but also traces of AlN, AlC<sub>3</sub> and Al<sub>2</sub>S<sub>3</sub>; (ii) non-soluble compounds in water, mainly corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), Al<sub>2</sub>S, spinel of the system MgO–Al<sub>2</sub>O<sub>3</sub>, quartz, and  $\beta$ -CaOSiO<sub>2</sub>.

Similar results were given by Gil, who presented the mineralogical characterization of Spanish salt slags [26,39]. Three are the main components: metal aluminium (6%), flux brines (28%), and oxides (nonmetal products: 66%) The composition of the non-metal products can be very variable, depending on the recycled material, making it difficult to find solutions for general recoveries. The average composition was (wt%):  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>: 40–80, MgAl<sub>2</sub>O<sub>4</sub> <40, MgO <10, Al(OH)<sub>3</sub> <5 and impurities (SiO<sub>2</sub>, M<sub>x</sub>SiO<sub>y</sub>, CaF<sub>2</sub>, AlN, etc.) <10.

Finally, Prillhofer et al. presented the differences in chemical analysis from salt slags produced at Rotary (RF) and Tilting Rotary (TRF) melting furnaces [40]. In case of RF, the chemical composition of the salt slag was: Al<sub>Metal</sub>: 10.2, Al<sub>2</sub>O<sub>3</sub>: 21.5, MgO: 3.7, SiO<sub>2</sub>: 2.8, CaO: 1.6, Na<sub>2</sub>O: 25.1, K<sub>2</sub>O: 11.5, F: 0.4, Cl: 21.9. The corresponding

values, in case of TRF, were:  $Al_{Metal}$ : 8.1,  $Al_2O_3$ : 28.6, MgO: 7.6, SiO\_2: 3.9, CaO: 1.7, Na<sub>2</sub>O: 16.2, K<sub>2</sub>O: 7.9, F: 0.7, Cl: 23.2. It should be noticed that the analyses were different, due to unequal salt factors used in Rotary (RF) and Tilting Rotary (TRF) melting furnaces. In case of TRF the Aluminium recovery was higher, but in case of RF the salt content in the final residue was lower.

#### 5. Salt slag treatment methods

The disposal of waste by-products did not constitute a major cost in aluminium production and there was no incentive to recycle reusable constituents of the waste products. In the last few years, however, public awareness and concerns about the quality of the environment have forced federal and local lawmakers to pass strict regulations on air pollution and on the disposal of various industrial wastes. As salt slag is difficult to dispose (because of the soluble nature of the salt and because of the production of toxic and explosive gases when it becomes wet) a lot of countries have banned the use of landfill for this material [41,42]. Besides, its disposal costs (operational cost) are very high, as it requires controlled landfills. Ending the need for landfill offers environmental benefits by eliminating any risk of leaching or electrolysis that could contaminate groundwater with aluminium and other metals. The increasing number of environmental regulations has forced the secondary aluminium industries in Europe and the United States to consider recycling technologies for the reduction of waste. On the other hand, the recovery of aluminium oxide became increasingly important as landfill costs increases. Processes that could convert the oxide content of salt cakes to value-added alumina products would be necessary for the profitability of salt cake recycling [31,43].

The conventional salt slag treatment consists of grinding the slag, sieving to recover the metal value, followed by water leaching at ambient or at higher temperature and pressure, to dissolve the salt in water from residue oxide [44,45]. The salt is recovered back by filtering and evaporation technique. The residue, which contains primarily alumina and other alloying elements can be used, after washing (or calcination) in various industries (cement, ceramic, building industries) [46,47].

#### 5.1. Salt slag treatment – industrial plants

The U.S. Bureau of Mines developed, in the late 1970s, a method to recover aluminium, aluminium oxide and fluxing salts from salt cake, without crushing it [48]. In this method, salt cake is leached with water, at room temperature, to produce a saturated brine slurry. The slurry is screened to yield an aluminium-rich fraction that can be returned to the rotary furnace. The remaining slurry is vacuum filtered, yielding a clear brine solution and an aluminium-oxide cake. Over 80% of the metallic aluminium and essentially all of the fluxing salts are recovered.

