

PHASE TRANSFORMATIONS IN CLAYS AND KAOLINS PRODUCED BY THERMAL TREATMENT IN CHLORINE AND AIR ATMOSPHERES

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Abstract—A study of the phase transformations generated by chlorine during the calcination of clays and kaolins is presented. The original samples and residues of the thermal treatment carried out in air and chlorine atmospheres are analyzed at different calcination times and temperatures. Sample characterization was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray microanalysis (EPMA). The results indicate that in samples of kaolin and ball clays the α -alumina phase (corundum) appears in the first chlorination stage. This phase disappears at longer chlorination times due to the volatilization of AlCl_3 . It is also observed that the kaolinite calcination in chlorine atmosphere favors the formation of the mullite phase. Other crystalline phases present in minerals, such as anatase and iron oxides, practically disappear after the samples chlorination.

Keywords—Kaolins, Clays, Chlorination, Calcination, Phase transformations

I. INTRODUCTION

The term kaolin is used to designate the white clays whose principal mineral is kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). Its particles are usually hexagonal with diameters ranging from 0.05 to 10 μm (average 0.5 μm). Since this mineral is a product of the decomposition of feldspars and micas present in pegmatites and micaceous schists, it is frequently found together with other minerals such as quartz, sulfides, feldspars, micas and iron and titanium oxides, among others (Norton, 1983).

Kaolin is used for different industrial applications due to its physical and chemical properties. It is mainly used in the paper industry (45 %), refractories and ceramics (31 %), fiberglass (6 %), cement (6 %), rubber and plastic (5 %), paint (3 %) and others (4 %) (Murray, 2002).

Kaolinite is also the principal mineral of ball clays, but it exhibits lower granulometry and crystallinity than the kaolin. Kaolinite is usually accompanied by other clay minerals such as montmorillonite, illite, etc. Clays contain organic matter, generally lignite, and other colloidal minerals that often provide typical colorations. Since red clays possess a high content of iron oxide, they usually contain a higher concentration of titanium accompanying the iron that is generally found as ilmen-

ite (Norton, 1983).

Iron is the principal contaminating agent in clays and kaolin. The presence of this element has a negative effect due to the color it gives to the product. Thus, the removal of iron from the kaolin used in industries, such as the paper industry, is of particular importance due to the requirements of high purity.

Numerous physical and chemical methods of iron extraction from these minerals have been investigated. The physical methods use separation techniques such as the flocculation and the high gradient magnetic separation (Chandrasekhar and Ramaswamy, 2002; Maury and Dixit, 1990). The chemical methods make use of leaching agents or leaching plus reductant agents (Ambikadevi and Lalithambika, 2000; Vèglio and Toro, 1994 and Atkinson and Fleming, 2001). Nowadays, leaching methods are being investigated using microorganisms (De Mesquita *et al.*, 1996; Lee *et al.*, 2002 and Came-selle *et al.*, 2003).

The use of chlorination in the procedures of the extracting metallurgy has notably increased in the last decades, and a future increase in the use of chlorine in pyrometallurgic processes can be anticipated. This increase is due to numerous factors that include the high reactivity, the low cost, the variety and availability of chlorinating agents, the development of materials resistant to corrosion and the facility with which the effluents can be treated and recovered (Jena and Brocchi, 1997).

The advantages of chlorination in the removal of iron and titanium from clay and kaolin minerals used for the paper and ceramic industries in Argentina were studied in a previous work (González and Ruiz, 2006). It was observed that, at high temperatures, chlorine not only removes iron and titanium quantitatively by the formation of the gaseous FeCl_3 and TiCl_4 species, but also produces phase changes in the chlorinated minerals (González *et al.*, 2003). The purpose of this work is to study the effect of chlorine on the phase transformations of clays and kaolins during calcination in chlorine atmosphere.

II. EXPERIMENTAL

A. Materials

The materials studied in this work were: high purity kaolin, provided by the Brazilian company CADAM and used in the Argentine paper industry, and ball clay, provided by the Argentine company Piedra Grande and