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The effect of molten sodium titanate and carbonate salt mixture on the alkali roasting of ilmenite and rutile minerals

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Worldwide TiO_2 is extracted from natural ilmenite, rutile, and anatase minerals via the sulphate and chloride processes. The sulphate process generates large volumes of less toxic wastes, whereas the chloride process, including the ilmenite-chloride process of DuPont, yields much lower volume of wastes, which are highly toxic and hazardous. The treatment and disposal of such hazardous chloride wastes is both expensive and difficult in terms of long-term monitoring. Besides the waste management and disposal, there is also a shortage of high-grade titanium dioxide minerals in nature, which consequently yields much larger tonnages of sulphate and chloride wastes.

In the present investigation we report the results of an alternative titaniferous mineral beneficiation process based on soda ash roasting of minerals. Compared to the conventional processes for beneficiation of TiO_2- ores, the alkali roasting of titaniferous offers several advantages including the zero process wastes. In the soda ash roasting process, the mineral is mixed with sodium carbonate and heated above 1023 K in air. The oxidative roasting of ores yields several complex alkali compounds, some of which produce a liquid mixture above 1123 K. In this paper, we have attempted to characterize the composition and physical chemistry of alkali-rich liquid phase. The phase equilibria in the Ti-(M:Fe)-Na-O system are evaluated and compared with the phases formed as a result of roasting reaction.

The experimental results revealed that the composition of complex alkali liquid at the reaction interface plays an important role in determining the transport of O^{2-} ions and decomposition of ilmenite. The roles of the crystal structure of mineral phases and their energetics are also emphasized in controlling their decomposition during alkali roasting. The presence of molten alkali in controlling the partitioning of water-soluble alkali salts and insoluble sodium titanate is also explained.

Keywords: ilmenite, anatase, alkali roasting, phase equilibria.

Introduction

Anatase, ilmenite, and rutile are three important Ti-minerals. These Ti minerals accumulate in secondary placer deposits along with zircon, monazite, leucoxene, and magnetite minerals[1]. These sand deposits are mined and upgraded by gravimetric, electrostatic or magnetic separation processes. However, need for higher grades of Ti minerals for the production of TiO_2 requires further upgrading to form synthetic rutile ($TiO_2 > 90\%$). Various techniques are used commercially for the production of synthetic rutile. The slagging, which involves smelting of ilmenite to produce a high-titania slag and iron byroduct, is the main process for beneficiation of ilmenite ores. The roasting of ilmenite via Becher process or roasting and acid leaching of ilmenite by Benelite process are also used for the production of synthetic rutile[2].

Approximately 94% of Ti minerals mined are used for the production of pigment grade TiO_2, which is used in paints and coatings (60%), plastic (20%), and paper (12%) industries[1,3]. The annual production of finished pigment grade TiO_2 is over 4.54 million tons, which is equivalent to US$6 billion annual sales. Natural rutile, ilmenite concentrates, anatase, leucoxene, synthetic rutile and titania-slag are the major feedstock for the production of TiO_2. The pigment grade TiO_2 is produced via two different processes: chlorination and sulphatation, both of which require different feedstocks.

The steady growth of pigment industries has encouraged the development of new minsand (heavy mineral sands) projects in Australia, South Africa, and India[2]. However, the present beneficiation techniques require high quality ilmenite ores and are not suitable for upgrading lower grade Ti ores [4]. Also the synthetic rutile or TiO_2 slag produced by the present beneficiation techniques, contain a significant amount of radioactive elements and other minor impurities. Minor and trace element oxides in the feedstock adversely affect the properties of finished products and create operational problems, e.g. sticky beds and hazardous wastes. The impurity oxides in the process wastes must be neutralized before being disposed of safely at landfill or at used mines, where they remain a potential source for environment pollution and groundwater contamination. Neither CaO nor minor and trace elements can be removed via acid leaching and electric-arc smelting.

In view of the above problems associated with the mineral phase concentration of Ti-based ores and production of pigment grade titanium dioxide, an alternative route, which is both flexible and more accommodating for processing difficult ores, is discussed in this paper. We have studied soda ash roasting and leaching for the beneficiation of various types of TiO_2 ores. In soda-ash roasting, the formation of liquid phase is a common problem that results in product granulation, formation of rings on the kiln walls and lump formation[5]. It is, therefore, important to analyse the formation of the liquid phase and its role in the soda ash roasting reaction, which will consequently aid in improving the process control for achieving a higher product yield.