Several companies process black dross and salt cake through wet milling to enrich the metallic concentrate and produce byproduct brines and oxides [49]. Engitec Technologies S.p.A. installed its first system in 1977, in Italy. The process used in recovering salt from salt cake consists of the following process steps: (a) Crushing/Screening, (b) Water Leaching/Filtering, (c) Gas Elimination/Brine Purification, (d) Evaporation/Crystallization [50]. The slag as produced in the aluminium foundry is pre-crushed in a mill (impact or jaw crusher). The big lumps of aluminium are separated by screening and then the pre-crushed slag is directly leached in the water by a milling operation in special drums. From the resulting slurry the remaining Al grains are washed, separated by means of a rotating screen and finally dried to obtain about 80% recovery efficiency. The oxides slurry is filtrated on a continuous vacuum belt filter, where the oxides cake is deeply washed from the chlorides. The resulting cake has a very low chloride content (<0.2%) suitable for industrial application, as the cement production. The gas evolved during leaching, together with the gas released from the other controlled points, are conveyed and burnt in a special designed combustor, where the pollutants (mainly hydrogen, ammonia, phosphine and methane) are transformed into water and inert gases. The heat produced to destroy the pollutants is recovered to produce live steam, which is finally used to run the crystallizer for the salt production. Finally, a single or a multistage crystallizer unit has been proposed to recover the salt in form of crystals. The energy source is the steam generated by the thermo-destruction of the gases produced during the leaching.

The method proposed by Berzelius Umwelt-Service AG (B.U.S.), can process both dross and salt cake. The company operates two plants: SEGL GmbH in Luren and HANSE GmbH in Hannover. It melts aluminium scrap to produce secondary aluminium and from the salt slag obtained, it additionally extracts the remaining metal portions, and obtains aluminium oxide and pure metal, as well as the original salt from the slag mix. The first system developed was installed in Germany and the salt cake processed at this plant is supplied by five secondary aluminium smelters and contains, on average, 7% metallic aluminium [51]. The process used by the B.U.S. system consists of the following process steps: (a) Grinding/Screening, (b) Leaching, (c) Gas Treatment, (d) Solid-Liquid Separation, and (e) Crystallization [11]. According to the above process, salt slag is completely reused and treated so that no waste is produced. After drying, the material is crushed and different metal fractions are obtained, which contain approximately 80% of metallic aluminium. These metal fractions are sold to the secondary smelters for the production of cast alloys. The residue which consists of salt and oxides is then processed in the wet stage of the plant. The salt is first dissolved in water at 80 °C for 2–3 h. About  $10 \text{ m}^3$  of hydrogen (H<sub>2</sub>), ammonia (NH<sub>4</sub>), phosphine (PH<sub>3</sub>), hydrogen sulphide  $(H_2S)$  and methane  $(CH_4)$  are produced per tonne of feed material. Ammonia is scrubbed from the off-gas with sulphuric acid solution and the ammonium sulphate produced is sold to the chipboard industry or is transformed into crystalline ammonium sulphate. Activated carbon filters absorb the toxic phosphine and the hydrogen sulphide from the remaining off-gas. After the leaching process the oxide residue, after washing with fresh water (chloride content < 0.2%), is dried with air and is used as raw material to cement industry. Finally the leach liquor is put into a five stage vaporizer for the salt recovery. The process is heated by steam. The salt product with 3% moisture consists of 30% KCl and 70% NaCl and is reused as fluxing salt for the melting process. Alsa Technologies, subsidiary of Germany's AGOR Group, also produces and markets products recovered from a similar process, with a high percentage of aluminium oxides, which can be used as a raw material in cement clinker, mineral wool, synthetic calcium aluminates, ceramics, refractory materials, abrasives, glass and filler.

Alustockach also developed and commissioned one of the first salt cake processing plant in Europe. The process results in recovering salt for reuse in the melting process, aluminium granules for feeding back into the aluminium resource cycle, aluminium oxide regenerated as raw material (substitute for bauxite, cement industry, refractory, steel, ceramics) and clean water for cooling purposes. The aluminium is separated from the flux by means of selective crushing, wet milling and screening. The different metallic fractions that are separated are forwarded again to the secondary aluminium casting process. The other fraction, which consists of salts and oxides, is processed in the plant humidity phase. The produced gases are collected and suitably treated and the insoluble solids are separated from the brine.

