

## Recovery of Flux Salts from Black Aluminium Dross

Upendra Singh<sup>1</sup> and Anupam Agnihotri<sup>2</sup>

1. Senior Principal Scientist

2. Director

Jawaharlal Nehru Aluminium Research Development & Design Centre, Nagpur, India

Corresponding authors: singhu@jnarddc.gov.in, upendra1970@gmail.com

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### Abstract

Aluminium smelter and re-melting operations generate a huge amount of industrial waste i.e. aluminium dross. This aluminium dross contains salts like NaCl and KCl which are hazardous for the environment.

Dross is classified based on aluminium content: high-grade (60–80 % aluminium, medium-grade (25–50 %), and low-grade/residual (< 25 %) based on recoverable metallic aluminium. India generates a huge amount of dross annually, mainly from primary production, recycling, and downstream processes. There are many research papers that report the hydrometallurgical methods that use aluminium dross to make aluminium alum and other products for industrial applications, these methods are also patented. Some of the recent applications of aluminium dross state its employment in manufacturing, refractory products, composite materials, concrete materials, and production of hydrogen, methane, and ammonia gases.

In recent years, extensive research has been done at JNARDDC on the recovery of flux salts at bench-scale and converting the residue into refractory to achieve the zero-waste concept. The paper reports the work expanded to salt-containing secondary dross (Black), recovering salts, and maximizing alumina content. More than 97 % of salts have been recovered during the process using leaching and precipitation. This approach transforms low-grade dross into a valuable alumina (> 98 %) source, converting refractory products. This will help the industry to curtail the expenses towards purchasing salt for metal recovery and save money.

This process will enhance the environmental sustainability of dross management by minimizing waste, enabling salt re-use, and alumina value addition. Also, a safe and cleaner technological process is the demand of time, and in this regard, the utilization of waste dross for the recovery of salt is an alternative to recycle/reuse which will not only reduce the slag generation but also solve environmental issues.

**Keywords:** Black aluminium dross, Sodium-Potassium Chloride salts, Dross slag, Refractory products.

### 1. Introduction

To produce secondary aluminium, the melting of aluminium scrap along with white dross is carried out within a rotary furnace, which contains an oxyfuel/air fuel burner [1–3]. The salt fluxes are added in the process to cover the surface of the molten aluminium bath. This will help in the agglomeration and separation of aluminium in molten form, within the solid oxide part, protecting the metallic aluminium from oxidation [4, 5]. The non-metallic components content will be entirely absorbed by this liquid flux, which generates a black color residue known as black dross (BD). Black aluminium dross (BAD) is a complex and contaminated byproduct formed during the secondary aluminium and aluminium dross recycling, mainly due to the use of chloride-based fluxes such as sodium chloride (NaCl), potassium chloride (KCl), and potassium aluminium

fluoride (PAF). These fluxes, typically used in rotary furnaces in a 3:1 or 2:1 NaCl to KCl ratio, along with small amounts of fluoride salts like  $KAlF_4$  or NaF, aid in metal recovery, prevent oxidation, and separate impurities. However, this process also leads to the generation of black dross, a residue containing salts, carbides, nitrides, and residual aluminium. This black dross is collected from the upper layer of the molten metal. Generally, 200–600 kg BD are generated in one tonne of aluminium metal, depending on the scrap mixture used [6, 7]. In 2013, it was reported that 1.1 million tonnes of BD were generated worldwide [7]. The black dross contains some amount of metal aluminium (Al), a high content of NaCl, KCl,  $Al_2O_3$ , and other impurities like  $Al_4C_3$  and AlN. Because of these contents and properties like leaching and impurities ( $Al_4C_3$  and AlN), BD is declared as a toxic and hazardous industrial waste. BD gives emission of  $NH_3$ ,  $CH_4$ ,  $PH_3$ ,  $H_2$ ,  $H_2S$ , etc., some poisonous, explosive and harmful gases if they come in contact with humidity [6, 8–11].

