Comparative study of alkali roasting and leaching of chromite ores and titaniferous minerals

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ABSTRACT

Extraction of titanium and chromium oxides may be achieved via roasting the respective minerals with alkali at high temperatures, followed by water and organic acid leaching. In this study, sodium and potassium hydroxides are used as alkali for roasting of chromite ores and ilmenite mineral concentrates. The thermodynamic analysis of the roasting process is discussed in terms of designing the process. Samples of chromite and titaniferous minerals were roasted with NaOH and KOH in a temperature range of 400 °C–1000 °C in an oxidising atmosphere. The roasted chromite and ilmenite samples were further processed in order to extract water-soluble Na_2CrO_4 from the reacted chromite and purify titanium dioxide from titaniferous minerals, respectively. The TiO_2 purity obtained after roasting at 400 °C with NaOH and double leaching was 49.2 wt.%, whereas when using KOH the purity was 54.5 wt.%. The highest TiO_2 purity obtained after roasting at 1000 °C for 2 h and double leaching with water and organic acids was 84 wt.%. At low temperature (400 °C) the recovery of chromium was higher for chromite roasted with KOH than for chromite roasted with NaOH. However, at high temperatures (700 °C and 1000 °C) chromium recoveries were similar when roasting with both hydroxides. Around 95% chromium extraction yield was achieved when chromite was roasted with sodium and potassium hydroxides at 1000 °C for 2 h and water leached.

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1. Introduction

For the last 40 years, global economic growth has resulted in a rapid increase in the demand for a range of metals and metal oxides for high technology applications, including titanium dioxide (TiO_2) and chromium oxide (Cr_2O_3) (Brown et al., 2015). This has led to a rise in the consumption of their mineral oxides, TiO_2 and Cr_2O_3, derived from ilmenite and chromite, respectively. As a consequence, the amount of waste generated and the energy required to treat the mineral feedstock has placed an increasing strain on the global environment. The world total production of titaniferous minerals and chromite ores and concentrates for the period 1971–2013, in millions of metric tonnes, is compared in Fig. 1.

Bearing the fact that the environment burden on industry is increasing, research must focus on the development of alternative processing routes, which alleviate the problem of wastes, materials and energy, by reducing the time for processing and reducing the waste volume at the end of the process. One of the reasons why we have undertaken comparative studies of chromite ore and titaniferous minerals is that often small concentrations of chromium oxide (0.1 to 0.5 wt.%) are found in ilmenite, and TiO_2 in chromite deposits, especially from S.

Africa. The presence of Ti metal as an impurity in Cr for steel making is undesirable, and also the strong green colour of Cr^{3+} in TiO_2 is not acceptable. For this reason, in this article a novel approach, based on alkali roasting at moderately high temperatures followed by leaching at low temperatures has been investigated for the treatment of titanium oxide minerals and chromium ores. The present work is focussed on studying the physico-chemical changes that occur during the alkali roasting of ilmenite mineral concentrates and chromite ores, using sodium and potassium hydroxides. The thermodynamics of alkali roasting for both minerals is also analysed by computing Gibbs energies of relevant reactions.

1.1. Production of TiO_2 from ilmenite mineral

Titanium is found in nature in a large variety of minerals of which ilmenite ($FeTiO_3$), rutile (TiO_2), anatase (TiO_2), brookite (TiO_2), perovskite ($CaTiO_3$) and leucoxene ($Fe_2O_3 \cdot TiO_2$) are the most representative (Habashi, 1997). Even though the demand for titanium metal from the energy and chemical industries is expected to increase during the next 10 years, the largest share (90%) of the titanium product market is still dominated by the paint and pigment industry, which requires white TiO_2 (Kogel, 2006). Ilmenite is the main feedstock for the extraction of TiO_2 pigment via the sulphate process, but increasingly the chloride process, which uses rutile or high-grade titanium slag, is being favoured due to the fact that it appears to be more favourable in terms of cost
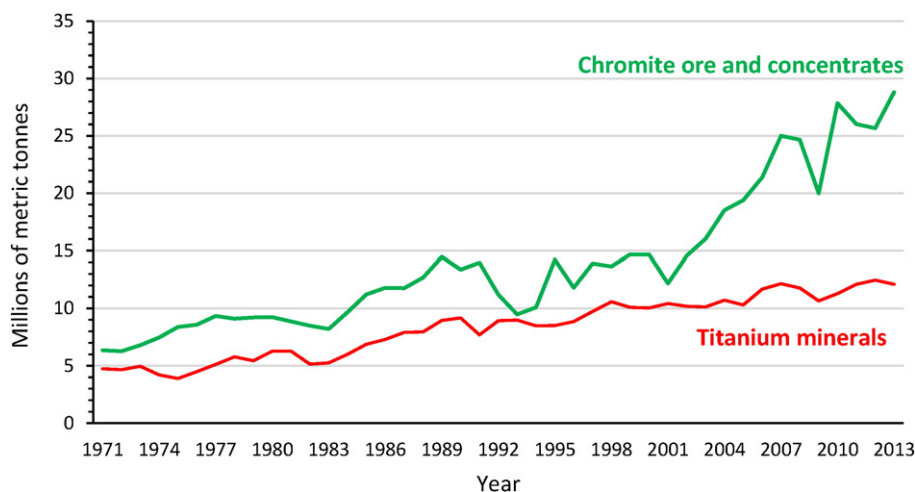
Fig. 1. World total output of titanium oxide based minerals and chromite ores and concentrates from 1971 to 2013. Brown et al. (2015).

and waste management, when compared to the sulphate process (Rosenbaum, 1982). However, due to the limited supply of natural rutile and increasing usage of the chloride process, it has become necessary to produce synthetic rutile by upgrading ilmenite (Mackey, 1994).