A similar process is employed by Kali & Salz AG in Germany [52]. After drying and crushing, metallic aluminium is recovered and sold to secondary aluminium smelters, whereas the residue (<0.6 mm) consists of salt and oxides and is first dissolved in water at 100 °C. The gases produced during the leaching process are cleaned and transformed into ammonium sulphate, sodium phosphate and sodium sulphate. The cleaned gas consists mainly of methane and hydrogen and is used in drying operations for the steam production (instead of natural gas). The hot leach liquor is pumped into the crystallization plant, where the potash is crystallized by cooling in a vacuum atmosphere. The dissolved sodium chloride remains in solution and is returned to the leaching stage. Potassium chloride and ammonium sulphate are used as high-quality fertilizers. Finally, the resultant leach residue (mainly aluminium oxide) is used to cover and foster the tailings piles (80% less waste water is to be found in the piles with this way).

The only plant in France treating salt slag was introduced by RVA and it was founded in 1990. After milling and screening of the salt slag the aluminium granules are sold to the secondary smelters for the production of metallic aluminium. The residue is leach with water and the salt flux is regenerated by evaporation–crystallization (NaCl 67%, KCl 28%, Fluorspar 2%). The leached residue (mainly Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub>, CaO) can be used as a raw material in cement or ceramic industry.

The salt slag recycling process operated by Befesa Escorias Salinas SA enables the recovery of free metal and flux salts, thus creating a product made up mostly of aluminium oxide. The first stage of the process is the mechanical grinding, whose target is the extraction of metallic aluminium from the salt slag and the reduction of particles to an optimum size to ensure the total dissolution of the salts. Dissolution is carried out with water. In order to control the emission of the gases during leaching, the slurry resulting from the dissolution is taken to reactors until the reaction is complete. Subsequently, the two existing phases, brine and leach residue, are separated using a vacuum filtration. The separation of the salts from the water is done through evaporation and subsequent condensation of the steam. In this way a mixture of NaCl and KCl is obtained. The last step of the process consists of an optional drying stage in which the salts in the earlier stage of crystallization or the aluminium oxide can be dried in a rotating dryer. The salt can be utilized again as flux in the secondary aluminium industry. Furthermore, it can be used in any application in which salt is commonly used (tanning, roadway cleaning, etc.). The insoluble residue, after washing, thanks to its high aluminium-content, can be used as a raw material in cement manufacturing, ceramics industry, chemical industry, metallurgical industry and agriculture.

Alumitech (Aleris) has developed and patented a closed-loop recycling system to recover aluminium and non-metallic materials and converts them into feedstock and products [53]. The crushed salt cake from the solids preparation section is fed to a leaching tank, where the salts are dissolved in water at ambient conditions. A brine with a concentration of 22 wt% salts is produced. The insolubles (mainly aluminium oxide) are separated from the brine and washed with water to remove residual salts. The wet oxide is further processed for sale. A portion of the aluminium oxide containing aluminium is sold to the steel industry for use in exothermic compounds, de-oxidations materials and slag conditioner. The oxides not containing aluminium metal are further processed to produce ceramic fibbers. The ceramic fibbers are used as insulation in industrial applications, where temperatures can reach upward of 1100 °C.

Alreco's (MHM Metals) is involved in salt slag and black dross recycling in USA and Australia (treat all of the aluminium salt slag produced in Australia). Using the ALNAK technology, it processes salt slag and separates it into its individual components of, aluminium metal (10–20%), aluminium oxide (30–40%) and a salt and potassium chloride blend (50%), removing the requirement for any portion of the salt slag to be sent to landfill. The technology results in total waste treatment and production of aluminium and other saleable products. The technology can also be used to recycle existing salt slag landfills, recovering material from the ground, recycling and reusing the recovered commodities.

On the other hand, Gil has supported that the total recovery process of the salt cake is not economically viable [26]. In the assessment process of salt cakes, three by-products can be considered: metal aluminium (6%), flux brines (28%), and oxides (66%). According to the authors the best solution was to maximize the recovery of aluminium and dispose of the residue in controlled landfills. In his study presented the process carried out at IDALSA, a Spanish company that has developed fusion technologies for the recycling of aluminium by-products and their transformation into ingots of various shapes and chemical compositions [54]. Regarding the produced salt cake from the rotary tilting rotary furnace, it was proposed the maximization of metal recovery by means of electromagnetic and mechanical processing.