The present investigation was carried out to understand the role of alkali liquid phase on soda ash roasting of ilmenite and anatase ores and its effect on the separation of impurities from ores.

Experimental work

Two types of TiO_2 ores, namely ilmenite and anatase, were used for this investigation. The chemical composition of the ores used is given in Table I. The X-ray diffraction patterns and microstructures of the anatase and ilmenite ores are compared in Figures 1 and 2 respectively. In Figure 1, the rutile and anatase phases were dominant in the ilmenite and anatase ores, respectively. The grains of the ores, as shown in Figures 2a and 2b, were highly porous and hematite-pseudobrookite type exsolved phases were also present on the surface of the TiO_2 grains, due to hydrothermal alterations and extensive weathering in a tropical environment. The zircon, monazite and silicate gangue were also present in the ore but these gangue phases were not identified in the XRD patterns in Figure 1 due to their very small concentrations, they may be present in an amorphous matrix.

The isothermal roasting experiments were carried out at different temperatures ranging from 1073 to 1273 K in and oxidizing atmosphere for 2 hours. For the roasting experiments, three types of alkali-to-ore ratios were used, which were based on the stoichiometric amount of soda ash required for the formation of alkali salts of:

- TiO_2
- $TiO_2 + Fe_2O_3$, and
- $TiO_2 + Fe_2O_3 + SiO_2 + Al_2O_3$.

The TiO_2 ore and sodium carbonate powder were weighed and mixed thoroughly. A ten-grams charge was transferred in an alumina crucible, which was then hung inside a silica reaction tube. The silica tube was then lowered inside a resistance furnace, which was preheated to the selected temperature. During the course of the roasting

Table I
Chemical composition of anatase and ilmenite ores used for roasting experiments (concentration in weight per cent)

Sample	Anatase	Ilmenite
TiO_2	57.80	70.65
Fe_2O_3	14.61	21.69
Al_2O3	7.64	2.51
SiO_2	1.65	2.13
P_2O_5	7.65	0.42
Mn_3O_4	0.71	0.72
MgO	0.36	0.37
CaO	2.13	<0.10
Na_2O	<0.30	<0.30
K_2O	<0.01	<0.01
Cr_2O_3	0.01	<0.01
LOI (at 1025°C)	6.19	2.01

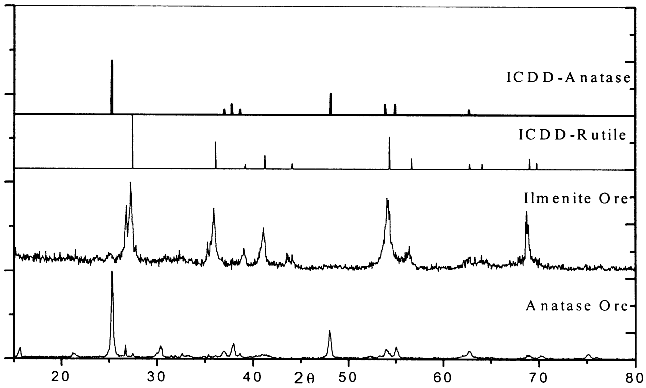


Figure 1. The comparison of XRD patterns of anatase and ilmenite ores. (ICDD Anatase file No. 21-1272 and ICDD Rutile file No. 21-1276)

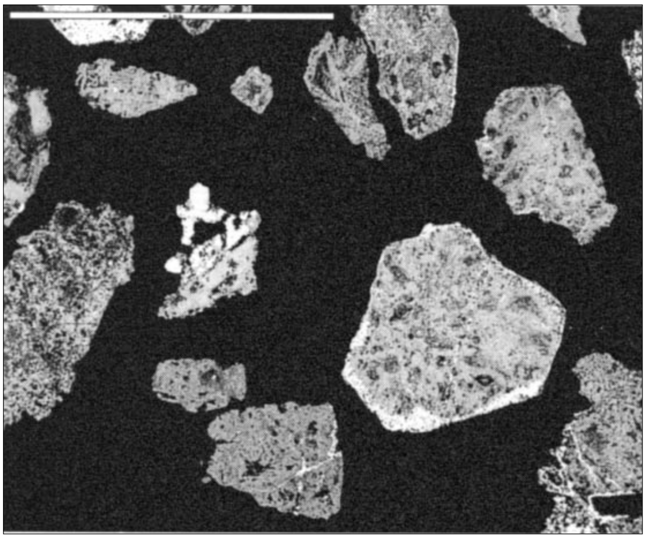


Figure 2 (a). The microstructure (BSE 200X) of the anatase ore. The anatase grains (grey colour) are highly porous due to weathering and have light grey colour rim/seams of Fe-rich exsolved phases