Iron, present in most aluminium scrap, forms intermetallic compounds like  $FeAl_3$ , while magnesium, especially from 5XXX series alloys, forms stable compounds such as  $MgO$ ,  $Mg_3N_2$ , and  $MgAl_2O_4$ . These Fe- and Mg-based compounds increase the non-metallic content of black dross, reduce aluminium recovery efficiency, and make the recycling process more challenging compared to white dross from primary production. Hence, the further treatment and disposal of this BD is very necessary for the betterment of environmental impacts. The proper disposal in the landfill will also solve the purpose of groundwater pollution. This will be decided by the economic and justifiable regulations of the particular country.

In general, the dross treatment processing can be of two types: hot and cold processing techniques. For white dross processing, generally hot processing route is adopted. The industrial approach for processing of black dross is the cold processing technique, which is either a wet or dry process. In this process, the BD is trapped directly and dried naturally by spreading it on the open floor before any further treatment [3]. After drying naturally, it is crushed and sieved to separate out the aluminium metal content from the salt cake [3, 12]. The wet process involves water leaching. The insoluble oxides will be filtered out and can be taken for recycling and extraction, and the salts will be contained in the filtration water, which is then evaporated and crystallised to extract the salts [3, 8, 10]. The present studies focus on the recovery of salt from waste aluminium dross and the application of the remaining dross in suitable refractories.

## 2. Methodology

### 2.1 Sample Collection

About 100 kg of aluminium dross sample was collected manually (Figure 1) from Shanark Industries, Butibori, a wholesaler of aluminium products and aluminium alloy sheet in Nagpur. The whole sample was packed in a plastic bag. The utmost care was taken while transporting the sample to JNARDDC. The sample was found to be heterogeneous as it contains metals and oxides of aluminium.

### 2.2 Sample Preparation

The aluminium dross sample was prepared by crushing and grinding using a ball mill machine for around 30 minutes. After homogenizing the whole lot, the quantity was reduced to around 1 kg using the quartering and coning method to make a representative sample of the same lot.

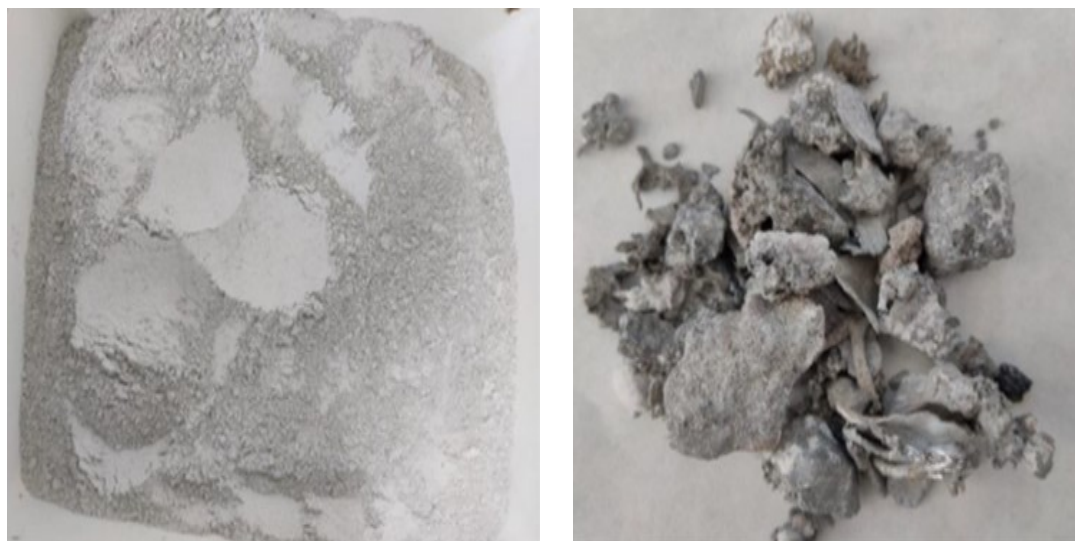
The whole sample was treated as a lot. The dross sample was pulverized and classified into two main parts, lumpy and powder dross. Big-size metals shown in Figure 2 were separated by hand picking and kept separately. The rest of the sample was screened using a standard sieve of mesh no 5 (i.e. 4 mm). The powder-fine dross sample shown in Figure 2 was screened from medium-