#### 5.2. Alternative salt slag treatment processes

crystallization, Alternative processes, such as freeze solvent/antisolvent extraction, common-ion effect, highpressure/high-temperature process, and capillary-effect systems have been proposed for procuring salt cake [13,55]. "Freeze-Crystallization Process" involved cooling of the solution beyond its saturation point. At this point, the salts start to crystallize and precipitate out of the solution. Cooling continued until pure ice crystals start to form and rise to the surface, resulting in the precipitation of more salts. The cooling of the solution achieved by means of indirect or direct heat exchange. With this method is possible to recover pure water and magnesium chloride from the solution in a marketable purity. Recovering the magnesium chloride is highly desirable to prevent its build-up in the recycled flux as an impurity. The "Solvent/Antisolvent Process" has been proposed as an alternative to evaporation. Initially, the crushed salt cake is leached with water at ambient temperature. The residue (aluminium oxide) in the leach effluent is washed with water to remove residual salts. The clarified brine solution is firstly concentrated to saturation using a forced-circulation evaporator. The saturated brine and recycle streams are then fed to the antisolvent reactor with acetone (acetone/water volume ratio of 1/1). "Common Ion Process" was based on the concept of salting out the salt-cake salts from a saturated solution by the addition of compounds that contain chloride ions. In case of using commercial hydrochloric acid (38% by weight hydrogen chloride), 55.2% of the salt content was precipitated. The residual acidified solution is filtered to remove the precipitated salts and reconcentrated by removing some of its water content by boiling or freeze crystallization. Finally, "High-Temperature/High-Pressure Process" was based on leaching the salts at elevated temperatures using pressurized liquid water. Increasing the temperature from about 200 °C to 300 °C, the solubility of the sodium and potassium chlorides in liquid water was increased by about 40% and 110%, respectively. Therefore, more salts could be leached at higher temperatures by each kilogram of water. The concept of leaching the salts at elevated temperatures could be integrated with more efficient separation methods, such as the freeze-crystallization processes. Except for the venting of gases generated during the leaching process (small amounts of steam), the process is closed and thus the water is recycled.

Wohlk et al. also proposed the recovery of salts and metallic aluminium for recycling, in order to produce an environmentally harmless alumina [56]. The salt slag produced in the aluminium foundry is firstly grinded in a hammer-mill. The metallic aluminium is merely deformed and is separated. The aluminium is recycled to the smelters, whereas, the salt slag is leached with water. The basic objective of the leaching process is: (1) the salt content of the slag has to be dissolved completely; (2) the solution should be concentrated as far as possible; (3) toxic gases should be removed completely; and (4) the residue (mainly oxides), after separating from salt solution, should be washed so that the chloride content to be kept less than 0.5 wt%. The leaching at temperatures near to the boiling point could lead to a fast and effective degassing reaction and the evolution of toxic gases could be completed within a short time. The salt recovery is carried out in a multi stage evaporator system, in order to reduce the energy consumption. In order to reuse the salt mixture of NaCl-KCl, as a cover salt in aluminium smelters, two are the main objective of the crystallization process: (1) a mixed salt of 65 wt% NaCl and 35 wt% KCl is preferred; and (2) the particle size distribution has to be suitable for furnace operation. The NaCl and KCl salts crystallize as the water is evaporated and liquor from the evaporator is then routed to product recovery.