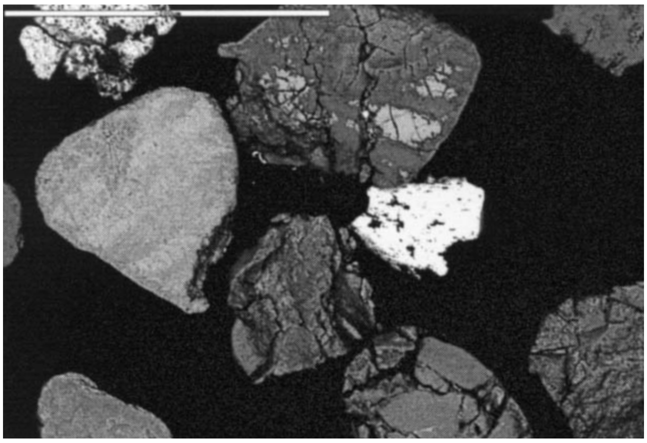


Figure 2 (b). The microstructure (BSE 200X) of ilmenite ore. The dark grey colour phase is rutile, the light grey colour phases are pseudorutile/ brookite (Ti-Fe-O) phases and bright colour phase is zircon grain. The phase contrast in light grey Ti-Fe-O phases is due to variations in Fe-contents of the phases

reaction, the flow of air was maintained at 500 ml min^{-1}. The sample temperature was recorded using a Pt / Pt13%Rh thermocouple. The schematic of the experimental set-up used is given elsewhere[5].

The roasted samples were then leached with hot water for 30 minutes at 363 K. The solution was agitated during water leaching by using a magnetic stirrer. After water leaching, the solution was filtered through Whatman filter paper and residue was washed with hot water repeatedly until the pH of the washed solution decreased to 7. The residue, after water leaching, was treated with a 5% hydrochloric acid solution for 20 minutes. The acid leaching was carried out at 343–353 K and a magnetic stirrer was used for agitation. The solution was filtered through Whatman filter paper and residue was washed thoroughly with hot water until pH increased to[6–7].

The samples collected after roasting, water and acid leaching were examined for the presence of reaction products. The physical and chemical properties of the samples were examined using several analytical techniques: e.g. the chemical composition was analysed by XRF, the phase composition of a sample was analysed using X-ray diffraction, SEM-EDX techniques. The results of the analysis of the samples are discussed in the next section

Results

Thermodynamic consideration

During the alkali roasting reaction, the constituent oxides in the Ti ores react with soda ash and form different alkali compounds. The Gibbs free energy change for the following reactions of TiO_2 and other oxide constituents in ore, with sodium carbonate was calculated using the FACT-Sage program[6]:

$$Na_2CO_3(s) \rightarrow Na_2O(s) + CO_2(g) \quad [1]$$

$$TiO_2(s) + 2Na_2CO_3(s) \rightarrow Na_4TiO_4(s) + 2CO_2(g) \quad [2]$$

$$TiO_2(s) + Na_2CO_3(s) \rightarrow Na_4TiO_3(s) + CO_2(g) \quad [3]$$

$$5TiO_2(s) + 4Na_2CO_3(s) \rightarrow Na_8Ti_5O_{14}(s) + 4CO_2(g) \quad [4]$$

$$3TiO_2(s) + Na_2CO_3(s) \rightarrow Na_2Ti_3O_7(s) + CO_2(g) \quad [5]$$

$$6TiO_2(s) + Na_2CO_3(s) \rightarrow Na_2Ti_6O_{13}(s) + CO_2(g) \quad [6]$$

$$Fe_2O_3(s) + Na_2CO_3(s) \rightarrow Na_2Fe_2O_4(s) + CO_2(g) \quad [7]$$

$$SiO_2(s) + Na_2CO_3(s) \rightarrow Na_2SiO_3(s) + CO_2(g) \quad [8]$$

$$Al_2O_3(s) + Na_2CO_3(s) \rightarrow Na_2Al_2O_4(s) + CO_2(g) \quad [9]$$

The plot of Gibbs free energy change verses temperature is shown in Figure 3. For comparison of relative thermodynamic stabilities of various TiO_2 compounds, the Gibbs energy of decomposition of Fe_2TiO_5 into hematite (Fe_2O_3) and rutile (TiO_2) via Reaction [10] is also presented in Figure 3.

$$Fe_2TiO_5(s) + TiO_2(s) \rightarrow Fe_2O_3(s) \quad [10]$$

It was observed from Figure 3 that in the roasting temperature range, the thermodynamic stability of Fe_2TiO_5 phase is less than sodium titanates and therefore Fe_2TiO_5 decomposes into sodium titanate and hematite. The TiO_2 forms various types of sodium titanates (Reactions [2] to [6] depending on the Na_2O:TiO_2 ratio.

