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Innovative methodology for recovering titanium and chromium from a raw ilmenite concentrate by magnetic separation after modifying magnetic properties

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HIGHLIGHTS

- A new process was proposed to recover Ti and Cr from a raw ilmenite concentrate.
- $FeTiO_3$ and Fe_2O_3 had better magnetic selectivity against $FeCr_2O_4$ after roasting.
- A commercial Ti concentrate assaying 47.94% TiO_2 was gained with recovery of 78.52%.
- A Cr concentrate assaying 28.65% Cr_2O_3 was obtained with total recovery of 84.18%.

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ABSTRACT

Raw ilmenite concentrate containing Cr can be either as a resource or as one kind of the most hazardous solid waste. In order to recover titanium and chromium from the raw concentrate which was separated from the Promenade deposit, Gaza province, Mozambique, an innovative technology using modification of magnetic property followed by magnetic separation was proposed. Magnetic property, phase and surface morphology of the sample before and after oxidizing roasting were firstly characterized by magnetism, chemistry, XRD and MLA analyses to interpret the mechanism of oxidizing roasting of the ilmenite. Then, these factors such as oxidizing roasting temperature, residence time and magnetic induction affecting on magnetic separation performance were examined and the optimum process parameters were determined. A commercial concentrate containing 47.94% TiO_2 and 0.23% Cr_2O_3 was obtained and the recovery of TiO_2 and Cr_2O_3 was 78.52% and 5.42%, respectively. The tailing obtained was preliminarily concentrated by a high-intensity magnetic separator and a rough chromite concentrate was gained. In order to further purify the rough one, reducing roasting was carried out to transform the minerals containing hematite into the minerals containing magnetite, followed by a low-intensity magnetic separation. The effects of these parameters such as temperature, carbon powder dosage, holding time and magnetic induction on magnetic separation performance were investigated and the optimal conditions were determined. A concentrate containing 28.65% Cr_2O_3 was obtained and the total recovery of Cr_2O_3 was 84.18%.

1. Introduction

The Promenade deposit, located in Chibuto town, Gaza province, Mozambique, is the largest heavy sand deposit containing separate Ti and Zr bearing minerals in the world, but so far it has not commenced its production [1]. Ilmenite is the major heavy mineral component in the deposit. However, it is usually considered to be

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of the lowest commercial value [2]. In order to realize the full economic value of the deposit, it is essential to process the ilmenite to a marketable product. For this type of deposit, gravity concentration using cone and spiral concentrators is usually applied to reject significant amounts of gangue in the first step while produce a raw heavy sand concentrate [3]. Then, magnetic or electric separation is carried out to produce a commercial ilmenite product [4], which can be used as feedstock for a smelting-chlorination or sulphate route pigment plant.

But for the raw ilmenite concentrate separated from the Promenade deposit, chromium represented a particular problem for processing. Previous mineralogical investigations have shown that chromium mainly occurs as free chromite particles and in principle, they can be separated along with other separate minerals such as zircon, rutile and monazite from the ilmenite grains by physical concentration procedures [5]. However, in practice, the separation is difficult because the physical properties of chromite grains, such as specific gravity, conductivity and magnetic susceptibility, are similar to the ilmenite grains and sometimes, the situation is more complex due to variable physical properties [6,7], resulting in considerable amounts of chromium reporting the ilmenite concentrate. This makes the downstream extraction of titanium more complicated and additionally, serious environment problems will be generated. Moreover, the presence of minute amounts of chromium compounds with a Cr_2O_3 content more than 0.0015% will considerably affect the light reflectance properties of titanium dioxide [8,9]. In other words, it is very possible that the raw ilmenite concentrate containing Cr will finally become one kind of the most hazardous solid waste. Therefore, the key factor impacting on the commercial exploitation of this heavy sand deposit is how to achieve a clean separation of the ilmenite from the chromite in the initial beneficiation stage.

Modifying the magnetic property of the ilmenite followed by magnetic separation has received much attention as a potential method for its recovery. Cui, Liu and Etsell [10] investigated oxidizing roasting of oil sands tailings in Athabasca. It was found that temperature had a considerable effect on the magnetic property of the ilmenite. Microwave radiation was also introduced to pre-treat the ilmenite ore. Compared with conventional heat treatment, it was considered as a more efficient and lower cost method [11,12]. However, for ilmenite ore containing chromite, it is also important to understand the magnetic property of the chromite under similar treatment. In the literature available [13,14], it was recognized that the magnetic susceptibility of the chromite was not significantly enhanced after oxidizing roasting, indicating that the ilmenite had better magnetic selectivity against the chromite.