Graziano et al. presented four potential salt cake recycling technologies [31]: (a) Base Case Process (leaching in water at 25 °C, with evaporation to crystallize salts); (b) High-Temperature Process (leaching in water at 250 °C, with flash crystallization to precipitate salts; (c) Solvent/Antisolvent process (leaching in water at 25 °C, with precipitation of salts by acetone addition; (d) Electrodialysis process (leaching in water at 25 °C, with concentration and recovery of salts by electrodialysis). In the solids preparation section, the salt cake is dry-crushed, screened, and magnetically separated to recover an aluminium-rich, iron-free by-product for remelting in a secondary aluminium furnace (Al recovery: 70%). When metallic particles, which can conduct electricity, pass through a magnetic field eddy currents are produced in the particles. The conducting particles are then deflected in the magnetic field and shot out of the material stream. According to this principle a separation can be made between conducting and non-conducting materials. Depending on the resistance against the magnetic field a separation between materials with variable electric conductivity is possible [57]. During leaching step with water, hydrogen, ammonia, methane, phosphine, and hydrogen sulphide are emitted. The gas treatment, for all options, consists of a thermal oxidizer, followed by a chlorine scrubber. In the "Base Case Process" the crushed salt cake from the solids preparation section is fed to a leaching tank, where the salts are dissolved in water at ambient conditions (25 °C, 1 atm) to yield a leach liquor with 22 wt% salts. The leach residue is separated from the liquor and washed with water to remove residual salts. The wet oxide residue, is landfilled or further processed for sale. The salt recovery is carried out in a forced circulation evaporator system. The NaCl and KCl salts crystallize as the water is evaporated. The slurry effluent from the evaporator is then routed to product recovery. According to the "High Temperature Process" the leaching with water is taken place at elevated temperature and pressure (250 °C and 51 atm) to yield a more concentrated brine solution (40 wt%). The hot leach effluent is then processed to remove the insoluble oxide residue. The wet oxide residue is landfilled or further processed for sale. The clarified brine is cooled and depressurized in a series of three flash crystallizers. As the water flashes and solution cools, the salts crystallize. The filtrate from the product centrifuge is recycled back to the leach reactor feed to maximize salt recovery. Finally, an alternative to evaporation is Electrodialysis [58,59]. For salt cake recycling, electrodialysis would be employed to transfer the salts from the leach effluent brine solution to a saturated brine solution, from which they would be precipitated for recovery. After water leaching at ambient conditions (25 °C, 1 atm), the clarified brine is combined with the ED cell diluate stream and fed to the ED cell. Salts in the feed stream are transferred, via the electrical driving force, through the alternating ion exchange membranes, into the saturated brine concentrate stream. The salts will precipitate as the concentration increases.

Experiments were carried out by Hazar et al. on the treatment of the salty slags, in order to obtain salt, aluminium and non-metallic products, which could be used for various purposes [60]. The original industrial salty slag was received from a plant producing Al-Si cast alloys in the rotary furnace under the presence of large amount of cover flux. The study of processing included the determination of solubility conditions of aluminium salty slags in water, precipitation of salt compounds from the solution, recovery of aluminium from aluminium rich part and separation of non-metallic products. In order to examine the effect of temperature, dissolution experiments were conducted using solid/water ratio of 1/15 at temperatures of 20, 40, 60, 80 and 100 °C for 1 h. The results showed that the temperature did not have any considerable effect on the solubility and therefore, the room temperature of 20 °C was considered to be sufficient for optimum salt solubility. The experimental results indicated that 30 min mixing period was enough for the dissolution process, within which the maximum recovery was achieved. In order to determine the usability of the recovered salt as a flux (after crystallization), aluminium rich parts of the slag (+0.125  $\mu$ m) were melted using the produced flux at 800–850 °C. The composition of the recovered flux (70% NaCl, 30% KCl) was almost the same with the original flux (69% NaCl, 29% KCl, 2% CaF<sub>2</sub>). In melting experiments carried out, using recovered and commercial fluxes the aluminium recovery ratios were estimated as 30% and 32%, respectively.

Davies et al. proposed an integrated process for the salt slag treatment and Al recovery [37]. The original salt cake consisted of rounded lumps up to about 150 mm in size with small fragments. After crushing to -2 mm, using a jaw crusher, the particles of distorted or flattened metallic aluminium contaminated with nonmetallic material were separated. Leaching tests were conducted not only on -2 mm crushed material, but on finely ground material as well, after wet grinding, at either room temperature (25 °C) or elevated temperature (60 °C), with initial pulp density of 30% solids (a liquid:solid ratio of 7:3). 90% of the Cl, 55% of the Na, and 45% of the K were extracted by aqueous leaching of -2 mm salt cake for 1 h at 25 °C. The residue from the aqueous leaching was then treated by Bayer-type digestion at 100 °C and 145 °C for 15 min was also investigated. The total Al<sub>2</sub>O<sub>3</sub> extraction (combined value from the atmospheric and pressure digestions) rose only marginally from 41.8% for the 'as-received' salt cake to 42.9% for the ground sample. Total Al<sub>2</sub>O<sub>3</sub> extraction for the water-washed sample was similar (41.2%). However, the major problem with using salt cake as part of a Bayer feed would be in the co-digestion of impurities. Of particular importance would be any remaining chlorides, phosphates, fluorides, and other salts which are in the original salt cake in higher concentrations than in bauxite. Bayer process liquors are sensitive to minor impurities in solid feeds due to the recirculating nature of the liquor.