Effect of roasting process parameters

The roasting experiments were carried out in the temperature range of 1073 K to 1273 K for 2 hours in air. The samples roasted at 1273 K fused to the crucible due to the formation of liquid phase and therefore these samples were not treated with either aqueous or acid solutions. The changes observed in the concentrations of TiO_2, Fe_2O_3, Al_2O_3, and SiO_2 after treatment of ores (roasting and leaching) are compared in Figures 4a and b. The concentrations of Al_2O_3 and SiO_2 reduced significantly with the increasing roasting temperature. The roasting-leaching experiments with different alkali-to-ore ratios were carried out at 1223 K for 2 hours. The chemical analysis of the final product after the roasting-leaching process indicated that the addition of excess soda ash improved the separation of Fe_2O_3, Al_2O_3, SiO_2, and P_2O_5 impurities from the ore. However, the average particle size of the final product, i. e. synthetic rutile, reduced significantly from ~200µ to ~75µ due to excess attack by the alkaline liquid present at the reaction temperature.

Water and acid leaching

The Eh-pH diagram of the Na-Ti-Fe-H-O system is shown in Figure 5. During water leaching, the excess alkali and sodium aluminate and silicates compounds dissolved in the water and the pH of the aqueous medium raised to 12–14 via the following reactions:

$$3Na_2TiO_3 + 2H_2O \rightarrow Na_2Ti_3O_7 + 4[Na^+] + 4[OH^-] \quad [11]$$

$$2Na_2Ti_3O_7 + H_2O \rightarrow Na_2Ti_6O_{13} + 2[Na^+] + 2[OH^-] \quad [12]$$

In this pH range, as seen in Figure 5, the $Na_2Ti_6O_{13}$ and Fe_2O_3 compounds are stable, which is why the sodium ferrite in the complex Na-Si-Al-Fe-O phase precipitated as $Fe(OH)_3$, which was separated via filtration.

In the acid leaching process, the pH of the solution was less than 3 and in this pH range (0-3) only TiO_2 is stable, as can be seen in Figure 5. This pH condition leads to the decomposition of sodium titanate into stable TiO_2 and sodium ions via Reaction [13]:

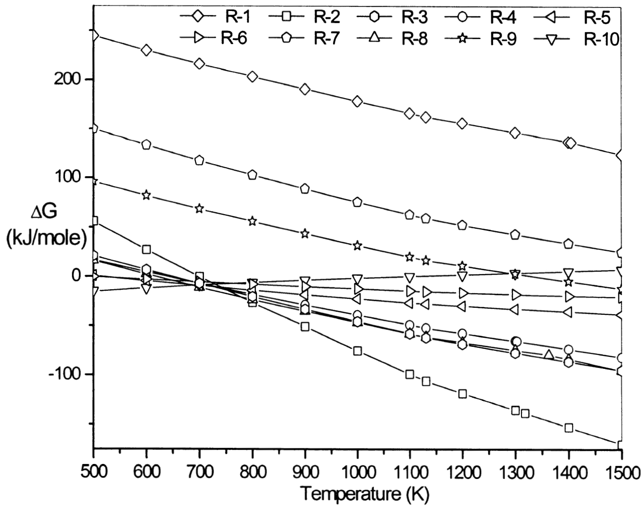


Figure 3. The plot of Gibbs free energy change verses temperature for the reactions of various oxide constituents in TiO_2 ores. R-#: reactions as listed in Equations [1–10] in the text

