Effects of Temperature on Ilmenite During Concentration of Iron in Laterites Using Charcoal and Separation using Magnetic Separation

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Abstract :Effect of temperature on ilmenite minerals found in laterites has been investigated. It was found that during reduction of iron minerals in laterites to magnetite using charcoal at temperatures of about 500-700°C, ilmenite minerals were not reduced. However when temperatures were raised to about 850-1200°C using acetylene flame, ilmenite minerals were reduce to rutile and iron. Currently, the mineral ilmenite (FeTiO3) is responsible for about 85% of the world's titanium requirements. The methods used to upgrade ilmenite are high temperature reduction and direct acid-leaching methods. Extraction of titanium from ores containing iron still remains a challenge. Laterite soils are currently being used mainly for surfacing roads. It has been proven that laterites can be a potential source of iron. This study set out to investigate whether the heat treatment that converts hematite in laterite to magnetite is adequate to decompose ilmenite. Laterite samples were concentrated by heating charcoal/laterite mixtures in the ratios of 1:10 by mass in a slow current of air and in the temperature range of 500-700°C. Elemental analysis was carried out on both the raw laterites and the concentrated samples using Atomic Absorption Spectroscopy (AAS). The minerals present were determined using a CubiX[3] Powder Diffractometer from PANanalytical Company. The results of elemental analysis showed that, raw laterites contain 28-31% iron and 1-2% titanium (IV) oxide depending on source. After the concentration, the level of iron in the heat-treated sample had increased to 55-64%, and titanium oxide increased to 3-5%. The X-ray diffraction data confirmed that, iron in the raw laterites was present predominantly as the minerals goethite, hematite and ilmenite since these are known to have diffraction peaks at angles 2θ= 21.51˚, 2θ= 54.11˚ and 2θ=32.7, respectively. After reduction (at 500-700°C), goethite and hematite peaks disappeared in the heat-treated magnet-separated samples and instead, a strong peak was observed at angle 2θ= 36˚and 2θ=32.7, which represents peaks for magnetite and ilmenite respectively. From the observation, this temperature (500-700°C), had no significant effect to ilmenite hence, was collected together with magnetite by a magnet. When reduction was done at temperature range of 850-1200°C, the ilmenite peak disappeared and a peak at 2θ=27.4, 2θ= 36˚and 2θ=44.6 appeared, attributed to rutile, magnetite and metallic iron respectively. The XRD of the tailing (non-magnetic waste) show distinct peak at 2θ=27.4 and 2θ=54.3 attributed by rutile. This shows that ilmenite minerals are reduced at high temperatures to rutile (non-magnetic) and metal iron (magnetic).

Key words: **Beneficiation; iron reduction; laterites; Magnetite; Hematite, ilmenite**
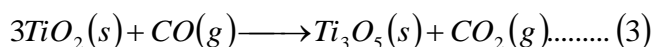
Introduction

The mineral Ilmenite is a naturally occurring iron titanate (FeTiO$_3$) and is abundant in nature. The sand formations are known to contain 3.4% of ilmenite which constitute 1.7% of the rutile before any concentration is done. Ilmenite mineral has the highest percentage of rutile compared to other minerals [7]. The commercial grades of Ilmenite contain 45 to 65.8 % TiO$_2$ and are regarded as a huge resource to the production of rutile (TiO$_2$) which can be used for manufacture of pigment grade TiO$_2$ or the metal itself. Rutile is used in plastics, paper, metallurgy, electronic applications and extensively in surface coating [8]. Titanium is also used in aerospace industries because of it lightness, strength, corrosion and heat resistance. It is widely used in making artificial hip joints, heart pace makers and spectacle flames [9].

