Characterization of aluminium black dross before and after stepwise salt-phase dissolution with glycerol and ethanol washing

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Introduction

Aluminium black dross, enriched with high amount of salts (e.g., 50-60 wt. % NaCl, KCl), is the by-product of the secondary aluminium industry. The Chemical and mineralogical composition of aluminium black dross varies significantly due to the different raw materials and metallurgical process used in production (Das *et al,* 2007). Generally, it contains a small amount of metallic aluminium, a large amount of the salt-flux mixture used during processing (e.g., NaCl and KCl), aluminium oxide (Al_2O_3), as well as other contaminants (e.g., Al_4C_3 and AlN) (Yoshimura *et al*, 2008). Black dross has a potential commercial value if it can be recycled in a proper way. However reactive contaminant species present in the black dross generate hazardous gases during the leaching stage of the salt recycling process. The toxic gases such as NH_3, CH_4, PH_3, H_2, H_2S, etc., are generated during the leaching stage. This factor significantly hinders the scale up process for industrial application. This is further complicated by the fact that black dross from various sources can contain different ratios of toxic components. This factor would require industry to adjust gas treatment methods and operational parameters every time they deal with a different type of black dross. The toxic components responsible for gas generation are minor phases in black dross, and consequently extremely difficult to identify and quantify by bulk characterization methods. It is reported that salt phases (such as NaCl, KCl) show significant solubility in glycerol, about a quarter of the solubility in water, without reacting with the gas evolving species (e.g., aluminium nitride) (Pinho & Macedo, 2005). Therefore, using water free glycerol and anhydrous ethanol washing the major components of the salt phases can be dissolved leaving the reactive components of black dross unchanged.

In this work black dross samples before and after non-aqueous salts dissolution have been investigated using various solid state microstructure characterization techniques (XRD, XRF, SEM/EDS, FTIR and Raman). In this case, the amount of the minor gas generating phases (e.g., aluminium nitride) before dissolving can be largely magnified making the toxic components more easily identified. These results can facilitate the setup of operation parameters and the control of the hazardous gases generation in industry process by providing a clearer methodology for the identification and quantification of hazardous components in black dross.

Experimental

Samples A_0 and B_0 from two different sources have been used in this study. with a particle size less than 1.2mm. Additionally, samples A_1 and B_1 have been obtained after aqueous free salt dissolution treatment of samples A_0 and B_0, respectively. All the solvents used for salt dissolution and washing were dried over 5Å molecular sieves. In the dissolution tests 20 g of black dross sample (A_0 or B_0) was added to 400 mL of anhydrous glycerol (40 min contact, 175 rpm agitation, 25 °C). The remaining residual solid was separated by centrifugation (15 min at 4000 rpm). The residual solid (A_1 or B_1) was washed and centrifuged (15 min at 4000 rpm) multiple times with anhydrous ethanol. The solid was then dried in an oven at 60°C for 3 hours.

Before microstructural characterisation, all samples were ground to fine particles using a pestle and mortar. 1 g sample powder was pressed into a tablet (with a diameter of 1.2 cm) using a Powder Tablet Press Machine (Specac Manual Hydraulic Press). The tablet samples were characterised by X-ray diffraction (XRD), X-ray Fluorescence analyzer (XRF), Scanning Electron Microscopy and Energy Dispersive Spectrometer (SEM/EDS), Fourier-transform infrared spectroscopy (FTIR) and Raman Spectroscopy.

Results and Discussion

The chemical compositions before and after salts dissolution in glycerol with ethanol washing of all four samples have been identified by XRF (Figure 1). Overall, black dross is a complicated material, about 30 elements have been detected from various source of samples. Both samples before dissolving consisted of soluble salts (Na, K and Cl), aluminium and alloying elements (Mg, Si, Fe, Mn, Ti, etc.). After dissolving, the salt content Na, K and Cl has been largely decreased. On the contrary, the content of most other elements (such as Al, Si, etc.) increased substantially.