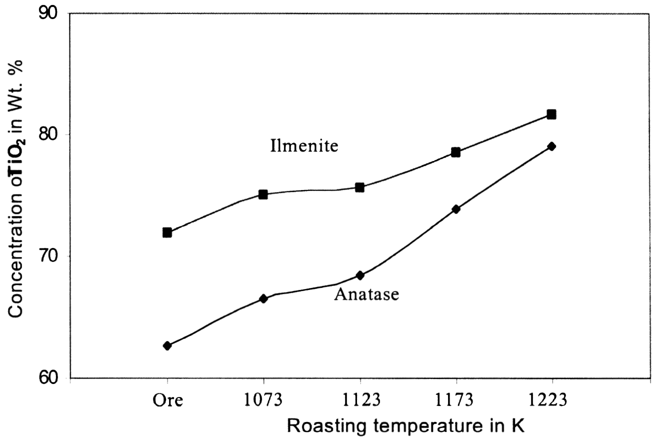


Figure 4 (a). The change in the concentration of TiO_2 in the anatase and ilmenite after roasting at different temperatures for 2 hours in air, followed by water and acid leaching

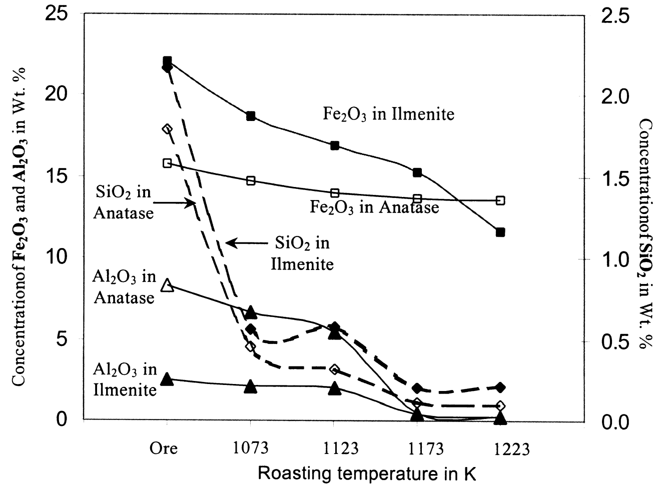


Figure 4 (b). The change in the concentrations of Fe_2O_3, Al_2O_3, and SiO2 in the anatase and ilmenite after roasting at different temperatures for 2 hours in air, followed by water and acid leaching

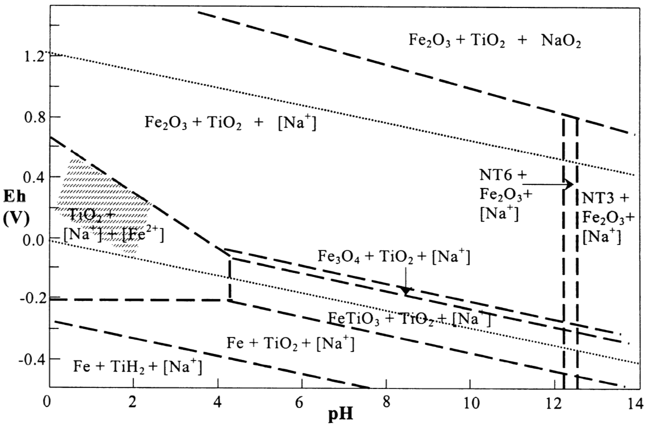


Figure 5. The Eh-pH diagram of Na-Ti-Fe-O system calculated by using FACT-Sage programme. The hatched areas show the water and acid leaching condition

$$Na_2Ti_6O_{13} + 2HCl \rightarrow TiO_2 + 2NaCl + H_2O \qquad [13]$$

The complex Na-Si-Fe-O and Fe-oxide phases in the water-leached residue were also dissolved in the acid medium. The microstructure (back scattered electron) of the ilmenite and anatase ores after roasting and water and acid leaching are compared in Figures 6 and 7, respectively. The microstructure of water-leached ores, in Figures 6a and 7a, shows the sodium titanate and Na-Si-Fe-Al-O phases. Whereas in the microstructure of acid-leached ores, see Figures 6b and 7b, rutile phase is dominant with only small fractions of unreacted ore. The comparison of the microstructures of the ore (Figure 1) with water-leached and acid-leached samples (Figures 6 and 7) also confirms the reduction in average particle size, which is mainly due to the fragmentation of porous grains of ore caused by attack of alkaline liquid phase and subsequent acid leaching.

