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Soda ash roasting of titania slag product from Rosetta ilmenite

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ABSTRACT

A soda ash roasting process for upgrading titania slag product of Rosetta ilmenite to a high grade titanium dioxide (TiO_2) is presented. The roasting process was carried out at moderate to high temperatures to yield a reaction product that would be easily decomposed by subsequent leaching procedures. Factors affecting the roasting process; namely the soda ash ratio to the slag material, the roasting time and temperature were studied. The optimised conditions used a Na_2CO_3 to slag ratio of 0.55:1 at a roasting temperature of 850 °C for 0.5 h duration period. The impurities associated with the roasted slag were subjected to leaching with water and dilute hydrochloric acid solution leaving synthetic rutile (TiO_2) as insoluble residue. To improve the quality of the synthetic rutile, an alkaline leaching step was added to remove the excess silica present in the treated titania slag. This method is capable of producing high purity synthetic rutile assaying about 97% TiO_2.

1. Introduction

Titanium is commonly found in nature in the form of ilmenite mineral ($FeO.TiO_2$) which assays from 40 to 80% TiO_2 whilst most mineral concentrates range from 45 to 67% TiO_2. Other mineral sands deposits include rutile (~95%TiO_2), anatase (>95%TiO_2) and leucoxene which represents a weathered form of ilmenite and contains up to 85% TiO_2. However, rutile deposits are much more scarce than ilmenite while those of anatase are yet to be commercially exploited and those of leucoxene are only exploited on a limited scale (Van Dyk et al., 2004). Other titanium minerals include brookite (rhombic TiO_2), perovskite ($CaTiO_2$), sphene ($CaTiSiO_5$) and geikielite ($MgTiO_3$).

Titanium is primarily used in the form of TiO_2 as white pigment in paints, plastics and paper. Commercial production of TiO_2 pigment uses either the sulfate process or the chloride process. In the former process, relatively low grade feedstock can be used, but it gives a higher volume of waste product that requires proper treatment and disposal. It is more preferable to use the chloride process which necessitates careful upgrading of low grade ilmenite deposits to increase their TiO_2 content.

To realize this objective, several processes have been developed that depend upon pyrometallurgical and/or hydrometallurgical treatment of ilmenite deposits to eliminate most of the iron content and other possible impurities (e.g. Schoukens et al., 2004; Mahmoud et al., 2004; Lasheen, 2005, 2006, Van Dyk et al., 2004; Jarish, 1977). These processes include the partial reduction of iron at high temperature to Fe(II) state which is more amenable to acid leaching or its pre-oxidation followed by partial reduction to Fe(II) or else to metallic iron. Alternatively, ilmenite ore can be smelted in the presence of a carbonaceous reducing agent in an electric furnace where two saleable products are obtained; namely high quality pig iron and a titania rich slag containing typically 80–85% TiO_2, (Sahu et al., 2006). In such a treatment, the composition of the titania slag product is chemically and mineralogically different from ilmenite. According to Van Dyk et al., (2004) all titanium is present in ilmenite as Ti(IV) and about 20% of iron is present as Fe(III) and the rest as Fe(II). However, titanium in the titania slag occurs as Ti(III) and Ti(IV) and most of the associated iron is present as Fe(II). While Ti and Fe atoms in ilmenite are arranged in the form of hexagonal crystals, ilmenite slag is composed of the following 4 phases:

1. pseudo-brookite or M_3O_5 phase (crystalline). This is the most abundant phase and can be regarded as a solid solution of iron oxide and titanium oxide.
2. rutile (TiO_2) (not always detectable by XRD)
3. an amorphous glassy phase consisting of mainly SiO_2, TiO_2, FeO, CaO and Al_2O_3.
4. finely disseminated metallic iron globules that are present on the grain boundaries of the rutile crystals and in the silicate rich glassy matrix.

Due to these differences and the complex nature of titania slag, the above processes developed for beneficiating ilmenite concentrates are not applicable in some cases for titania slag. Other processes have thus been developed for its beneficiation including chlorination or fluxing of the associated impurities, sulfatisation and oxidation–reduction roasting or else salt roasting. The first process of chlorination has been suggested by Gueguin in 4 successive U.S. Patents (1978, 1990, 1991, 1995) for treating of titania slag containing at least an alkaline earth impurity. In this procedure, the slag is treated with HCl gas at high

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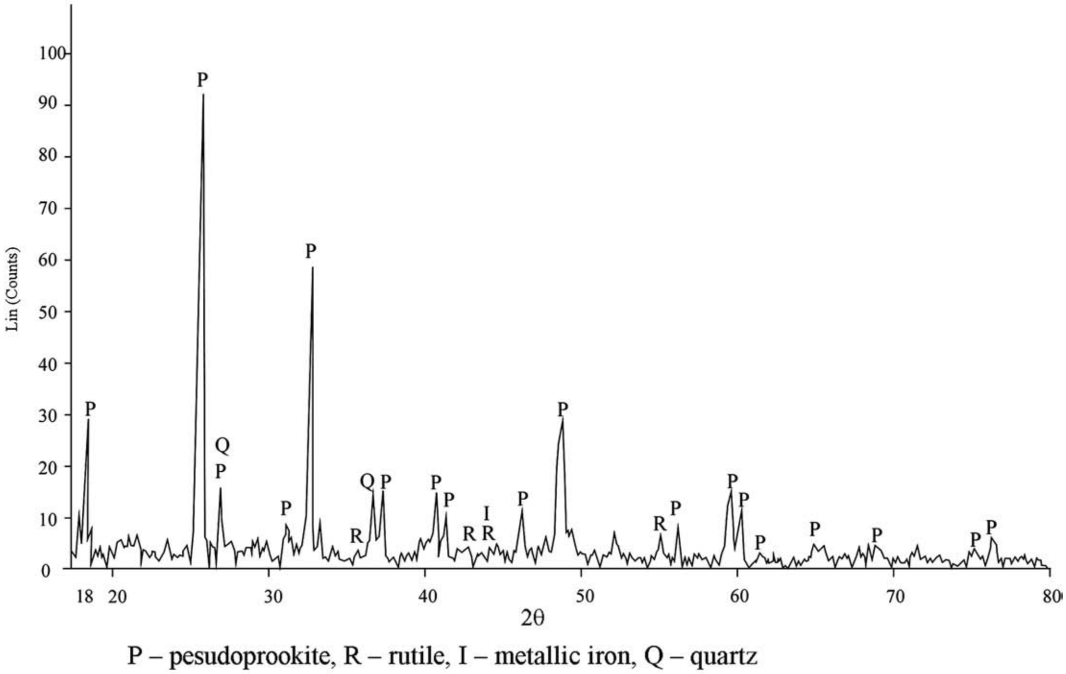