sized particles. The undersize was treated as low-grade aluminium dross as it contains a lower metal value and is uneconomical for metal recovery by conventional metallurgical processes such as melting.

Undersize mainly consists of metal oxide and a small portion of metallic aluminium. Oversize (+ 5 mesh) was obtained to be 0.2 kg and undersize (-5 mesh) was found to be 0.8 kg. Undersize mainly consists of metal oxide and small portion of metallic aluminium. Over size consists of metallic aluminium in lumpy form and used for recovery of metal. Under size around 0.5 kg was further pulverised and homogenized for chemical characterization. Finally, a 100-g sample was taken for physicochemical characterization



**Figure 1. Manual collection of aluminium dross.**

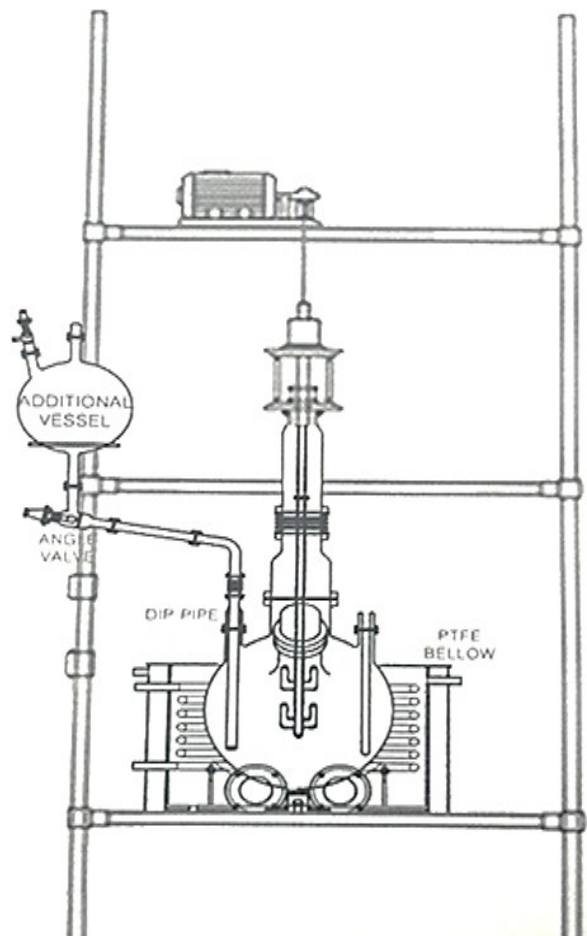


**Figure 2. Fine dross and recovered metal.**

### **2.3 Leaching Reactor**

A flat-bottomed borosilicate glass reactor (1 L) with a PTFE agitator fitted with a heating mantle was used to handle the acidic reactants (Figure 3). A stirrer with variable speed from 0 to 150 rpm was used for mixing solid and acid. The reaction was initiated by introducing 160 mL of 3NHCl solution through the side vessel neck. Around 100 g of Al dross was poured in the flask from side neck. The agitator was continuously stirring at 100 rpm at the time of addition. The temperature

of the process was maintained at 90 °C and it was measured by a specially designed thermometer. After the dross introduction, the flask was corked to minimize any further gaseous loss.



