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Recovery of vanadium and gallium from solid waste by-products of Bayer process

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ABSTRACT

In this study, recovery of vanadium and gallium from solids waste by-products (vanadium sludge and electrofilter dust of calcination plant) of Bayer process was investigated. An efficient purification process was developed based on the removal of impurities such as phosphate by water leaching, neutralisation using CO_2-enriched air and addition of aluminate solution. Recovery of V_2O_5 from the purified solution via the precipitation of ammonium metavanadate, its conversion into polyvanadate by the addition of ammonium sulphate and sulphuric acid, respectively, and then the ignition of the latter at 560 °C was demonstrated. Effects of various parameters on the purification and precipitation processes were shown. A treatment process involving sintering and two-stage of carbonisation was also demonstrated to produce a Ga-rich precipitate. A gallate solution suitable for electrolysis of Ga was also shown to be prepared from this precipitate. A complete flowsheet was proposed for the treatment of vanadium sludge and electrofilter dust.

1. Introduction

Gallium is an important metal with extensive application in high-tech industries (Moskalyk, 2003). Wide use of gallium in electronics, atomic, laser, missile industry and power sector driven by the development of technology (Font et al., 2007; Gupta et al., 2007; Chou et al., 2008) have increased its demand, which is estimated to increase 20-fold by the year of 2030 (Angerer et al., 2009). The search of potential sources for gallium has become ever important for meeting the current and future demand for gallium. Bauxite ores are the primary sources for gallium production in that approximately 90% of world primary gallium is produced from leach solutions of Bayer process (Ibragimov and Budon, 2010). In Bayer process, about 70% of gallium is leached together with aluminium from bauxite ore into the caustic soda solution and the balance is disposed of with the red mud. Gallium accumulates in Bayer liquor to a concentration of 100–300 mg/l as the solution is recycled within the process after the recovery of aluminium as hydroxide (Figueiredo et al., 2002). Recovery of gallium from Bayer solutions involves precipitation, re-solution and electrolysis (Habashi, 2008). Some gallium also precipitates together with aluminium during hydroxide precipitation stage.

Previous studies have concentrated essentially on the recovery of Ga from leach solutions in that solid wastes received only very limited attention. Electrofilter dust of calcination plant is a waste product produced during the calcination of alumina and contains a significant amount of gallium. However, most studies appeared to focus on the recovery of aluminium rather than gallium from electrofilter dust and Sancho et al. (2009) reported that 40% aluminium was recovered from the electrofilter dust that contained 91% Al_2O_3. Ayala et al. (2010) studied sulphuric acid leaching of electrofilter dust (89% Al_2O_3) to obtain aluminium sulphate, abrasive and aluminium alum as commercial products. On the other hand, the recovery of gallium from the dust of aluminium electrolysis plant has received interest since gallium tends to accumulate in the dust fraction during the electrolysis (Carvalho et al., 2000; Abisheva et al., 2012). Abisheva et al. (2012) characterised the dust products from fused-salt electrolysis of aluminium, which were found to contain 0.071–0.125% Ga and 26.6–29.9% Al_2O_3. They also examined acid leaching of these dusts and found that 64–83% of gallium can be extracted from the dust products under the conditions of 1.0 mol/dm^3 H_2SO_4, 1:4 solid:liquid ratio, 90 °C

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and 1 h leaching period. In hydrochloric acid leaching, gallium recoveries for both dusts were lower than those in sulphuric acid leaching i.e. 52–63%. They also reported that two step counter current leaching of the dust with sulfuric and hydrochloric acids improved the gallium recovery by 10–20%.

Bauxite ores also contain vanadium at appreciable levels (Mahanty et al., 1967; Moskalyk and Alfantazi, 2003). In the Bayer process, vanadium dissolves to some extent (~30%) and builds up in solution up to a certain level at which the solution is treated by evaporation and then by cooling down to 15 °C so as to crystallize/remove vanadium as a sludge of complex salts. Low vanadium content (16–17% V_2O_5) coupled with its high content of impurities such as fluoride, phosphate, and arsenic renders the sludge less attractive source for vanadium. The removal of impurities or selective recovery of vanadium from the sludge has proved difficult (Mahanty et al., 1967). Mahanty et al. (1967) tested various options to selectively recover vanadium from the complex salt. They found that vanadium could be selectively separated from phosphate by precipitation as ammonium metavanadate at pH 6. Mukherjee et al. (1990) proposed a recovery process that incorporated water leaching, activated carbon adsorption and ammonia precipitation. Yuzer et al. (1990) reported the removal of impurities (Al, As and P) by the addition of gypsum at pH 6–8.5 and 98.5 °C at which vanadium loss was only 2.3%. They recovered vanadium as pentaoxide (99.5% V_2O_5) after ammonia precipitation followed by calcination. In Seydisehir Aluminium Plant, there is currently no production gallium, which is lost to solids wastes and products. In the plant, vanadium is removed as sludge from leach solutions to control impurity levels and the sludge is stored as a waste of no economic return due to its relatively low vanadium, but, high impurity content.