A similar integrated flowsheet for the treatment of salt cakes was also proposed by Bruckard and Woodcock [35]. The process involved crushing and screening of the salt cake (to recover coarse aluminium metal), followed by wet grinding and screening (to recover fine metallic aluminium). Screen undersize material was then leached in cold water and the pulp filtered and washed. The solution was evaporated in solar ponds to recover the dissolved salts for recycling, while the leach residues was proposed to be treated in a Bayer digestion plant to recover residual aluminium units. All leaching tests were conducted for 4 h at either room temperature ( $25 \circ$ C) or elevated temperature ( $60 \circ$ C), with initial pulp density of 30% solids (a liquid:solid ratio of 7:3). Tests were conducted either with tap water at  $25 \circ$ C or with 16% (w/v) NaOH at  $60 \circ$ C on the  $-2 \,$ mm crushed head samples and on the dried finely ground samples. The data from the Bayer digestion process

of the leached residue indicated that total  $Al_2O_3$  extraction (combined atmospheric and high temperature extractions) was 41.9% for the crushed (-2 mm) salt cake and only slightly higher (42.9%) for the ground salt cake. The  $Al_2O_3$  extraction from the water-leached material was similar (41.2%), while extraction from salt cake previously reacted with alkaline solutions were low (typically 25–27%). These levels of  $Al_2O_3$  extraction were reasonable and were comparable to those from bauxite.

Finally a wet milling process, in combination with Eddy Current separation, for recovering aluminium metal from varied size clumps of salt cake, has been proposed [61]. The salt cake clumps have varied concentrations of aluminium metal. The method includes steps of segregating the varied size clumps into smaller clumps and larger clumps (by size) and separating (by aluminium metal concentration) the larger clumps. Separation is carried out by eddy current process. Magnetic forces are created by a conventional eddy current separator, where the magnetic forces repel the pieces having significant aluminium metal concentration from along the pieces having lower aluminium metal concentration. The reject clumps of lower aluminium metal concentration are grinded and the steps of segregation/separation are repeated. The recovered aluminium is melted and sold on the open market. Aluminium oxide, which is a by-product of the wet-milling process, is sold for use in making Portland cement. The salt is recovered from brine by evaporation and is reused as a flux in the melting process.

#### 5.3. Non metallic residue utilization

The end use of the non metallic residue (NMR) depends on the chloride content and further washing may be necessary to reduce this chloride content to manageable levels. It can be used to introduce alumina into the clinker burning process of the cement kiln, as its high alumina content is important for the formation of calcium aluminate phases. It can be also used in ceramic and refractory industry. Products resistant to high temperature are made from materials such as alumina, bauxite, corundum, spinel and aluminate cement. The NMR can act as a source of alumina in ceramic and refractory applications (building bricks, pavers, firebricks). Other possible uses of NMR are shown below:

- Civil works: inert filling for constructions, pavements, mortar components.
- Chemical industry: production of hydrate aluminium oxide and aluminium salts, epoxy resin mortar, inert load in polymers.
- Metallurgical industry: synthetic steel refining slags to remove sulphur, phosphorus and aluminium oxide from molten steel.
- Agriculture: artificial soil, fertilizers.
- Mineral wool.

Pereira et al. worked at a two-phase study, in order to determine the effect of waste additions on mechanical properties of cement mortars, involving partial replacements of either sand or cement [33]. They used a salt slag from a Portuguese aluminiumalloy producing industry, which had been firstly water leached in several conditions. Mortar preparation was conducted according to the EN196-1 procedure. Flexural and compression strengths were measured on prismatic samples after curing periods of 3, 7, 28, and 90 days in a standard testing conditions. The addition of coarse slag grains promoted deleterious effects on the mechanical properties of the mortars. Samples containing 20% and 30% of slag seemed to be weaker than the others, but the differences were decreased for longer curing periods. After 28 days, the resistance of all samples was more similar. On the contrary, the addition of washed fine-grained slag (up to 30 wt%) did not decrease the mechanical properties of the mortars. In case of cement substitutions, both compression and flexural strengths decreased with increasing slag

contents, irrespective of the curing period, a fact that would also be expected for any kind of cement for inert substitution, whatever the nature of the inert material. According to the tests results, lower tolerable levels were accepted (up to 10 wt%).

