



# A novel technology for the refinement of low-grade ilmenite concentrate

Xuewen Wang\*, Xuehui Liu, Yiqian Ma, Mingyu Wang, Yi Wang, Xingming Wang

School of Metallurgy and Environment, Central South University, Changsha 410083, China



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## ABSTRACT

In this paper, the refinement of low-grade ilmenite concentrate was studied. It was found that by transforming in NaOH/NaNO<sub>3</sub> molten salt, and then leaching in water and in dilute hydrochloric acid, the low-grade ilmenite concentrate containing 3.09 wt% Mg, 1.03 wt% Ca, 3.38 wt% Si and 1.54 wt% Al can be refined well, meanwhile the contents of Ti and Fe are not affected. The lattice of ilmenite concentrate can be completely destroyed in the molten salt with NaOH/NaNO<sub>3</sub> weight ratio 7:3 at 400 °C for 6 h. The removal rates of Mg, Al, Ca and Si are 86.62%, 90.55%, 92.62%, 92.90% respectively by leaching the transformed concentrate in water with L/S ratio 2:1 mL/g at 60 °C for 0.5 h, and leaching the water leached residue in dilute HCl solution with L/S ratio 4:1 mL/g under pH 1.2 at 40 °C for 2 h. The contents of Mg, Al, Ca and Si are 0.41 wt%, 0.13 wt%, 0.08 wt% and 0.21 wt% respectively in the refined concentrate, which is suitable for arc reduction smelting to produce high-quality titanium slag.

## 1. Introduction

Titanium tetrachloride, TiCl<sub>4</sub>, is an important intermediate for titanium metallurgy and is widely used in the production of high-quality titanium dioxide and titanium sponge (Akhtar et al., 1991). TiCl<sub>4</sub> is obtained by reducing chlorination of natural rutile or titanium slag in a fluidized bed furnace. Titanium slag is mainly used as raw material of TiCl<sub>4</sub> production as there is few natural rutile in China (Tao et al., 2012; Xiao et al., 2013). Titanium slag is obtained by treating ilmenite concentrate in electric smelting furnace (Lv et al., 2017). Then gaseous TiCl<sub>4</sub> is formed by reduction chlorinating titanium slag (Xu et al., 2006). After cooling the gas containing TiCl<sub>4</sub>, crude TiCl<sub>4</sub> liquid is obtained (Xiang et al., 2014). During TiCl<sub>4</sub> producing, the low-boiling-point chlorides, such as AlCl<sub>3</sub>, SiCl<sub>4</sub>, VOCl<sub>3</sub> etc. are enriched in the crude TiCl<sub>4</sub>, while the high-boiling-point chlorides, such as CaCl<sub>2</sub>, MgCl<sub>2</sub>, MnCl<sub>2</sub> etc. deposit naturally at the bottom of fluidized bed (Den, 2010). The presence of impurities Ca, Mg, Al and Si in the titanium slag not only affects the production cost of TiCl<sub>4</sub>, but also causes the fluidized bed to fail to operate normally (Xu et al., 2006). Therefore, many methods have been posited to refine low-grade ilmenite concentrate and its titanium slag (Sahu, 2006; Huang et al., 2016).

The refinement of low-grade ilmenite concentrate is mainly acid leaching and alkali leaching. Acid leaching of ilmenite concentrate is mainly used to produce synthetic rutile (Mahmoud et al., 2004; Li et al., 2008). By alkaline leaching, Si and Al can be effectively removed from low-grade ilmenite concentrate, but Ca, Mg and Mn cannot

(Mazzocchitti et al., 2009). Although the grade of titanium has been greatly improved in synthetic rutile (TiO<sub>2</sub> > 99%) after alkaline leaching and acid leaching, its granularity is too fine to be used in boiling chlorination process, because in fluidized bed furnace, a large number of fine particles of synthetic rutile directly enter the flue gas without reaction (Den, 2010). Moreover, the acid leaching is expensive because iron is completely leached from the ilmenite concentrate, and the wastewater containing Fe needs to be treated. As a result, there is no factory in China that produces TiCl<sub>4</sub> from synthetic rutile, although its TiCl<sub>4</sub> production is currently the world's largest.

