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Tungsten recovery from alkaline leach solutions as synthetic scheelite

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Abstract

The recovery of tungsten from alkaline leach solutions has been studied examining the effect of temperature, pH, Ca/WO_3 molar ratio and nature of the precipitated calcium tungstate. The precipitation kinetics of calcium tungstate, upon the addition of aqueous sodium tungstate to calcium solutions, was followed by potentiometric measurements using a calcium ion-selective electrode. Two models, a crystal growth model and a second-order reaction opposed by zero-order reaction, have been used to test the experimental data. Both models show that the apparent activation energy of $CaWO_4$ precipitation falls in the range 58 to 67 kJ mol^{-1}.

The kinetic data shows that the maximum recovery of precipitated calcium tungstate occurs at pH ≥ 8.5 with a 10% excess of $CaCl_2$ at 50 °C over a period of 20 min using sodium tungstate solutions of 100 g L^{-1} and 150 g L^{-1} WO_3.

Keywords: Calcium tungstate; Synthetic scheelite; Kinetics; Crystal growth

1. Introduction

Tungsten is one of the most important refractory metals used in several industrial applications taking into account its hardy and heat-resistant performance in the form of tungsten carbide. The main sources of tungsten are the high-grade concentrates of wolframite and scheelite ores. Currently, synthetic scheelite is a strong contender as a third source of tungsten. Under normal circumstances the medium-grade concentrates of tungsten have reduced commercial value and are difficult to place in the market (Martins et al., 2003; Martins, 2003). One of the methods to refine these products is through their conversion to ortho-tungstate in alkaline medium, followed by its precipitation to calcium tungstate by addition of calcium salts or solutions. The different methodologies (Delmas and Casquinha, 1976; Burwell, 1955; Fruchter and Moscovici, 1982) used by industry to obtain synthetic scheelite have varying costs and mainly affect the grain size of tungstic acid (Martins et al., 2002). Hence there is interest in the kinetics and crystal growth of its precipitation.

The precipitation reaction kinetics depends on the predominance of a slow step in the mechanism of crystal growth. If the equilibrium at the crystal surface is rapid, the transport of the lattice ions from solution to the primary nuclei will be the rate-limiting step. The rate of

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crystal growth is then proportional to the supersaturation, through Fick's law of diffusion. Conversely, if the interface controls the reaction, the rate of growth is proportional to the square of the supersaturation. Many precipitation reactions follow this latter mechanism, such as calcium carbonate (Nancollas and Reddy, 1971; Reddy, 1977) and calcium sulphate (Liu and Nancollas, 1971).

The kinetics of crystal growth of calcium tungstate from sodium tungstate melts have been performed by Roy and Appalasami (1978). They found that the reaction is rate-controlled by the development rate of excess solute concentration. In the case of aqueous solutions, no work appears to have been performed on the kinetics of calcium tungstate, except for the synthesis and characterization of calcium tungstate nanocrystals for application as luminescent material (Chen et al., 2003; Sun et al., 2006).

This paper reports the kinetics of calcium tungstate precipitation from alkaline sodium solutions and the influence of temperature, supersaturation, pH and nature of calcium tungstate on tungsten recovery using a calcium ion-selective electrode. This potentiometric technique has the advantage of being non-destructive and measures high to low concentrations directly.

2. Experimental

2.1. Reagents and solutions

All chemicals were analytical grade from Merck and used without further purification.

Orion (92-20-01) was the ion exchanger used to prepare the calcium ion-selective membrane electrodes.

All solutions were prepared by diluting a stock concentrate. Since the ionic strength influences the kinetics and morphology of crystal growth (Nancollas and Liu, 1975; Nielsen, 1964) and electrode potential, potassium nitrate was added to maintain a constant ionic strength. Since the ion selective electrode shows a linear response between 0.001 mM to 100 mM Ca^{2+}, the initial concentration of calcium ion was chosen as 10 mM, and the ionic strength was fixed as 0.1 M.

The titration of the calcium and tungstate concentrated solutions was performed by potentiometry using a solution of EDTA (0.1 M) and lead perchlorate (0.1 M) (Orion 94-82-05), together with calcium and lead ion selective electrodes, respectively.

2.2. Preparation of selective electrode

The construction of the calcium ion-selective electrode was performed according to Moody and Thomas' technique (Moody et al., 1970; Davies et al., 1972). The sensor composition was 0.17 g of PVC powder and 0.40 g of ion exchanger Orion (92-20-01). The sensor solution immobilized in PVC was a mixture of calcium bis-di(*n*-decyl)phosphate as ion exchanger and di-*n*-octylphenyl-phosphonate as solvent mediator and plasticizer. The ion-selective electrode was calibrated by increasing the calcium ion concentration stepwise from zero to 14.7 mM and evaluating the respective potentials over three consecutive days. The prepared electrodes showed a slope between 28 and 33 mV and a linear response from 0.05 mM Ca^{2+} using an Orion millivoltmeter model 801A.

2.3. Equipment

To obtain the kinetic data the reaction was performed in a glassware with the solution stirred magnetically and monitored for pH and calcium ion concentration. Calcium tungstate was then precipitated from sodium tungstate solutions of 100 g L^{-1} and 150 g L^{-1} WO_3 using 150 g L^{-1} and 250 g L^{-1} calcium chloride solutions in a 1-L batch reactor thermostatically controlled at 50 ± 1 °C and stirred with a pitched blade turbine.

Scanning electron microscopy micrographs were obtained on a JEOL JSM-6301F instrument.

2.4. Experimental procedure

Since sodium ions can act as interfering species in calcium ion selective electrodes it was necessary to evaluate the extent of sodium ion interference in the potentiometric measurements performed with the constructed electrodes.

The calcium ion-selective electrode potential, E, in the presence of sodium ion is given by the modified Nernst equation,

$$E = \text{const} + \frac{RT}{2F}\ln[a_{\text{Ca}} + k^{\text{pot}}_{\text{Ca,Na}}(a_{\text{Na}})^2] \quad (1)$$

where is $k^{\text{pot}}_{\text{Ca,Na}}$ the potentiometric selectivity coefficient.

The interference of sodium ion was analysed according to the Srinivasan and Rechnitz (1969) method by plotting $e^{\Delta E/RT}$ against $(a_{\text{Na}})^2/(a_{\text{Ca}})$. The calculated $k^{\text{pot}}_{\text{Ca,Na}}$ value at 0.1 M ionic strength was 0.011 which fully agrees with literature data (Moody et al., 1978; Ammann et al., 1975). We conclude that the constructed electrode picks up interference from Na^+ when the $[Na^+]/[Ca^{2+}]$ ratio is higher or equal than 135, where the yield of the precipitation reaction is already about 99%. Nevertheless, to avoid any memory effect of the membrane