Lopez et al. presented a preliminary study, which looked at the possibility of producing a mixture of alumina and spinel by sintering the waste produced after leaching salt slag from aluminium remelting in rotary furnaces [38]. The process initially involved grinding the slag and carrying out grain screening and sizing, which leads to the recovery of most of the aluminium metal found in the original material. It then involved the water leaching of the non-metal part of the slag, once this has been ground to a grain diameter of less than 500  $\mu$ m. The fraction which was not soluble in water was pelletized and then calcined in an oxidizing atmosphere. By calcination at high temperature (1300–1500 °C), most of Al and its compounds in the residue were converted into a-Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> (spinel). It was estimated that the calcination product can be applied in fused grain, cement and glass foundry and steel mixes, refractory, mineral wool, abrasives and ceramic fibres.

A similar work has been carried out by Prillhofer et al. [40]. For the utilization of the oxidic residue in branches where alumina-rich products are used as base, the content of undesirable components such as F, Cl, metallic aluminium and Na, K, should be as low as possible. This was accomplished by thermal treatment at 1200 °C in a calcinations process. As a result, the refined residue could be used as a "value added product", in materials with high content of alumina. However, large scale industrial utilization of refined residues still have to be developed, as well-established industrial branches are hesitating to substitute their conventional materials with alternative ones [21].

Hryn et al. examined the chemical and the mineralogical composition of eight residue-oxide samples from various secondary processors [62]. It was found that the composition of residueoxide was independent of source or alloy family being processed, with the exception of slightly elevated silicon levels in two cases. The major phases detected in the residue-oxide were alumina, spinel, and aluminium hydroxides. Preliminary economic analyses indicated that the refractory market appears to be the best choice for high value-added products produced from residue-oxide with minimum processing. According to bench-scale tests, the low silicon-containing residue-oxide could be used as a raw material in the refractory market.

The NMR has been also tested as a refractory raw material for applications in the aluminium industry, especially for the bottom lining of the aluminium reduction pots [63]. Pressed tablets of the oxide residue, with a diameter of 50 mm and a height of 25 mm, were filled in drilled bores of fire-clay bricks. The tablets were covered with pieces of aluminium metal or pressed tablets of powdered cryolite bath melt. From the test with aluminium melt (800 °C for 72 h) no attack to the NMR was detected. The main components of the residue (corundum and spinel) are thermodynamically stable against aluminium metal [64]. On the other hand, in case of the test with NMR and cryolite melt (950 °C for 24 h), the NMR presented the behaviour of metallurgical alumina, while it was penetrated, but only partially and not attacked. The advantage of NMR compared to metallurgical alumina is the significantly less open porosity of the stamped material, so that less cryolite can infiltrate.

Lightweight expanded clay aggregates (LECA) were produced using clays with a high content of carbonates and thermal treated NMR in different compositions [65]. Based on the results obtained from the mineralogical investigations of preliminary experiments, NMR heat treatment was carried out in the temperature ranging of 1150-1280 °C in order to eliminate impurities, such as aluminium nitride, iron sulphite, aluminium chloride and to produce a material reach in Al<sub>2</sub>O<sub>3</sub> and spinel. Clay was mixed with ground NMR in different proportions, ranging from 9 to 37.5 wt%. The raw materials were ground and mixed in the ball mill. Plastic mass was prepared by adding 20–25 wt% of water. Comparative ceramic aggregates were also produced from the clay without adding NMP. Sintering was carried out in electric furnace for 5 min, at various sintering temperatures ranging from 1150 °C to 1270 °C. The expansion degree, density and pore structure of the produced LECA depend on the composition and sintering temperature. Apparent density of LECA sintered at the maximum expansion temperature is between 0.4 and 0.6 g/cm<sup>3</sup> irrespective of the composition. The water absorption values of LECA sintered at the maximum expansion temperature increased along with the increase in the proportion of NMP in clay composition. Fully developed pore structure, which was typical for LECA sintered in the maximum expansion temperature, consisted of macropores with mean diameter 1 mm and micropores with diameter smaller than 0.2  $\mu$ m.