The treatments of titanium slag mainly included oxidation roasting, oxidation-reduction roasting, sulphidization, chlorination, and salt roasting, in which impurities were subsequently removed by water or diluted hydrochloric acid leaching (Gueguin and Cardarelli, 2007; Pistorius and Motlhamme, 2006; Wang et al., 2006). By these methods, Ca and Mg can be effectively removed from titanium slag, while the impurities similar to titanium, such as Si and Al, are difficult to be removed (Liu et al., 2013). Moreover, in order to remove impurities effectively, the titanium slag must be finely ground in the treatment process. As with synthetic rutile, powder titanium slag cannot be used in the reduction chlorination process as well.

To overcome the shortcomings of above technology, the ideal method is to remove impurities Ca, Mg, Al, Si and so on from ilmenite concentrate, and then use the refined ilmenite concentrate to produce titanium slag because the titanium slag produced by arc smelting of ilmenite concentrate is not powdery but sandlike. In this paper, a novel

\* Corresponding author.

E-mail address: [wxwesu@163.com](mailto:wxwesu@163.com) (X. Wang).

**Table 1**  
Experimental results of the refinement of low-grade ilmenite concentrate, wt%.

Elements	Ti	Fe	Mg	Ca	Si	Al	Mn	V	Na
Ilmenite concentrate	27.52	30.41	3.09	1.03	3.38	1.54	0.63	0.08	0.15
Water leached residue	23.39	25.85	2.63	0.87	1.28	0.55	0.52	–	10.53
Refined concentrate	30.36	33.62	0.41	0.08	0.21	0.13	0.06	–	0.18

technology for the refinement of low-grade ilmenite concentrate is presented. After transforming in NaOH-NaNO<sub>3</sub> molten salt, and then leaching in water and in dilute HCl solution, impurities Ca, Mg, Al, Si and so on can be effectively removed from ilmenite concentrate, while the contents of Ti and Fe are not affected.

## 2. Experimental

### 2.1. Materials and analysis

The low-grade ilmenite concentrate used in the study was obtained from Panzhihua city, Sichuan province, China. The concentrate was ball milled to 270 mesh (100% through 270 mesh, 53 μm) before refining. The composition of the low-grade ilmenite concentrate is listed in Table 1. Sodium nitrate, sodium hydroxide and hydrochloric acid were used in the experiments, which are all analytical grade.

The compositions of experimental samples were determined by chemical methods and inductively coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu Kα X-ray radiation at 35 kV and 20 mA. The pH was determined with ORION-230A which was made in USA, the degree of accuracy is 0.01.

### 2.2. Experimental procedure

The transformation of low-grade ilmenite concentrate was carried out in a 50 mL iron crucible. For each experimental run, 10 g low-grade ilmenite concentrate, 12 g NaNO<sub>3</sub> and predetermined weight (20–40 g) NaOH were added into the crucible, which was heated by a molten salt bath (40 wt% NaNO<sub>2</sub>, 7 wt% NaNO<sub>3</sub>, 53 wt% KNO<sub>3</sub>) at the desired temperature (360–500 °C) to make the concentrate transformed under stirring (150 r/min) for 2–8 h. Then the liquid (molten salt) in the crucible was drained as soon as possible. The solid (transformed concentrate) was moved from the crucible to a 150 mL conical flask which contains 50 mL water to dissolve the entrainment molten salt. After stirring (250 r/min) for 0.5 h at 60 °C, filtration was performed. The filtrate was used to recover the molten salt, and the filter cake (water leached residue) was leached with dilute HCl solution under pH 0.1–3.0 at 25–100 °C stirring (250 r/min) for 1–8 h to remove impurities Ca, Mg, Mn and so on. At last, the refined concentrate was obtained after filtering once again.

