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Extraction of titanium (IV) from acidic media by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester

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Abstract

The extraction of titanium(IV) from sulphate, chloride and nitrate solutions has been investigated using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) in kerosene. The kinetics of extraction was slow, requiring 60 min for the complete extraction of titanium and was improved with the increase of the extractant concentration in the organic phase. When the acid concentration in the aqueous feed phase was varied from 0.5 M to 4 M, the distribution ratios of titanium showed minimal values at 1–2 M acid. The effect of the initial concentration of titanium on extraction was found to be negligible, indicating the presence of mononuclear species in the aqueous phase. The stripping of titanium was studied using H_2SO_4, H_2SO_4+H_2O_2 and Na_2CO_3. The kinetics of the stripping was very slow when sulphuric acid was used, but was improved with complex forming stripping agents (H_2SO_4+H_2O_2 and Na_2CO_3). The extraction and stripping of titanium were 100% using an aqueous nitrate medium and sodium carbonate strip. Hence, results generated would be applicable to separate titanium from secondary sources such as fly ash originated from incinerators of Municipal Solid Waste.

Keywords: Titanium(IV); Sulphuric acid; Hydrochloric acid; Nitric acid; Solvent extraction; EHEHPA; Stripping

1. Introduction

Titanium and its alloys, due to their excellent characteristics as industrial materials, are used for various purposes in industry. In particular, titanium has been widely used in the aerospace industry while titanium dioxide finds application as pigment in the paint industry. Moreover a larger-scale output of lower-cost titanium and titanium alloy products for use in automotive parts and buildings is increasing.

The recovery of titanium from secondary sources such as fly ash generated from the Municipal Solid Waste (MSW) incineration could minimise landfill disposal and the waste of natural resources. Generally a medium size incineration plant (170 tons/day of MSW) annually produce about 80 tons of fly ash which contain 7000–12 000 mg Ti/kg (Wiles, 1996; Pietrelli and Porzio, 2002). Fly ash can be effectively leached by H_2SO_4, HNO_3, HCl

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and mixed acid solutions. A preliminary study shows that in terms of titanium yield, the best result was obtained by H_2SO_4+HNO_3 (Giacco, 2003). The selective separation of titanium from fly ash is a tough task considering the presence of many metal ions and impurities such as Fe, Zn, Al, Mn, etc., at various concentrations.

Many reagents have been tested for the extraction of titanium(IV) from aqueous solutions. It is recognised that neutral organo-phosphorous compounds are effective extractants for tetravalent metals, particularly for titanium(IV). Among these, tri-*n*-butyl phosphate (TBP), tri-octylphosphine oxide (TOPO) and Cyanex 923 (TRPO) have been used widely for the extraction of titanium(IV) from acidic chloride solutions (Allal et al., 1997; Sheng et al., 1983; John et al., 1999a). However, the use of TBP and TOPO leads to third phase formation when titanium(IV) is extracted from concentrated metal ion solutions (Allal et al., 1997). Quaternary amine extractants such as Aliquat 336 extract titanium efficiently at low acidity range from HCl solutions (Sundaramurthi and Shinde, 1989). Organo-phosphorous acid derivatives such as dodecyl phosphoric acid (Ritcey and Ashbrook, 1979), di-*o*-tolylphosphoric acid (Islam et al., 1985) and *p*-(1,1,3,3-tetramethylbutyl) phenyl phosphoric acid (Mellah and Bauer, 1995), di(2-ethylhexyl) phosphoric acid (D2EHPA) (Biswas and Begum, 1998, Biswas et al., 2002), have been used by several investigators but they are found to have very slow kinetics and to be less selective. Mixtures of extractants, seems to give faster kinetics (Kislik and Eyal, 1993a). Critical reviews of published data on titanium(IV) extraction appeared in 1993 (Kislik and Eyal, 1993b) and 1999 (Sole, 1999a). The review by Kislik and Eyal, in particular, showed that titanium extraction passes through a minimum, depending on the acidity of aqueous phase. Moreover, mono-2-ethylhexyl phosphate (MEHPA) was found to be better and more selective than its counter part D2EHPA, because of its strong chelating capability and less sterically hindered sites. Among the acidic organo-phosphoric compounds, EHEHPA (commercially known as PC88A or Ionquest 801 or P507), has been widely used for Ni–Co separation (Sarangi et al., 1999). Titanium extraction by EHEHPA has been studied by Jayachandran and Dhadke (1998), John et al. (1999b, 2003) and by Sing and Dhadke (2002) in H_2SO_4, HCl and $HClO_4$ solutions, respectively.

In this paper the solvent extraction of titanium(IV) from HCl, HNO_3, H_2SO_4 solutions by EHEHPA has been investigated to evaluate if the recovery of titanium from the fly ash produced by a MSW incineration plant could be carried out after leaching. Therefore, the extraction of titanium using sulphate, nitrate and chloride as medium was compared to determine the best extraction and stripping conditions for the effective recovery of titanium from other impurity elements.

2. Experimental

2.1. Reagents

The extractant 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) was supplied by Albright and Wilson (now Rhodia), and was used without further purification. As small amounts of di-acid, such as 2-ethylhexyl phosphonic acid, are usually present in this commercial extractant, EHEHPA was titrated by KOH in a 70% (v/v) aqueous/acetone solution and its content was found to be 96.4%. Low odour kerosene (Aldrich) with a boiling fraction: 180–250 °C was used as a diluent due to the high extraction efficiency observed when kerosene was employed (Saji and Reddy, 2003). All other chemicals used were of analytical grade.

Titanium(IV) stock solution was prepared by leaching titanium dioxide in concentrated H_2SO_4 (98%) and ammonium sulphate at 230 °C for about 120 min until the solution turned from yellow to colourless. The final stock solution contains 0.04 M Ti and <0.02 M H_2SO_4 as free acid, therefore the experimental tests were performed with solutions containing a maximum of additional H_2SO_4 of 0.01 M. It is necessary to note that the actual fly ash leach solution would be a mixed acid (H_2SO_4+HNO_3) in order to produce a salt sludge that can be subsequently dissolved by an acid solution and give the best titanium yield.

A typical MSW leaching solution contains Ti, Fe, Zn, Al and Pb; therefore three simulated solutions containing 0.5 g/L for each metal were