The Mineralogical phases before and after salts dissolution in non-aqueous media recognised by XRD are shown in Fig. 2. Obviously, after salts dissolution, the intensity of the salts peaks are significantly reduced. By contrast, other phases' characteristic peaks have been largely magnified. It can be seen that before dissolving, aluminium nitride (AlN), was hard to be detected. However, after dissolution, it can be detected and analysed easily. The common

ingredients, such as halite (NaCl), sylvite (KCl), corundum (Al_2O_3), spinel ($MgAl_2O_4$), cryolite (Na_3AlF_6), were identified.

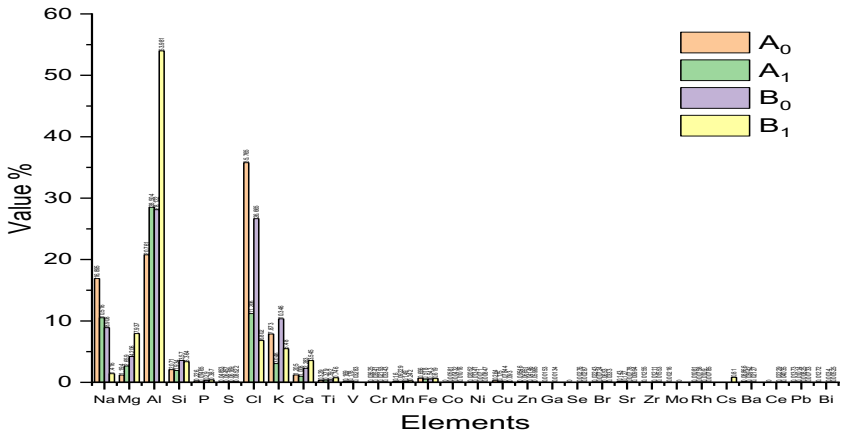

Figure 1. Chemical analysis of aluminium black dross from two different sources before (A_0, B_0) and after (A_1, B_1) salt-phases dissolution in glycerol and ethanol

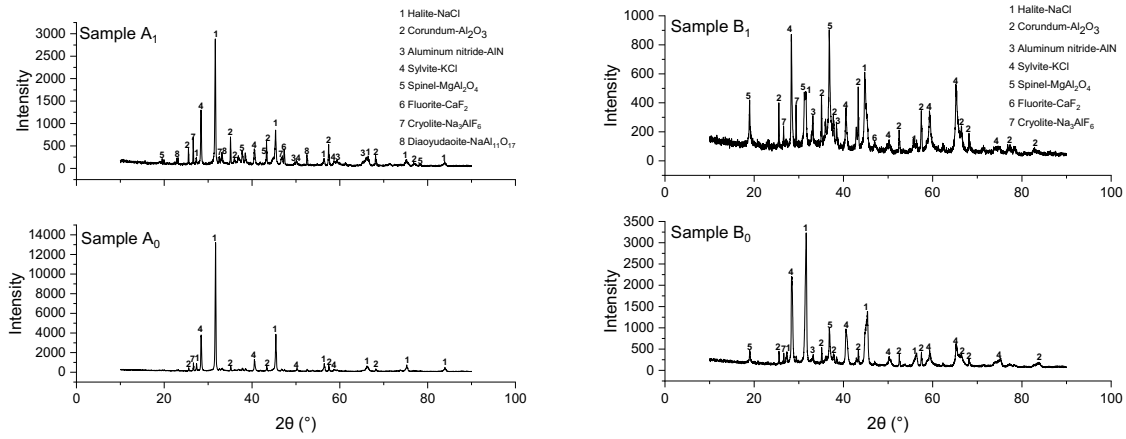

Figure 2. Mineralogical phases of aluminium black dross from two different sources before (A_0, B_0) and after (A_1, B_1) salt-phases dissolution in glycerol and ethanol

In addition, based on the SEM/EDS results, the problematic element N was obvious in the sample after salts dissolving. From the Raman and FTIR characteristic peaks of mineral phases compared to online database and literature, it can also confirm the presence of cryolite, elpasolite, calcite etc., especially, AlN.

Conclusions

Aluminiun black dross is a complex mixture of salts, various metals and oxides. It contains about 30 elements in total. Pre-treatment of black dross was an effective way to determine minor phases using various characterisation methods, especially when characterized by XRD. For example, the minor aluminium nitride resulting in toxic gas generation can be much easier to be identified.

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