In the year 2011, about 1,340 metric tons of titanium was produced worldwide. China was the top producer followed by Australia, India and South Africa [10]. Kenya remains the importer of Titanium products yet there are deposits known to contain the mineral. Titanium bearing minerals identified in Kenya comprise mainly of ilmenite FeTiO$_3$, rutile TiO$_2$, ilmenorutile, (Ti, Nb, Fe) O$_{26}$, titanite CaTiSiO$_5$ and perovskite CaTiO$_3$ [11]. Recent studies at Kwale by Tionim Kenya limited technical report of February 2006, reveals the existence of a low grade Ti ores containing ilmenite, rutile and zircon in large quantities [12]. Laterite deposits found around Mbeu in Meru County-Kenya contain 2.4% TiO$_2$, according to report from mines and Geology (Ref No. Original Cert NO 3390/11). Magnetite minerals at Uyoma Peninsula in western Kenya contain titanium content of 13.8 per cent. Beach sand at Ras Ngomeni in Malindi contains 3.84 percent ilmenite with even higher value of 13.7 percent near the mouth of the Sabaki River [13]. Iron ore from Marimante in Meru-Kenya contains millions of tons of massive iron containing about 46 % Fe. High titanium content of 5 to 15 % TiO$_2$ makes it unlikely to be workable unless a cheap method is found to reduce the titanium oxide from the ore to about 2 % [5].

The extraction of the iron from the Ilmenite has been, and still is an expensive undertaking. Therefore the search for an environmentally friendly, cost effective extraction method remains a strong industrial imperative. In a commonly used extraction process (Becher process), Ilmenite is reacted with coal in iron reduction kiln at 860 to 1,100 °C. The iron is reduced from Ilmenite to the metallic form and titanium oxide at 860 °C as shown in the equation 1[1].

$$FeTiO_3(s) + C(s) \longrightarrow Fe(s) + TiO_2(s) + CO(g)...(1)$$
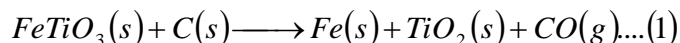
Gaseous reduction then took place at temperatures above 1,000 °C. Above 1,200 °C reduction of rutile takes place as shown by equations 2 and 3.

$$FeTiO_3(s) + CO(g) \longrightarrow TiO_2(s) + Fe(s) + CO_2(g)..(2)$$

$$3TiO_2(s) + CO(g) \longrightarrow Ti_3O_5(s) + CO_2(g)........(3)$$

Carbothermal reduction of ilmenite with charcoal powder has also been studied between 975 °C and 1,100 °C. Ilmenite was reduced by CO and products obtained were studied using SEM and XRD. The major products obtained are α-Fe and TiO_2 at temperatures below 1,000 °C; at 1,050 °C, α-Fe and Ti_9O_{17} were observed; at 1,100 °C, α-Fe and Ti_4O_7 were observed [2,3].

Reduction of ilmenite minerals using charcoal at temperatures of 1200 °C has been investigated. Before reduction, the XRD pattern of the raw ilmenite gave intense peaks of the ilmenite, and rutile at 32.7(2θ), and 27.5(2θ) respectively. After the reduction by heating of the ilmenite/charcoal mixture, the pattern of reduced ilmenite shows a marked emergence of metallic-iron peaks at 44.6 (2θ) and 65.3(2θ), together with a significant increase in the intensity of the rutile peaks [4]. In this study, laterite soils from Tunyai in Kenya were found to contain about 1% rutile in form of Ilmenite mineral. Effort of concentrating iron from laterite containing Ilmenite was meant to investigate if titanium could be reduced in the concentrate at temperatures 500 to 700 °C, a temperature used to convert hematite to magnetite [6].

MATERIALS AND METHODS
Sampling
Sampling was done randomly from quarries from five localities of Tunyai Division in Tharaka Nithi County. These localities were Kithino, Kamujwa, Kinyuru, Mithigini and Tubui regions, located at latitudes 0° 10' 26" S to 0° 12' 52" S and longitudes 37° 48' 40" E to 37° 49' 12" E. Three sampling sites from each location were selected within a distance of about a km apart. Within a given sampling site, Three Samples were obtained from a distance of ten metres apart. The samples were mixed and

about one kg of the sample-mixture packed in plastic bags for analysis.

Sample Treatment and Analytical Procedures
About a kilogram of each laterite sample was weighed and put in a paper bag and transferred to the oven for drying at 105 °C for 9 hours. Samples were then removed from the oven and cooled. A mass of 100 g of the sample were pulverized to 300 microns (150 meshes) using a pulverizer. Minerals present were determined using a CubiX^3 Powder Diffractometer. Chemical analysis was carried out by AAS. The remaining amount of pulverized laterite was used in concentration using charcoal for magnetic separation.