## 3. Results and discussion

### 3.1. Transformation of low-grade ilmenite concentrate

#### 3.1.1. Effect of time on impurities removal

Fig. 1 is the experimental results obtained by adding 10 g low-grade ilmenite concentrate into the molten salt containing 12 g NaNO<sub>3</sub> and 28 g NaOH to make it transformed at 380 °C under stirring in a 50 mL iron crucible. After transforming for scheduled time, the liquid of molten salt was drained from the crucible as soon as possible. Then the transformed concentrate was moved from the crucible to a 150 mL conical flask which contains 50 mL water to dissolve the entrainment

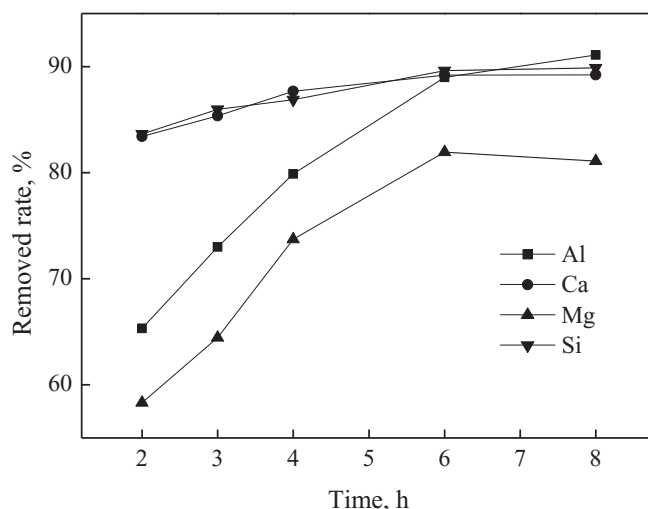
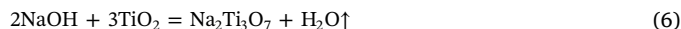
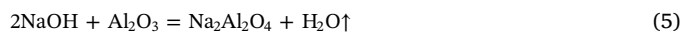
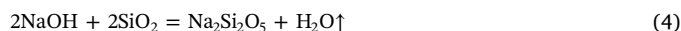
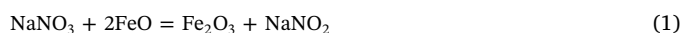


Fig. 1. Effect of transformation time on impurities removal.

molten salt. After stirring for 0.5 h at 60 °C, filtration was performed. Then the water leached residue was leached in dilute HCl solution with L/S ratio 4:1 mL/g under pH 1.5 at 60 °C stirring for 2 h. From Fig. 1 it can be seen that the removal rates of Ca and Mg increase sharply with the increase in transforming time from 2 h to 6 h. At the same time, the removal rates of Al and Si increase as well, but slower. Then their removal rates all increase slowly with the further increase in transforming time. Therefore, the transforming time should be ≥ 6 h.

The XRD patterns of low-grade ilmenite concentrate are shown in Fig. 2a, which reveals that there are four crystal mineral phases, FeTiO<sub>3</sub>, (Fe,Mg)(Ti,Fe)O<sub>3</sub>, Ca<sub>19</sub>MgFe<sub>2</sub>Al<sub>10</sub>Si<sub>18</sub>O<sub>70</sub>(OH)<sub>8</sub> and Ca<sub>3</sub>Fe<sub>3</sub>(SiO<sub>4</sub>)<sub>3</sub>. The main existence form of impurities Ca, Mg, Al and Si in ilmenite concentrate is (Fe,Mg)(Ti,Fe)O<sub>3</sub>, Ca<sub>19</sub>MgFe<sub>2</sub>Al<sub>10</sub>Si<sub>18</sub>O<sub>70</sub>(OH)<sub>8</sub> and Ca<sub>3</sub>Fe<sub>3</sub>(SiO<sub>4</sub>)<sub>3</sub>. The XRD patterns of the water leached residue of the ilmenite concentrate transformed for 6 h are shown in Fig. 2b, which indicates that the lattice of ilmenite concentrate has been completely destroyed, and there are six crystal mineral phases, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> and MgFe<sub>2</sub>O<sub>4</sub> in the transformed concentrate. In the transforming, the main chemical reactions can be expressed by the following equations:



As can be seen from the above reactions, NaNO<sub>3</sub> is the oxidant of ilmenite concentrate, and NaOH is its transformation agent. It was found that no amount of NaNO<sub>3</sub> could completely oxidize the iron in ilmenite concentrate without NaOH.

#### 3.1.2. Effect of temperature on impurities removal

Fig. 3 is the experimental results obtained by transforming the low-grade ilmenite concentrate at different temperature for 6 h, and the other conditions are the same as that in Fig. 1. As can be seen, the removal rates of Ca and Mg increase sharply with the increase in transforming temperature from 360 °C to 400 °C. Then their removal rates are decreasing with the further increase in transforming

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