In this study, research and development of environmentally acceptable, technically sound and low-cost processes were undertaken for the recovery of gallium, aluminium and vanadium solid waste by-products (electrofilter dust of calcination plant and vanadium sludge) of the Bayer process. The treatment processes proposed in this study are based essentially on the technology, which is a commercially proven technology and is currently exploited in Pavlodar Aluminium Plant of Kazakhstan (Ibragimov and Budon, 2010).

Table 1
Chemical composition of the vanadium sludge and electrofilter dust.

Vanadium sludge		Electrofilter dust	
V_2O_5	14.3%	V_2O_5	0.02%
P_2O_5	2.1%	Ga_2O_3	0.0038%
Al_2O_3	1.44%	Al_2O_3	89.5%
Na_2O	30.0%	Na_2O	0.5%
Na_2CO_3	35.6%	SiO_2	0.3%
CaO	0.5%	CaO	0.01%
F^-	1.5%	Fe_2O_3	0.031%
A loss on ignition	14.56%	A loss on ignition	9.6352%
	100%		100%

2. Materials and method

Samples of electrofilter dust of the calcination plant and vanadium sludge were obtained from Seydisehir Aluminium Plant, located in Konya province of Turkey. By X-ray Fluorescence Spectrometer with wave dispersion Venus 200 PANalytycal BV (PANalytycal B.V., The Netherlands). The survey was made using diffractometer D8 Advance ("Bruker"), α-Cu, voltage across tube 40 kV, current 40 mA. Processing of obtained data of diffractograms and estimation of interplanar distances were carried out using EVA software. Identification of phases was made using a search/match program (the Base of Powder Diffractometric Data PDF-2 Rel. 2012 (ICDD)).

2.1. Treatment of vanadium sludge

The chemical composition of the sludge sample XRF (by X-ray Fluorescence Spectrometer with wave dispersion Venus 200 PANalyical BV) is shown in Table 1. The sludge was determined to contain 14.3% V_2O_5 and impurities such as phosphate and fluoride. XRD analysis XRD (by Bruker D8 Advance X-ray Diffractometer) of the sludge showed the presence of various complex salts (Fig. 1).

Treatment of the vanadium sludge involved leaching, neutralisation and precipitation stages. A thermostated stainless steel reactor equipped with an anchor impeller was used in the tests. Leaching of the sludge (dissolved at a ratio of liquid to solid matter is equal 2.0-2.5:1.0) in distilled water was performed at 90–95 °C

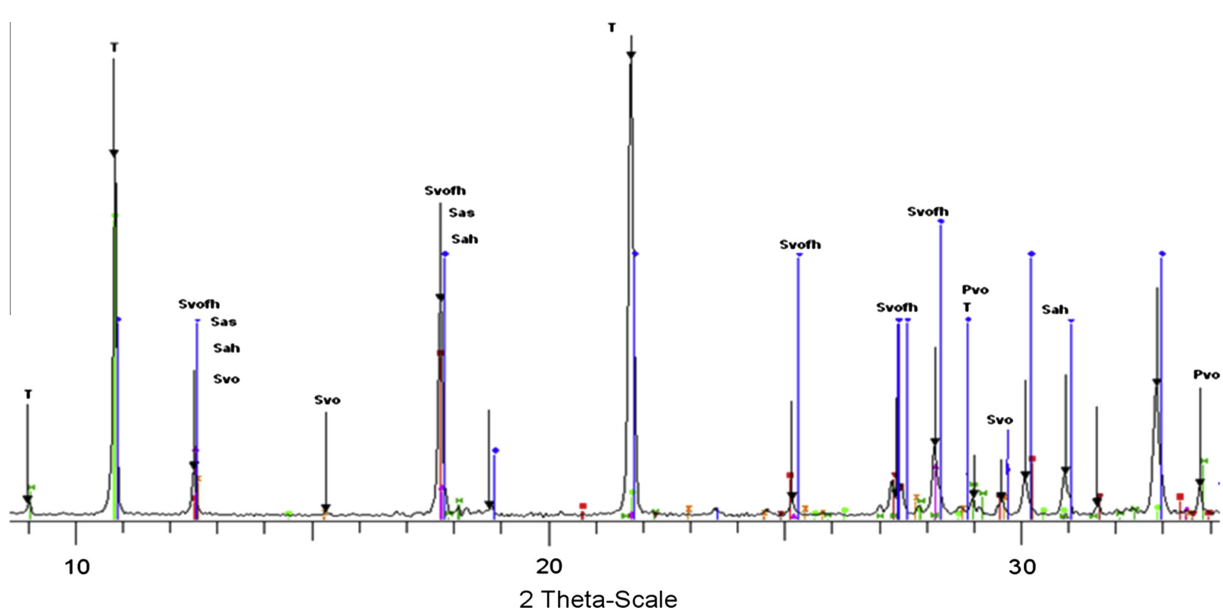

Fig. 1. X-ray pattern of vanadium cake used in this study (Phases: M: Metamunirite; Svofh: Sodium Vanadium Oxide Fluoride Hydrate; Pvo: Potassium Vanadium Oxide; Sas: Sodium Aluminium Silicate; Sah: Sodium Aluminium Hydride; Svo: Sodium Vanadium Oxide; T: Trona).