Several processes exist for the upgrading of ilmenite, with the Becher process being an example of one employed on a commercial scale (Zhang et al., 2011). In the Becher process, ilmenite is pre-oxidised in air to form pseudobrookite ($Fe_2O_3 \cdot TiO_2$) and TiO_2, converting the Fe^{2+} ions to Fe^{3+} ions. This follows reaction (1.1):

$$4\ FeTiO_3 + O_2 \rightarrow 2\ Fe_2O_3 \cdot TiO_2 + 2\ TiO_2. \tag{1.1}$$

The pre-oxidised ilmenite is reduced with coal at 1200 °C in a rotary kiln, converting the iron oxide to metallic iron:

$$Fe_2O_3 \cdot TiO_2 + 3\ CO \rightarrow 2\ Fe + TiO_2 + 3\ CO_2. \tag{1.2}$$
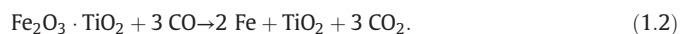
The metallic iron is oxidised and precipitated using an aeration process where ammonium chloride is used as a catalyst (Farrow et al., 1987). After the removal of precipitated iron, any remaining iron is removed by leaching with sulphuric acid, leaving behind synthetic rutile with around 93 wt.% TiO_2 (Becher et al., 1965; Filippou and Hudon, 2009):

$$2\ Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3. \tag{1.3}$$

Indeed the Becher process involves high-temperature oxidation, followed by metallisation and then leaching. The iron derived is not available in a suitable metallic form for iron or steelmaking.

Alkali treatment of ilmenite and titanium bearing ores at high temperatures has been extensively studied. This includes work by Foley and MacKinnon (1970) that involved roasting of ilmenite with potassium and sodium carbonates, at 860 °C, and subsequent leaching of the alkali titanates formed, with hydrochloric acid (HCl). Kinetics and reaction mechanism of soda ash roasting of ilmenite, in the 600 °C–900 °C temperature range, was studied by Lahiri and Jha (2007). Sanchez-Segado et al. (2015a) further studied alkali roasting of Bomar ilmenite with sodium, potassium and lithium carbonates and hydroxides, followed by acid leaching in order to produce synthetic rutile. They were able to achieve 97% pure TiO_2 from a feedstock containing 75% TiO_2, after leaching for 5 h. Further studies have focussed on direct leaching of ilmenite in aqueous solutions of potassium or sodium hydroxide and followed by acid leaching. Nayl and Aly (2009) decomposed ilmenite in an aqueous solution of KOH and investigated

this route by using a range of acids to produce high-grade TiO_2. Amer (2002) pressure-leached ilmenite at a high temperature with NaOH before leaching with HCl to produce high-grade TiO_2. Lahiri and Jha (2009) roasted ilmenite with KOH and were able to selectively separate the rare earths that were present. Manhique et al. (2011) investigated the roasting of ilmenite with NaOH at different temperatures but no comparison was made with other alkali salts.

1.2. Chromium extraction from chromite ore

Chromium is present in many different minerals, nevertheless, just chromite ore, which can be expressed with the general formula $(Fe_aMg_{(1-a)})(Cr_bAl_{(1-b)})_2O_4$, is used for commercial extraction of chromium (Maliotis, 1996). Chromites often have up to 1.5% TiO_2, with Ti ions occupying octahedral sites in the spinel structure. Chromium compounds are widely used in manufacturing of metals and production of chromium-based chemicals and refractory materials (Ding and Ji, 2003). The estimated world production of chromite ore in 2014 was 29 million metric tonnes (Brown et al., 2015). The global resources of shipping-grade chromite are more than 12 billion tonnes, with about 95% of them located in Southern Africa and Kazakhstan (U.S. Geological Survey, 2015). Chromium is an important alloying element for increasing the oxidation resistance of iron and nickel in high-alloy steels and super alloys. Different chromium chemicals are also used as pigments, in electroplating, as mordant in the leather industry and for manufacturing of refractory materials.

Current technologies for chromite ore processing present serious environmental problems associated with waste disposal. Previous research reported that around 15 wt.% of chromium oxide present in chromite does not react in traditional alkali roasting process, which then generates a chromite ore processing residue (COPR) containing about 0.1 to 0.2 wt.% Cr^{6+}. Landfilling is the traditional method of waste disposal and has become a significant source of hazardous hexavalent chromium (Antony et al., 2001). Various processes such as soda-ash roasting (Antony et al., 2001), acid leaching (Geveci et al., 2002; Zhao et al., 2014), alkali leaching (Xu et al., 2005; Zhang et al., 2010) and alkali fusion (Hundley et al., 1985) have been developed for the processing of chromite ores in order to produce sodium chromate (Na_2CrO_4), which is the primary product used for the manufacturing of different chromium chemicals. Because of economic and technical reasons, just soda-ash roasting has been used worldwide on a commercial scale, either in a rotary kiln or in a rotary hearth furnace. In this process, the extraction of chromium is achieved via roasting the mineral with alkali salts (usually sodium carbonate). Chromite ore and sodium carbonate are roasted at temperatures ranging between 900 °C and