However, little work has been reported on the high-efficiency utilization of a material simultaneously containing ilmenite and chromite by modifying magnetic property followed by magnetic separation. Oxidizing roasting of the raw ilmenite concentrate was firstly carried out, resulting in a distinct discrepancy of magnetic susceptibility between the ilmenite and the chromite. After low-intensity magnetic separation, a commercial ilmenite concentrate and a tailing containing Cr were obtained. Then, the tailing was preliminarily concentrated by a high-intensity magnetic separator and a rough chromite concentrate was gained. In order to further purify the rough one, reducing roasting was performed to transform the minerals containing hematite into the minerals containing magnetite, followed by low-intensity magnetic separation and finally, a chromite concentrate was obtained. In this study, the magnetism changes, phase transformation and morphology variation during oxidizing roasting process were detected by magnetism, chemistry, XRD and MLA analyses to interpret the mechanism of oxidizing roasting of the ilmenite. The oxidizing and reducing roasting conditions such as roasting temperature, carbon powder dosage, roasting time and magnetic induction were further optimized. The goal of this paper was to find a feasible way to realize the full economic value of the ilmenite deposit.

Table 1
Chemical composition of the raw ilmenite concentrate (%).

Constituent	TiO_2	Cr_2O_3	Fe	Zr_2O_3	SiO_2	CaO	MgO	Al_2O_3	P
Content	42.56	2.95	36.90	0.15	0.96	0.041	0.48	1.61	0.02

Table 2
Distribution of Ti and Cr oxides at different size ranges (%).

Size range (mm)	Yield	Grade		Distribution	
		TiO_2	Cr_2O_3	TiO_2	Cr_2O_3
+0.2	9.88	34.41	7.21	8.04	23.1
−0.2 + 0.074	84.45	43.62	2.72	87.15	74.46
−0.074 + 0.037	4.71	41.6	1.40	4.64	2.14
−0.037	0.96	7.41	0.99	0.17	0.30
Total	100.00	42.27	3.09	100.00	100.00

2. Experimental

2.1. Materials

Representative sample provided was a raw ilmenite concentrate separated from the Promenade beach placer using cone and spiral concentrators, whose chemical composition is shown in Table 1, which reports a high Cr content sample. Scanning electron microscope (SEM) images of the original and colored sample are presented in Fig. 1 where the particle size, shape and the minerals were exhibited at different colors (Fig. 1(b)) for easier recognition. Statistical results shown that the major constituents of the sample, in decreasing order of wt%, were the following: ilmenite (78.58), V-Ti-bearing magnetite (12.7), chromite (3.8), rutile (2.39), almandine (1.35) and that the liberation degree of the ilmenite and the chromite reached 90% and 96%, respectively, indicating that their effective separation were promising. The distribution of Ti and Cr oxides at different size ranges are exhibited in Table 2 and it can be known that more than 95% of them were distributed in the particle size above 0.074 mm, which was beneficial for the physical concentration.

2.2. Theoretical fundamental

2.2.1. Oxidation roasting

Reactions during oxidation roasting of the ilmenite [15,16] are listed as follows:

$$12FeTiO_3(s) + 3O_2(g) \rightarrow 4Fe_2O_3 \cdot 3TiO_2(s) + 2Fe_2O_3(s) \quad (1)$$

$$Fe_2O_3 \cdot 3TiO_2(s) \rightarrow Fe_2O_3 \cdot 2TiO_2(s) + TiO_2(s) \quad (2)$$

$$2FeTiO_3(s) + 1/2O_2(g) \rightarrow Fe_2O_3 \cdot 2TiO_2(s) \quad (3)$$

$$Fe_2O_3 \cdot 2TiO_2(s) \rightarrow Fe_2O_3(s) + 2TiO_2(s) \quad (4)$$

$$yFeTiO_3(s) + (1-y)Fe_2O_3(s) \rightarrow yFeTiO_3 \cdot (1-y)Fe_2O_3(s); \quad (0 < y < 1) \quad (5)$$

$$Fe_2O_3 \cdot 2TiO_2(s) \rightarrow Fe_2O_3 \cdot TiO_2(s) + TiO_2(s) \quad (6)$$

$$Fe_2O_3(s) + TiO_2(s) \rightarrow Fe_2O_3 \cdot TiO_2(s) \quad (7)$$

The ilmenite is firstly oxidized to an intermediate phase of $Fe_2O_3 \cdot 3TiO_2$ or $Fe_2O_3 \cdot 2TiO_2$, and then decomposed into hematite and rutile (Eqs. (1)–(4)) in the temperature range of 500–800 °C. Meanwhile, the generated hematite is reacted with the ilmenite