**Figure 3. A Schematic of the leaching reactor for Al dross.**

The schematic process flow chart for processing the Al dross is shown in Figure 4, it includes the following steps: Pulverization and Sieving of the waste aluminium dross to obtain a homogeneous sample, Conditional leaching of the dross at various parameters (pH, time, volume, solid/liquid ratio), Filtration, evaporation and separation of leach liquor from the dross. Washing and calcination of dross residue after recovery of salts, Product validation for suitable application.

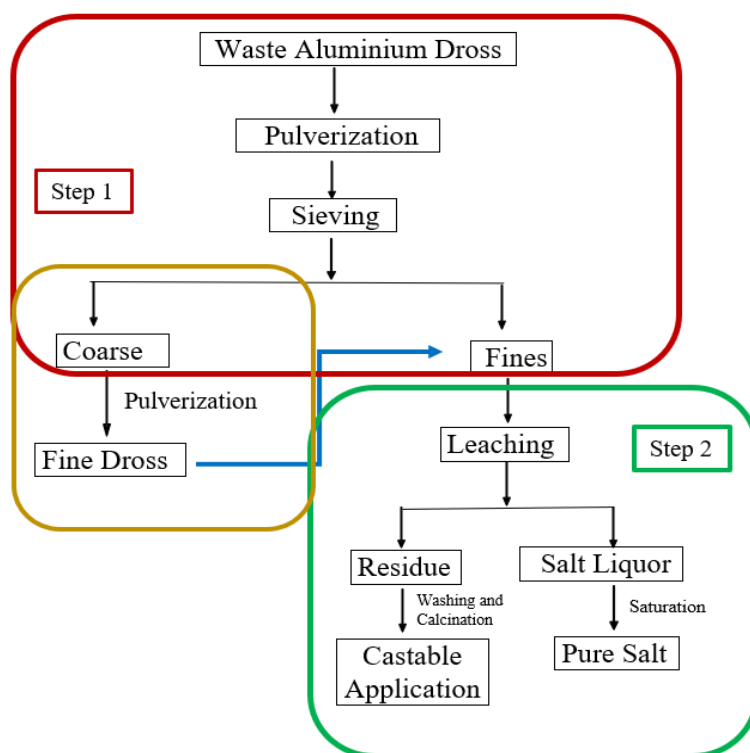


Figure 4. Process flow sheet.