Discussion

Phase equilibria calculations

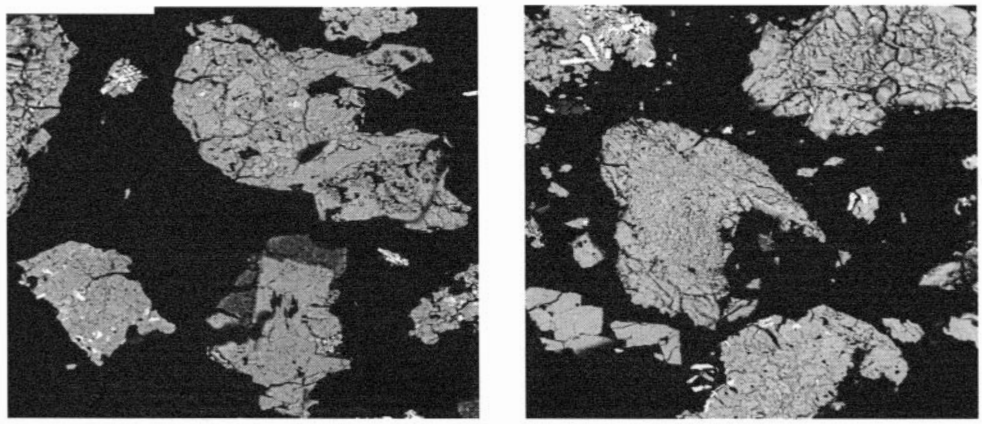
The phase diagram of the Na_2O-TiO_2 binary system[7] is given in Figure 8. The Na-Ti-O binary system forms 5 different alkali titanates, namely $2Na_2O.TiO_2$ (N2T), $Na_2O.TiO_2$ (NT), $4Na_2O.5TiO_2$ (N4T5), $Na_2O.3TiO_2$ (NT3), and $Na_2O.6TiO_2$ (NT6). The Na-Ti-O binary system also has the following three eutectics invariants:

- $4Na_2O.5TiO_2$ and $Na_2O.3TiO_2$ at 1258 K and 70.6 wt% TiO_2
- $2Na_2O.TiO_2$ and $Na_2O.TiO_2$, at 1135 K and 45 wt% TiO_2, and
- Na_2O and $2Na_2O.TiO_2$, at 1131 K and 24 wt% TiO_2.

Thermodynamic modelling of mineral-salt equilibrium, to determine the coexisting equilibrium compositions at any fixed temperature and pressure, can be estimated by using the Gibbs energy minimization technique. For this purpose thermodynamic activities of components in multicomponent solution are required and, as the experimental activity data are not available, different types of solution models are used for estimation of thermodynamic properties. In the present study, the free energy minimization calculations for the Ti-mineral-sodium carbonate system were carried out using the FACT Sage program[6]. The equilibrium phase compositions in molar fractions in the Na-Ti-Fe-Si-Al-O system, at different alkali-to-ore ratios, deduced from FACT Sage calculations are given in Table II. The calculated proportions of equilibrium alkali titanate phases (Na_2TiO_3, Na_2TiO_4) are in good agreement with experimental results. The calculations show that the hematite (Fe_2O_3) and nepheline ($NaAlSiO_4$) are present as two separate phases, however, the results of roasting experiments indicate that most of the hematite is in the complex Na-Ti-Al-Si-Fe-O phase. Since the solution data for the Na-Fe-O salt phase are not available for computation, the results of computation show hematite and nepheline as two separate phases.

Effect of Na-Ti-Fe-Al-Si-O phase on roasting reaction:

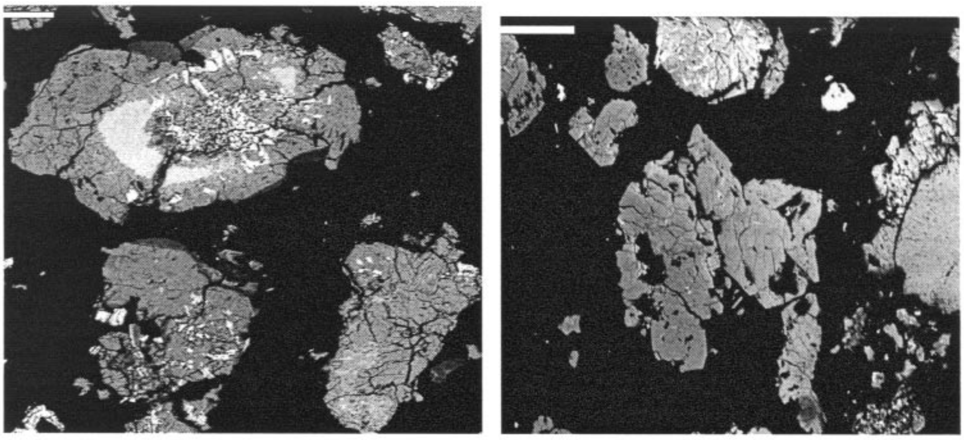
During the alkali roasting reaction, liquid phase forms above 1123 K depending on the Na_2O:TiO_2 ratio. However, in the presence of impurities, the alkali salts (sodium ferrite, aluminate, and silicate) formed during the early stages of the roasting reaction alter the properties of the alkali liquid phase. Therefore in the roasted samples with the lowest alkali-to-ore ratio in Table II, high alkali Na_4TiO_4 (N2T) phase was not observed; instead the Na_2TiO_3 (NT) phase was dominant as most of the alkali was consumed by the gangue oxides. The NT phase melts incongruently at 1223