Due to the fact that 50% of the world's aluminium production is used for AlSi-based cast alloys in the automotive industry, a process was proposed for the production of AlSi master-alloys, using oxide residues from of aluminium slag treatment, via carbothermic reduction [66]. The NMR used (originates from Alustockach GmbH) was a product after the treatment of salt-slags by leaching and crystallization. Silicon dioxide in the form of quartz sand was added to the aluminium residue in order to adjust the lack of silicon in the final raw meal. The reduction agent was lignite coke (with 86% of carbon) and was agglomerated together with silicon dioxide and the aluminium residues. Because of this grain size of the NMR, raw meal was agglomerated before charging into the furnace. The tests were conducted in a AC-laboratory electric arc furnace. Heating was maintained by filling the crucible with coke and forming of an electric arc. The heating period was between 30 and 60 min after reaching a temperature between 1400 and 1500 °C. According to the results, the implementation of the carbothermic reduction of used oxidic material was possible for AlSi alloy production and the electric arc furnace was proved to be a suitable technology. However, the metal yield was considered relatively low, mainly owing to the small scale equipment.

Daniels et al. have proposed the recovery of sodium aluminate from salt cake by water leaching at high temperature and pressure [67]. The salt cake was leached in a treatment tank with water at 250 °C for a time sufficient to dissolve halide (to form a saturated brine solution) and to hydrate aluminium oxide. The hydrated aluminium oxide was then separated from the saturated brine solution (and residual aluminium oxides) and thereafter mixed with caustic to form sodium aluminate which was separated for further treatment. The saturated brine solution was cooled at 20 °C to precipitate halide salts, which were recovered.

NMR has been also used in the production of mineral wool, an insulation product, which plays a significant energy conservation role in residential and industrial buildings [52]. Mineral wool is manufactured from melting natural basic rock (basalt, diabase, gabbro, amphibolites) with small amount of organic content (thermosetting resin binder and oil), using different type of fluxes (limestone, dolomite, olivine). The raw material mix needs to comprise an appropriate level of alumina (bauxite, anorthosite). The molten material is processed into fibres or wool, which undergoes further treatment, eventually being formed into various finished products of mineral wool, such as rolls, batts, and boards. A source of alumina is added in the manufacture of mineral wool in order to reduce solubility of dust particles in lung fluids preventing bronchial problems for operatives. As an alternative source has been used a NMR of aluminium salt slag with the following typical composition: 63-67% of Al<sub>2</sub>O<sub>3</sub>, 2-4% of CaO, of 7-14% SiO<sub>2</sub>, 4-8 of MgO and 1-2% of Na<sub>2</sub>O + K<sub>2</sub>O. It was observed that one of the benefits of using NMR in mineral wool production is its help in saving energy costs by decreasing the sintering and burning temperature. Depending on the furnaces' total feed mix and the chemical analyses of the desired mineral wool product, the NMR content ranged between 5% and 30% by weight.

Recently, salt cake residue has been tested as unconventional adsorbent for water and wastewater treatment (removal of Cu(II) from aqueous solutions), as this type of waste material is a mixture of oxides, with high surface reactivity and capable of removing several contaminants for removal of heavy metals from water [68]. The fractions with particle size less than 1 mm were used for activation treatments with HNO<sub>3</sub> solution (0, 0.5, 1, 1.5 and 2 mol/L) for 0.5, 4 and 24 h, at room temperature. According to the results the residue could be used as potential adsorbent. The amount of Cu(II) adsorbed per unit of mass of salt cake residue increases with increasing initial concentration of Cu(II) reaching its maximum at 0.0096 mg/g.

#### 6. Conclusions

Salt slag, a mixture of salts, aluminium oxide, aluminium metal and impurities, is a typical residue generated during remelting of scrap/dross under a salt layer in rotary furnaces (up to 500 kg of salt slag per tonne of aluminium metal). As it has been classified as toxic and hazardous waste (highly flammable, irritant, harmful and leachable), its landfill disposal is forbidden in most of the European countries and it should be recycled. The conventional salt slag treatment consists of grinding the slag, sieving to recover the metal value followed by water leaching to dissolve the salt in water, which is finally recovered by filtering and evaporation. The non metallic residue could be landfilled or further reused. However, processes that convert the oxide content of the residue to value-added alumina products are necessary for the profitability of the total process recycling. The non metallic residue can be used in a variety of applications, such as the production of cements, in ceramic and refractory applications, in chemical and metallurgical industry. Its utilization in such manners will reduce the cost of disposal and will also lead to less environmental problems.

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