Chemical Analysis using AAS
About 0.100 g of the pulverized sample was weighed using analytical balance Model Mettler AJ150 and put into a labeled 125-ml plastic bottle. About 1 ml of concentrated aqua-regia (mixture of concentrated HCl and HNO_3 in the ratio 3:1) was added followed by 3.0 ml of hydrofluoric acid. The samples were left to digest for 8 hours. A 50.0 ml of concentrated boric acid was added in each container and left to digest for one hour. Distilled water was added to make the total volume of 100.0 ml. Syenite (SY-3) and Mount Royal Gabbro (MRG) rock standards were also digested following the same procedure used to digest the samples. Dilutions of the sample solutions were made by putting 5.0 ml in 100-ml labeled volumetric flask and made up to the mark using distilled water [6]. The samples were analyzed using AAS instrument (Spectr AA.10 model from SEANAC Company).

X-ray Diffraction (XRD) Analysis
About 30 g of pulverized laterite samples were put in sample holders. They were then loaded for analysis of minerals using data collector software. Results of analysis of minerals present in each sample were given using CubiX^3 Powder Diffractometer from PANanalytical company.

Concentration of Iron in Laterites
A 30.0 g of laterite sample and 3.0 g of charcoal powder were mixed and transferred into fire clay crucibles. The mixture was heated at temperature range of 500 - 700 °C in controlled current of air for 2 hours using a charcoal burner. The fire was monitored by looking at the amount of charcoal consumed. Charcoal was then added into the burner every time there was weight reduction. After 2 hours, the roasted samples were allowed to cool to room temperature, and then transferred into a rotating magnetic separator. Serial separation was done on the samples by returning the concentrate three times into the rotating magnetic separator. The samples were concentrated using a strong magnetic of about 92 millitesla. The mineralogical and elemental compositions for the concentrate were determined using XRD and AAS [6].
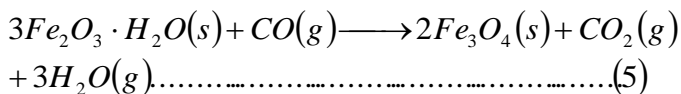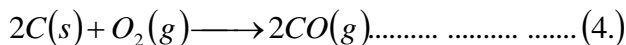
RESULTS AND DISCUSSION
Determination of Appropriate Ratios of Charcoal to Laterites Needed for Complete Beneficiation

Samples from each region were first used to determine the appropriate ratios of charcoal needed to reduce iron minerals

The mean of the results obtained using 3.0 g of charcoal per 30.0 g of laterites was economical for reduction of laterite samples. All the samples were therefore reduced using a ratio of 1:10 by mass of charcoal to laterites and the concentrate obtained analyzed for mineralogical and chemical composition.

Mineralogical Composition of the Raw and Beneficiated Laterite Samples Using Magnetic Separation Method
Laterite samples from identified sampling sites were analyzed for their mineral content using X-ray diffraction technique. The figure 1 shows XRD spectra for a raw and beneficiated laterite sample from one of the quarry. The results from the spectra show that all goethite and hematite minerals were converted to magnetite at a temperature range of 500-700°C. This is confirmed by the disappearing peaks from goethite (2Θ of $21.51°$) and hematite (2Θ of $54.11°$ & $33.51°$) spectra of raw samples, and increasing intensity of the magnetite peaks (2Θ of $36°$) from beneficiated sample.

$$2C(s) + O_2(g) \longrightarrow 2CO(g) \ldots\ldots\ldots \ldots\ldots\ldots \ldots\ldots (4.)$$