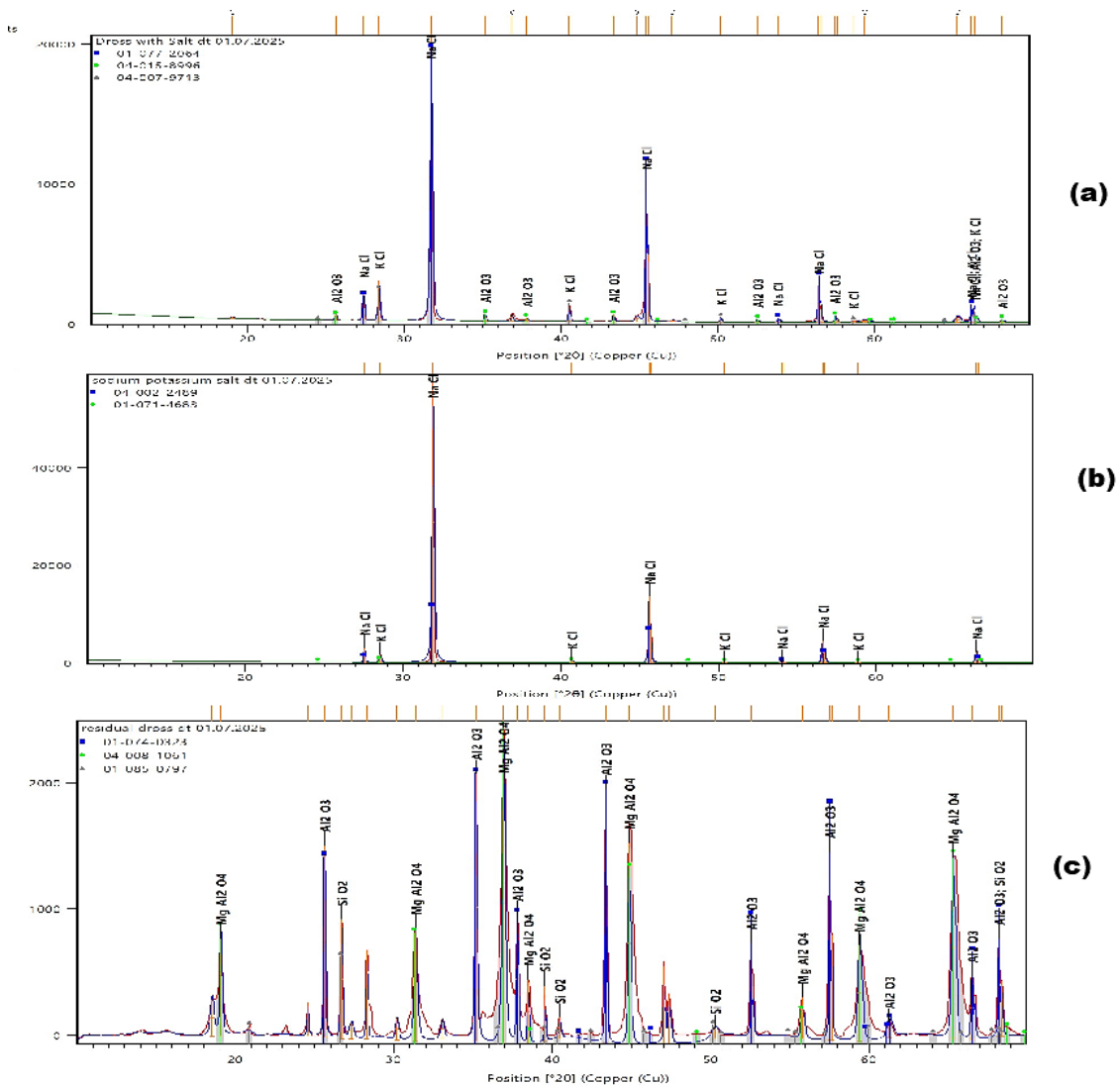
### 3. Results and Discussion

After screening, a dross sample was taken for chemical analysis and leaching tests. 5 g of dross was mixed with HCl and kept on a hot plate for 1 hour. After cooling, the solution was filtered and analyzed for metallic aluminium and other constituents. The characterization of the dross of the major elements was performed using conventional wet analysis procedures, while ICP-OES for the trace elements and complete analytical data are presented in the Table. 1

Table 1. Typical chemical analysis of black aluminium dross.

Sr. No.	Constituents	% Concentration
1.	Al <sub>2</sub> O <sub>3</sub>	21.313
2.	CaO	0.704
3.	Fe <sub>2</sub> O <sub>3</sub>	0.318
4.	MgO	3.246
5.	MnO <sub>2</sub>	0.055
6.	TiO <sub>2</sub>	0.458
7.	Na <sub>2</sub> O	35.227
8.	SiO <sub>2</sub>	1.426
9.	P <sub>2</sub> O <sub>5</sub>	0.045
10.	SO <sub>3</sub>	0.073
11.	Cl	32.865
12.	K <sub>2</sub> O	2.347
13.	Total Fluoride	1.849

