DETERMINATION OF KINETIC ASPECTS FROM THE NON-ISOTHERMAL CHLORINATION OF TUNGSTEN MINERALS

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Abstract— **The main kinetic aspects of the chlorination of tungsten minerals with chlorine and sulphur dioxide were analyzed from data obtained under non-isothermal conditions. The tungsten minerals studied were wolframite, scheelite and a scheelite-wolframite concentrate. The collected minerals were milled and then concentrated by means of gravity separation. Chlorinations were made in a vertical reactor with a static bed and upward flow of reactive gases using an empirical methodology that was established taking into account the most important physicochemical features of the system. The rate equation and the apparent activation energy for each tungsten mineral were determined by the integration method using a characteristic temperature to evaluate the temperature integral. An easy applicable criterion was used to determine the corresponding values of the characteristic temperature. Results obtained allowed to establish that the movement of an interface controls the wolframite chlorination and that the presence of non-volatile reaction products affects the chlorination of scheelite and of the scheelite-wolframite concentrate. An operative sequence was proposed to determine the temperature range (initial and final) in which the respective rate equation selected from non-isothermal data maintained its validity. Finally, the characteristic temperature was calculated by a frequently used route and results obtained were compared in each case.**

Keywords— **Kinetic aspects, non-isothermal chlorination, tungsten, wolframite, scheelite.**

I. INTRODUCTION

The determination of kinetic parameters under non-isothermal conditions is an alternative method of analysis that allows to obtain acceptable results in thermal decomposition reactions (phyllosilicates, metal carbonates, sulphates, nitrates, nitrites, oxyhalides, chromites, etc.). The decomposition evolution is determined in a unique experiment when the sample is exposed to a systematic and controlled variation of the reaction temperature. Parameters are calculated from the curve that shows the conversion degree as a function of the reaction temperature (Popescu and Segal, 1998; Brito *et al.*, 1996; El-Awad and Mahfouz, 1989; Felix and Girgis, 1989; Aglietti *et al.*, 1988; Bamford and Tipper, 1980; Vallet, 1972; Horowitz and Metzger, 1963). Some authors consider that kinetic parameters obtained from a single experiment are less reliable than those determined from multiple experiments (Gotor *et al.*, 1998; Criado *et al.*, 1987).

The main tungsten minerals are wolframite ($Fe_XMn_{1-X}WO_4$) and scheelite ($CaWO_4$). The wolframite consists of an isomorphous series of ferberite ($FeWO_4$) and hübnerite ($MnWO_4$) (Blackburn and Dennen, 1994). In the nature, wolframite and scheelite can be found separately or associated between them. When this natural association occurs, both minerals are distributed in an irregular way in each tungsten-bearing grain and their separation is difficult to be performed under favourable economic conditions. In our country, sufficient resources of associated tungsten minerals were found so as to be used at industrial scale. At the same time, scarce resources of minerals without association are known (Angelelli, 1984).

The chlorination is an alternative process to recover tungsten from its bearing minerals (Menéndez, 1999; Nolasco et al., 1991; Yih and Wang, 1979). The reaction starts with adsorption of chlorine on the surface of the reactive solid. Then, the exchange of lattice oxygen by chlorine and the respective desorption of oxygen into the gaseous phase are produced. The efficiency of the process may be improved if a reducing agent is