$$3Fe_2O_3 \cdot H_2O(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g)$$
$$+ 3H_2O(g) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Note: Each value is mean±SE of 18 replicates
The results of the beneficiated samples gave values which ranged between 69 and 79 % iron (III) oxide. This occurred because hematite and goethite minerals in the heated laterite-charcoal mixture were converted to magnetite. The ilmenite concentration increased from about 1-2% to about 2-5% depending with the location. This shows that ilmenite minerals
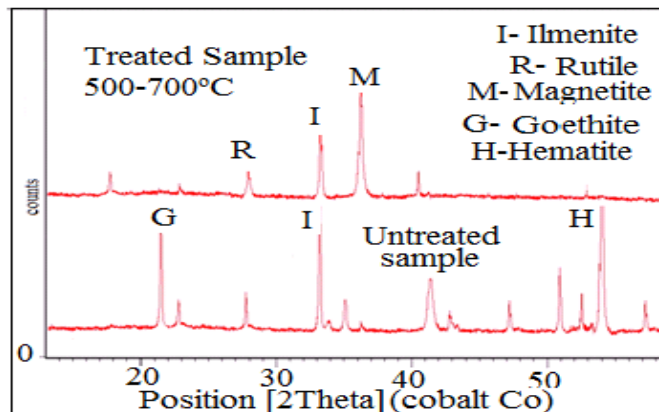
**Figure 1 : XRD spectra for raw and beneficiated laterites sample**
The peak for Ilmenite mineral found at 2Θ of $33.12°$ reduced but present in the spectra of the concentrated samples. This shows that not all ilmenite minerals were able to be reduced at temperatures of 500-700 °C. The reactions involved are given by equations 4 and 5.

Elemental Composition of Raw and Beneficiated Laterites Using Magnetic Separation and Analyzed Using AAS
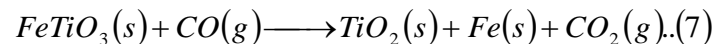Laterite samples from identified sites in Tunyai Division were reduced at temperature range 500-700°C and analyzed for elemental composition and the results are given in tables 2 an

are not affected by temperature range of 500 to 700°C. The same sample was again reduced using acetylene flame which raised temperatures from about 850-1200°C. The magnetic separated and the residue sample was analyzed for mineralogy and spectra given in figure 2.

The iron is reduced from Ilmenite to the metallic form and titanium oxide at temperatures of 860 °C and above as shown in the equation 6.
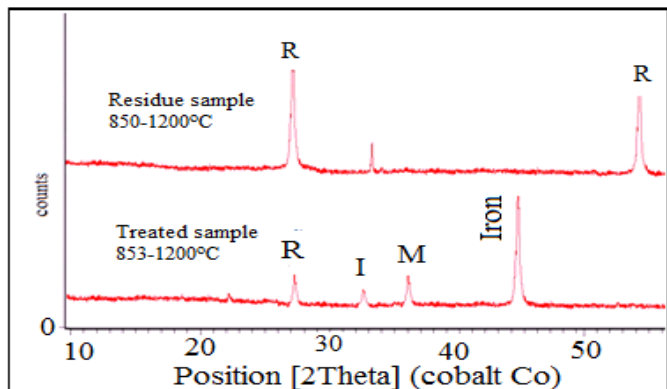$$FeTiO_3(s) + C(s) \longrightarrow Fe(s) + TiO_2(s) + CO(g) \ldots (6)$$
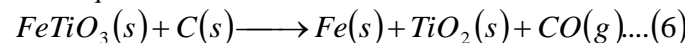
The CO produced reduced further ilmenite to rutile and iron. Since rutile is not magnetic, it was left as residue as shown in equation 7.

$$FeTiO_3(s) + CO(g) \longrightarrow TiO_2(s) + Fe(s) + CO_2(g) . (7)$$

Figure 2 : XRD spectrum for beneficiated sample and residue at 850-1200°C

CONCLUSION
From the results, the reduction of ilmenite is a factor of temperature. Therefore, the method can be used to concentrate

titanium from laterite containing iron minerals. However, the method needs to be investigated in large scale to determine its viability.

ACKNOWLEDGEMENTS

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Table1 : Determination of Appropriate Ratios of Charcoal to Laterites Needed for Complete Beneficiation

		Masses of charcoal used per 30.0 g of laterites				
	Sample site	1.0 g	2.0 g	**3.0 g**	4.0 g	5.0 g
Percentage iron in the concentrate obtained after magnetic separation and analyzed using AAS	**Kithino**	46.95±0.03	48.48±0.06	**50.57±0.02**	50.28±0.07	50.02±03
	Tubui	48.44±0.03	50.30±0.02	**51.59±0.03**	51.45±0.01	51.57±0.02
	Mithigini	49.43±0.04	50.64±0.03	**55.97±0.06**	55.74±0.03	55.78±0.06
	Kamujwa	49.95±0.04	51.76±0.01	**53.84±0.01**	53.05±0.01	53.11±0.05
	Kinyuru	37.05±0.01	38.61±0.04	**48.48±0.02**	48.36±0.03	48.19.02

Table 2: Percentage Elemental Composition of Raw Laterite Analyzed using AAS.