The secondary aluminium dross used in the present work contains a flux ratio of 9:1, i.e., 9 % NaCl + 1% KCl. This ratio of the fluxes used in the dross can be more clearly seen from the XRD analysis results. In the XRD diffractogram Figure 5(a), the spectra shows the diffraction pattern of the dross used in the present study, it shows the presence of NaCl, KCl, and Al<sub>2</sub>O<sub>3</sub>. In Figure 5(b), the spectra of the recovered fluxes shows that both NaCl and KCl phases appear in the diffractogram. The Figure 5(c) spectra of residual dross shows the presence of alumina in various phases. The significant phase of recovered alumina is certainly corundum, which is also known as alpha-alumina. Analysis of the diffractogram shown in Figure 5(c) indicates a sharp peak at (2θ - 38.5°), which is attributed to the presence of aluminium metal in the dross. Other trace analysis reveals the presence of aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), Spinel (MgAl<sub>2</sub>O<sub>4</sub>), diaoyudaoite (NaAl<sub>11</sub>O<sub>17</sub>), Al<sub>4</sub>C<sub>3</sub>, and aluminium nitride (AlN). The phase NaAl<sub>11</sub>O<sub>17</sub> is called β-alumina.



**Figure 5: XRD analysis of aluminium black dross.**

After leaching of the aluminium black dross, two fractions were obtained, on one side the residual waste which can be used in the castable, and on the other side the recovered salt liquor which then undergoes filtration and crystallization to get the pure NaCl salt.

Figure 6 shows the residue and the salt after leaching.



Figure 6. Residue and salt after leaching.

The obtained salt is taken for elemental analysis through ICP-OES, the result obtained is shown in Table 2.

Table 2. Chemical analysis of leached liquor for Na and K salt extraction.

Constituents	F	Na	Mg	Al	Si	P	S
% Conc.	0.890	35.133	0.143	0.064	0.012	0.014	0.146
Constituents	Cl	K	Ca	Br			
% Conc.	59.011	4.524	0.057	0.004			

Total extracted salts after crystallization:



NaCl = 89.353 g

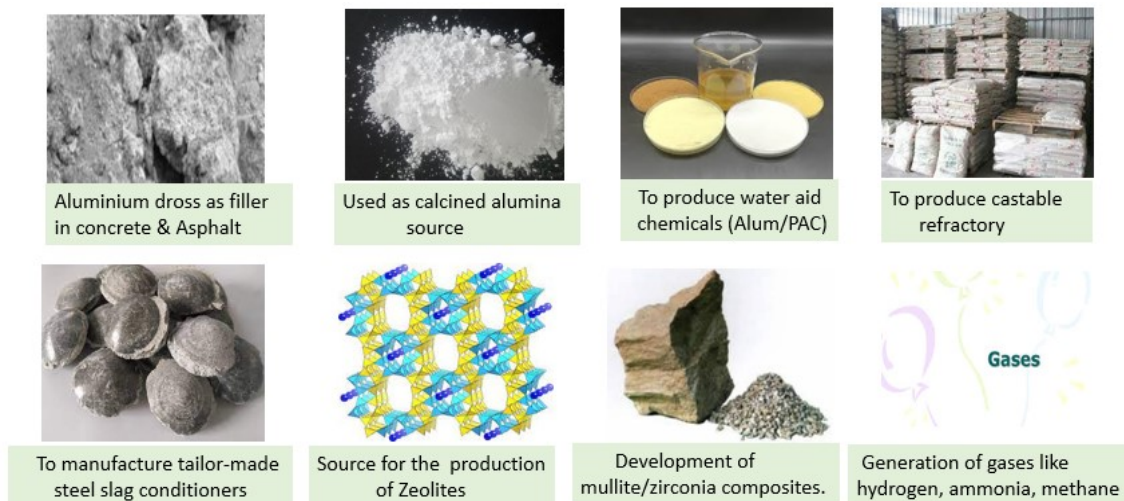
KCl = 8.645 g

As the Na and K salts are recovered from the Al black dross, the residue is left, containing mainly Al and Fe. The elemental analysis for the residue is shown in Table 3.

Table 3. Chemical analysis of dross residue obtained after leaching.