(a) After water leaching

(b) After acid leaching

Figure 6. The microstrusture of anatase ore after alkali roasting at 1223 K for 2 hours followed by water and acid leaching. Dark grey phase in (a) is complex Na-Fe-Si-O salt phase, which is not disolved in the aquoues medium, whereas the grey colour grains are sodium titanate. The grey colour grains in (b) are rutile



(a) After water leaching

(b) After acid leaching

Figure 7. The microstrusture of ilmeniate ore after alkali roasting at 950°C for 2 hours followed by water and acid leaching. Dark grey phase on the surface of the grey colour sodium titanate grain in (a) is complex Na-Fe-Si-O salt phase, which is not disolved in the aqueous medium, whereas the brigh phase in the core is unreacted pseudorutile phase. The grey colour grains in (b) are rutile with small bright colour particles of unreacted ore particles

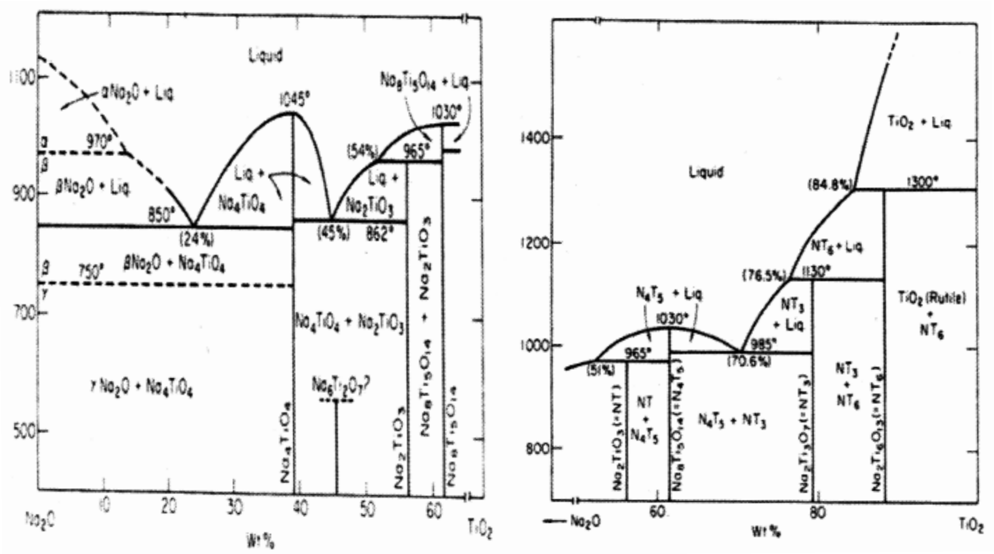


Figure 8. The binary phase diagram of the Na_2O-TiO_2 system[7]

Table II
Composition of roasting charge and the equilibrium phase composition derived from the FACTSage program for roasting of ilmenite and anatase ore at 1223 K

	Ilmenite ore			Anatase ore		
Alkali-to-ore ratio	0.90	1.03	1.10	0.73	0.82	0.99
Species	Roasting charge (in mole fraction)					
TiO_2—rutile (s)	0.846	0.846	0.846	0.692	0.692	0.692
Fe_2O_3—hematite (s)	0.125	0.125	0.125	0.086	0.086	0.086
SiO_2—quartz (s)	0.039	0.039	0.039	0.041	0.041	0.041
Al_2O_3—gamma (s)	0.030	0.030	0.030	0.061	0.061	0.061
$(P_2O_5)_2$ (s)	0.001	0.001	0.001	0.013	0.013	0.013
Na_2CO_3 (s)	0.846	0.971	1.042	0.692	0.778	0.893
Species	Equilibrium phase composition (in mole fraction)					
Na_2TiO_3 (NT)	0.743	0.742	0.671	0.176	0.606	0.556
$Na_8Ti_5O_{14}$ (N4T5)	0.021	0.000	0.000	0.103	0.017	0.000
Na_4TiO_4 (N2T)	0.000	0.105	0.175	0.000	0.000	0.137
$NaSiAlO_4$ (Nepheline)	0.039	0.039	0.039	0.041	0.041	0.041
Na_3PO_4 (Phosphate)	0.002	0.002	0.002	0.052	0.052	0.052
$NaAl_9O_{14}$ (Beta-alumina)	0.002	0.002	0.002	0.009	0.009	0.009
Fe_2O_3	0.125	0.125	0.125	0.086	0.086	0.086
CO_2 (gas)	0.846	0.971	1.042	0.692	0.017	0.238