Fig. 1. X-ray diffraction pattern of titania slag of Rosetta ilmenite.

temperature in the absence of oxygen to prevent oxidation of Ti(III). Iron and alkaline earth chlorides are formed and subsequently water or HCl acid leached. Alternatively, Elger and Kirby (1976) have proposed upgrading the slag through heating in presence of a glass forming fluxing agent, such as P_2O_5 or the oxides of Na, K or Si, which results in the formation of a crystalline rutile phase and a glassy phase containing most of the impurities which would be removed by treatment with a mineral acid. In titania slag sulfatisation, Elger and Holmes (1982) propose mixing of the slag with an alkaline salt e.g Na_2CO_3 before reaction with either SO_3 or with mixtures of SO_2 and O_2 at 700 °C to 1100 °C. Alternatively, sulfidisation in presence of a mixture of H_2S+N_2 and S_2+C at 1100 °C was proposed by Borowiec (1991), followed by water or HCl acid leaching of the iron sulfides at room temperature.

More recently, both Van Dyk et al. (2004) and Borowiec et al. (1998) have indicated that slag can be directly upgraded by oxidation–reduction thermal treatment before HCl leaching. Borowiec et al. (1998) described a process that is now commercially employed for upgrading Sorel slag (78.3–84.84 TiO_2%) produced by QIT. It involves thermal treatment where oxidation is accomplished at temperature (1000 °C–1050 °C) for 1–1.5 h, and the succeeding reduction step is performed at 800 °C for 1 h using smelter gas. In the oxidation step, Fe (II) and Ti(III) are converted to Fe(III) and Ti(IV) which help in decomposing the glassy phase. In the subsequent reduction step Fe (III) is reduced back to Fe(II) and a MgO rich ilmenite–geikielite solid solution is formed which is more amenable to leaching than the original phases. However, proper pre-treatment of the slag is required involving fine sizing of the titania to allow iron reactions at the exposed surfaces during oxidation and reduction. The treated slag is then leached at 145–155 °C in a two stages procedure using 20% HCl for 6 h or in one stage procedure for 8 h under pressure. The assay of the beneficiated slag after washing and calcinations attains 95 TiO_2%.

The presently proposed method is an alternative process for the successful treatment of slags that have a relatively large amount of impurities (20–30%). It can summarized in the following main points

- roasting of the ground slag in the presence of soda ash at a relatively low temperature (850 °C) for a contact time of only 0.5 h.
- atmospheric acid leaching of the destroyed refractory structure for only 30 min.
- potential to further separate useful by-product (V, Cr) besides Mn and Fe.

The fineness of the obtained titanium dioxide concentrate can be easily overcome in order to be suitable for the chloride process feed. Finally, the proposed process represents a promising trial to upgrade impure titania slag in an economic manner into a high TiO_2-containing product (~97 TiO_2%).

A treatment comparable to soda ash sintering-roasting of an Egyptian ilmenite from Abu Ghalga (Morsi et al., 1993) has also been applied by Jarish (1977) to a Canadian titania slag (Sorelslag); viz, an alkali salt or a mixture of these salts (carbonates, chlorides, sulfates, nitrates or their oxides or hydroxides) at 600–950 °C. In the former work, it has been concluded that the formation of the higher titanates $Na_8Ti_5O_{14}$ and $Na_6Ti_2O_7$ during sintering favors the formation of the lower titanates such as Na_2TiO_4 during subsequent roasting which is easily soluble in dilute sulfuric acid. For the latter work, the mentioned alkali salt treatment results in the destruction of the refractory slag thereby the associated impurities as iron and silica are amenable to acid leaching. Prior to acid leaching, wet grinding of the treated slag allows leaching of Cr and V as their alkali salts.

The present paper relates to the development of soda ash roasting process for treating the titania slag product of northern Rosetta ilmenite for producing a high grade synthetic rutile. The experimental parameters affecting the roasting process were investigated and optimized.

2. Experimental

2.1. Materials

A titania slag sample was prepared from Rosetta ilmenite by its carbothermal reduction in an electric arc furnace and was kindly

Table 1
Chemical composition of the titania slag

TiO_2	Fe_t[a]	Al_2O_3	CaO	MgO	P_2O_5	MnO	Cr_2O_3	V_2O_5	ZnO	SiO_2
72.00	12.65	1.80	0.78	0.60	0.06	1.63	0.32	0.55	0.002	9.0

[a] As Fe_2O_3.