Sample Source	SiO_2 Mean ±SE	Al_2O_3 Mean ±SE	K_2O Mean ±SE	Na_2O Mean ±SE	CaO Mean ±SE	TiO_2 Mean ±SE	MnO Mean ±SE	Fe_2O_3 Mean ±SE	MgO Mean ±SE	LOI Mean ±SE	Total Mean ±SE
Kithino	22.71± 6.13	16.78± 2.09	0.24± 0.10	0.18± 0.08	0.08± 0.01	**1.21± 0.13**	1.50± 0.41	43.84± 0.32	0.14± 0.04	16.83± 4.62	103.58± 1.50
Tubui	22.34± 6.13	10.32± 1.78	0.30± 0.07	0.20± 0.08	0.10± 0.01	**1.13± 0.32**	1.63± 0.75	43.50± 0.69	0.14± 0.02	16.67± 1.97	96.98± 6.06

Mithigini	24.99± 2.33	10.97± 3.84	0.24± 0.10	0.22± 0.06	0.09± 0.02	**0.94± 0.27**	1.07± 0.43	44.50± 0.84	0.14± 0.03	17.67± 4.13	100.64± 2.09
Kamujwa	18.43± 3.70	17.20± 4.73	0.28± 0.14	0.19± 0.10	0.08± 0.03	**0.76± 0.33**	1.27± 0.39	42.47± 0.58	0.12± 0.03	19.67± 3.88	100.54± 2.82
Kinyuru	22.49± 4.53	14.72± 3.16	0.25± 0.06	0.19± 0.07	0.07± 0.01	**0.89± 0.42**	1.33± 0.27	40.81± 0.65	0.13± 0.02	17.83± 2.23	98.98± 5.66

Note: Each value is mean±SE of 18 replicates

Table 3: Percentage Elemental Composition of Beneficiated Laterites Samples and Analyzed using AAS.

Sample Source	SiO_2 Mean ±SE	Al_2O_3 Mean ±SE	Fe_2O_3 Mean ±SE	CaO Mean ±SE	MgO Mean ±SE	Na_2O Mean ±SE	K_2O Mean ±SE	TiO_2 Mean ±SE	MnO Mean ±SE	LOI Mean ±SE	TOTAL Mean ±SE
Kithino	8.61± 2.10	7.62± 1.71	72.24± 0.90	0.35± 0.05	0.18± 0.06	0.21± 0.07	0.60± 0.24	**4.12± 0.21**	0.82± 0.61	8.60± 2.29	100.99± 3.07
Tubui	7.75± 0.88	6.67± 0.89	73.70± 0.16	0.41± 0.06	0.17± 0.04	0.25± 0.16	0.65± 0.08	**5.02± 0.67**	1.25± 0.71	9.00± 2.98	98.90± 4.55
Mithigini	11.5± 1.29	7.27± 1.11	78.97± 0.99	0.37± 0.06	0.23± 0.04	0.28± 0.10	0.53± 0.15	**2.49± 0.49**	0.47± 0.40	8.82± 1.67	101.19± 3.38
Kamujwa	8.81± 2.74	6.93± 1.95	76.92± 0.90	0.39± 0.14	0.18± 0.92	0.20± 0.76	0.52± 0.26	**3.96± 0.28**	0.75± 0.91	9.44± 3.61	99.10± 5.09
Kinyuru	9.85± 1.27	6.97± 1.37	69.26± 0.98	0.38± 0.07	0.17± 0.12	0.28± 0.14	0.68± 0.17	**5.98± 0.46**	0.76± 0.25	7.82± 4.05	98.99± 5.41

Note: Each value is mean±SE of 18 replicates