K and therefore the volume of liquid phase was very small in the samples roasted in the temperature range from 1073 to 1223 K. However, the samples roasted at 1273 K fused to the alumina crucible due to melting of NT phase and the formation of large volumes of liquid phase.

In the samples roasted with high alkali-to-ore ratios, N2T phase was present along with the dominant NT phase. The NT and N2T phases form a eutectic at 1135 K and 45 wt% TiO_2 as seen in Figure 8, which is why the excess addition of soda ash increased the volume of liquid phase. The formation of Ti-rich liquid phase also reduced the average particle size of the final product and increased the loss of TiO_2 in a complex alkali phase

The microstructure of ilmenite and anatase ores, in Figure 1, shows the exsolved Fe-rich phases on the surface of the Ti-rich grains. Consequently, in the early stages of roasting reaction, the sodium carbonate reacts with these Fe-rich oxides on the surface and forms Na-Fe-Ti-O compounds. As the roasting continues, the siliceous gangues phases in the ore react with soda ash and form sodium alumino-silicates. These alkali salts form low-temperature eutectic liquid with sodium carbonate, which then reacts with Ti-rich phases in the ore. The microstructure and elemental X-ray maps of the anatase ore after roasting, shown in Figures 7a and b, confirms the reaction of complex Na-Fe-Al-Si-O phase with Ti-rich phase. Sodium ferrite is thermodynamically less stable than to the sodium silicate, aluminate and titanate as seen from Figure 3. But the formation of Na-Ti-Al-Si-O complex salt phase increases the thermodynamic stability and solubility of sodium ferrite in the complex phase, which is confirmed from Figure 7b. Thus the formation of complex liquid phase helps to separate the iron oxide from the Ti-rich phases, which is then removed by the water and acid leaching process.

During the reductive alkali roasting techniques, the iron oxide is separated as a pure iron at 1373–1473 K. At high temperatures, most of the alkali compounds form the liquid phase, which hinders the diffusion of gaseous species formed during the reduction reaction and therefore conversion of Fe_2O_3 to Fe remains incomplete. The high temperature during the reduction roasting reaction also significantly reduces the particle size of the final product. However, in the oxidative alkali roasting process, the small fraction of FeO present in the ilmenite ores oxidizes to Fe_2O_3 in the early stages of the reaction. This oxidation reaction generates vacancies in the ilmenite lattice and increases the reactivity of mineral phases. The oxidative alkali roasting reaction also helps to remove the Cr_2O_3 and V_2O_5 oxide impurities, which are detrimental to the safe operation of the chlorination process, by forming water soluble sodium chromate and vanadate. In the reductive roasting process, Cr_2O_3 forms sodium chromite, which is not water-soluble and hence remains in the final products or requires strong acid medium in a leaching stage, which consumes the excess acid.

Conclusions

The oxidative alkali roasting process can be used for the production of synthetic rutile from different types of TiO_2 ores. The formation of complex alkali salt phase during the roasting process helps to separate the Fe_2O_3 and other impurities from the ores, which are removed subsequently in the water and acid leaching processes. The results of the phase equilibria calculation using FACT Sage agreed broadly with the experimental data. Increasing the roasting temperature up to 1223 K improved the separation of the impurities. However, above 1223 K, the roasted mass fused with the crucible due to the formation of large volumes of liquid phase. The excess addition of alkali in the roasting reaction improved the purity of synthetic rutile. But the particle size of the synthetic rutile reduced significantly (< 100µ) due to the formation of N2T-NT eutectic liquid. The chief impurities such as Cr_2O_3, Al_2O_3, CaO, and V_2O_5, which are undesirable for the pigment manufacturing process, were also successfully removed by the oxidative alkali roasting techniques.

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