PHASE TRANSFORMATIONS FROM GOETHITE TO HEMATITE AND THERMAL DECOMPOSITION IN VARIOUS NICKELIFEROUS LATERITE ORES

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ABSTRACT

This study presents an evaluation of the thermal transformations and decomposition kinetics of different nickeliferous laterite ores using thermogravimetric analysis technique. Nine different nickeliferous laterite ores of Class-C and Class-B were analyzed. Transformations from goethite to hematite and decomposition of chlorite and serpentine were identified.

Keywords: nickeliferous laterite, goethite, hematite, thermal decomposition, TGA/DTA.

INTRODUCTION

Generally, the industrial production of nickel is based on two types of ores such as nickel oxides (laterites) and nickel sulfides. According to international reports, the world nickel supply is covered predominantly by sulfide ores (60 % versus 40 % by laterites), but participation of the laterite ores has risen from about 200 000 tons/year or 10 % before 1950 to about 1,200,000 tons/year or 42 % in 2003 and it reached 1,454,000 tons in 2008 [1]. Keeping in mind that the additional nickel demands are expected to be mainly satisfied by mining of laterite deposits, the optimization of the metallurgical laterite processing methods represents a further step for the nickel industry. Thermogravimetrical data are of great interest in the planning of the pyrometallurgical operations for the exploitation of these materials.

Based on the literature data, laterite deposit profiles are mainly classified according to their mineralogical content into the following four categories: (i) Limonite zone, (ii) Nontronite zone, (iii) Serpentine zone and (iv) Garnierite zone [1]. Based on the Fe and MgO content laterite ores are classified in three classes: (a) Class A – garnieritic type of laterite (Fe < 12 % and MgO > 25 %); (b) Class B – limonitic type (high Fe content of 15-32 % and MgO < 10 %) and (c) Class C – intermediate type of laterite (Fe 12-15 % and MgO 25-35 % or 10-25 %) [2].

Most of the research on these materials was focused on their characterisation and the application of the extraction methods for the production of various products [3, 4]. The literature survey includes numerous studies on goethite thermal analysis but there is not many data on the transformation kinetics and thermal decomposition of goethite in low-grade nickeliferous laterite ores [5-8]. Thermogravimetric data are of great interest from the industrial point of view in the planning of pyrometallurgical operations.

The main aim of this study is to evaluate and to compare the effects of the thermal transformations and decomposition kinetics of different types of nickeliferous laterite ores using thermogravimetric analysis. Having in mind the mineralogical composition of these ores, the kinetics was based on the study of the goethite dehydroxylation reaction.

EXPERIMENTAL

Nine different types of low-grade nickeliferous laterite ores were taken for the analysis: Ore1 (Indonesia-Saprolite), Ore 2 (Indonesia-Limonite), Ore 3 (Philippine-Saprolite), Ore 4 (Philippine-Limonite), Ore 5 (Turkey-Bandirm), Ore 6 (Turkey-Toros), Ore 7 (Albania-Class A), Ore 8 (Albania-Class B), Ore 9 (MK-Rzanovo). All the samples were ground and vacuum dried as for the chemical composition testing. The average chemical composition was obtained using Atomic Absorption Spectroscopy (AAS) using a Perkin Elmer 2100 instrument. Chemical composition data of the low-grade nickeliferous laterite ores are presented in Table 1.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG/DTG) were obtained simultaneously using the Perkin Elmer Diamond System. The samples were heated from 30 to 1100°C, at
heating rate varied between 10 and 40°C min⁻¹. The amount of sample used in each test was from 16 to 22 mg. The kinetic study was carried out on the basis of the derivative thermogravimetric (DTG) curves [9].

### RESULTS AND DISCUSSION

The results obtained for the chemical composition of the studied nickeliferous laterite ores are presented in Table 1. It was determined that the Ores 1 and 3 are typical intermediate type Saprolite from the Class C (Fe 13-16% and MgO 20-22%); Ores 2 and 4 are Limonitic type from the Class C with low Fe = 13-16% and lower MgO = 10-13%. Both samples of nickeliferous laterite ores from Turkey as well as Ore 7 from Albania could be classified in Class B with low Fe content of 25-32% and MgO < 10% (MgO = 2-5%). The second ore from Albania, Ore 8, could be classified in the Class B with high Fe content of 35-45% and MgO lower than 10%, MgO = 2-5%. Macedonian ore 9 from Rzavovo should be classified in the Class C because of the high content of MgO 12-16% but also with high Fe content of 25-33%.

Characteristic TG/DTA thermograms of the studied low-grade nickeliferous laterite ores are presented in Figures 1-9. Generally, for all studied samples five temperature regions were analysed: T-1 (50-100°C), T-2 (150-300°C), T-3 (400-600°C), T-4 (600-750 °C) and T-5(750-850°C). The total mass loss varied from $D_m = 4\%$ for Ore 9 to $D_m = 15\%$ for Ore 3 in the studied temperature range 30-1100°C. These values are somewhat lower than those reported in the literature for nickeliferous laterite ores the mass loss values of which are between 15-18% in the range 100-1000°C [10]. For the Ore 1 four main thermal effects were observed in Fig. 1 (Indonesia Saprolite). The DTG curve of Ore 1 (Fig.1) shows four intense peaks about 70, 260, 580 and 800°C with a mass loss of 1.77, 4.93, 7.82 and 13 %, respectively. The DTA curve of Ore 1 shows three endothermic and one exothermic peaks. The first DTG peak at 69.9°C corresponds to the elimination of absorbed water. The water in the nickeliferous ores can be divided in free water, crystal water, and hydroxyl group. During the heating process, the temperature range for the removal of the free water is 25 - 140°C, for the crystal

![Fig. 1 TGA/DTA of Ore-1 Indonesia Saprolite.](image1)

![Fig. 2 TGA/DTA of Ore-2 Indonesia Limonite.](image2)
water it is 200 - 480°C, and for the hydroxyl group it is 500 - 800°C. For the analysed nickeliferous ores, the first DTG peak and removal of the free water was between 49°C and 70°C, except for the Ore 9 where it was at 133°C.

The second strong DTG peak at 266.7°C for Ore 1 corresponds to the mass loss of the crystal water. The strong DTG peak in the region of 292-355°C is caused by the dehydroxylation of poorly crystallized goethite which is transformed into hematite in accordance with eq. 1.

$$2\alpha-\text{FeOOH} \rightarrow \alpha-\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$$

(1)

Generally, this DTG peak, representing goethite-hematite transformation, is sharp at 385 °C for highly crystalline goethite, but for the finely grained and poorly crystallized goethite, the dissociation temperature is always lower [11]. For the studied nickeliferous laterite ores, this peak is mainly at lower temperatures of 257 to 318°C. This indicates that all studied nickeliferous ores contain a significant amount of amorphous goethite whose crystallite size is comparatively small.
DTG peaks at higher temperatures - above 800°C, were registered only for Ore 2 at 832°C and for the Ore 9 at 895°C. They were attributed to the transformations in the nickeliferous serpentine. In the range above 800°C to 825°C exothermic DTA peaks were registered for Ores 1, 2, 3, and 4. This peak was not found for Ores 5 to 9. The DTA exothermic peak at 816°C is attributed to recrystallization phenomena.

CONCLUSIONS

Using the TGA/DTA technique, evaluation of the phase transformations and thermal decomposition kinetics was performed. Nine different nickeliferous laterite ores of Class-C and Class-B were analyzed. Transformations from goethite to hematite and decomposition of chlorite and serpentine were identified.

REFERENCES