Constituents	F	Na	Mg	Al	Si	P	S
% Conc.	4.558	0.094	12.003	71.749	4.521	0.001	0.002
Constituents	Cl	K	Ca	Fe			
% Conc.	0.231	0.021	1.817	1.282			

The commercial applications of residual dross remaining after the recovered fluxes are as shown in Figure 7. The residual dross has been tested for castable application and further studies are under progress for other suitable application in refractory.



**Figure 7. Commercial applications of residual dross.**

#### 4. Conclusions

- This process enhances the environmental sustainability of dross management by minimizing waste and enabling salt reuse.
- A safe and cleaner technological process is the demand of time and in this regard, the utilization of waste dross for recovery of salt from it is an alternative to recycle/reuse which will not only reduce the waste generation but also solve environmental issues.
- Process know-how for NaCl and KCl salt extraction and residual dross for suitable refractory applications.
- The dross residue after recovering the fluxes is rich in  $\text{Al}_2\text{O}_3$  and can have potential refractory applications like filler in concrete & asphalt, as a calcined alumina source, water aid chemicals (Alum/PAC), castable refractory, steel slag conditioners, production of zeolites, mullite/zirconia composites, gasses generation like hydrogen, ammonia, methane, and others.

#### 5. References

1. Antonio. Gil et.al., Management of the Salt Cake from Secondary Aluminum Fusion Processes, *Industrial & Engineering Chemistry Research*. Vol. 44, No.23 (2005), 8455-8944.
2. J.A. Tenorio and D.C.R. Espinosa, Alloy Production and Materials Manufacturing, in *Handbook of Aluminum*: CRC Press, 25 April 2003, 115–155.
3. M.E. Schilesinge, *Aluminium Recycle*, 2nd ed. Boca Raton,FL: Taylor & Francis, 2013.
4. O. Majidi, S.G. Shabestari, and M.R. Aboutalebi, Study of fluxing temperature in molten aluminum refining process, *J. Mater. Process. Technol.* Vol. 182, No. 1–3, 2 February 2007, 450-455
5. C.F. Beur, J.H. Hussey, B. Langston, and N.M. Parikh, Process for preparing substituted 5-fluoro-1H-pyrazolopyridines, *U.S. patent 4501614*, 1985.
6. X.-L. Huang, A.E. Badawy, M. Arambewela, R. Ford, M. Barlaz, and T. Tolaymat, Characterization of salt cake from secondary aluminum production, *J. Hazard Mater*, Vol. 273, (2014) 192-199.
7. P.E. Tsakiridis, P. Oustadakis, and S. Agatzini-Leonardou, Aluminium recovery during black dross hydrothermal treatment, *J. Environ. Chem. Eng.* Vol. 1, No.1-2, (2013) 23-32.
8. W.J. Bruckard and J.T. Woodcock, Characterisation and treatment of Australian salt cakes by aqueous leaching, *Miner. Eng.*, Vol, 20 (2007), 1376-1390

9. W.J. Bruckard and J.T. Woodcock, Recovery of valuable materials from aluminium salt cakes, *Int. J. Miner. Process*, Vol. 93 (2009), 1-5
10. S.R. Rao, *By-Product Processing and Utilization*, New York: Elsevier, 2006.
11. H. Shen and E. Forssberg, Black dross: processing salt removal from black dross by thermal treatment, *Waste Manag.* Vol. 23, (2003).
12. O. Manfredi, W. Wuth, and I. Bohlinger, Characterizing the physical and chemical properties of aluminum dross. *JOM*, Vol. 49 No.11, (1997) 48-51.
13. M. Davies, P. Smith, W.J. Bruckard, and J.T. Woodcock, Treatment of salt cakes by aqueous leaching and Bayer-type digestion, *Miner. Eng.* 21, 605 (2008).
14. J.Y. Hwang, X. Huang and Z. Xu, Recovery of metals from aluminium dross and salt cake, *Journal of Minerals & Materials Characterization & Engineering*, Vol. 5, No. 1, (2006), 47–62

