Analysis of Water Produced during Thermal Decomposition of Goethitic Iron Ore

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Abstract—The aim of this study was to investigate the non-ferrous elemental composition of water produced during thermal decomposition of goethitic iron ore. A typical goethitic iron ore was heated, while the released vapour was condensed by liquid nitrogen trap, and the elements contained in the condensate were measured and grouped. Results showed that Ba in the group of alkali and alkali earth metals, Mn, Ni, Cu, Zn, and Hg in the group of heavy metals, and P and S in the group of non-metal elements were the most abundant elements with present in the chemically bound water. Other technologies including thermogravimetric analysis, Computer Aided Thermal Analysis, and Fourier transform infrared spectroscopy were also used to reveal the thermochemical behaviour of goethite during its thermal processing.

Index Terms—Goethite, decomposition, heat of reactions, FTIR.

I. INTRODUCTION

The ironmaking industry produces considerable pollutants and greenhouse gas emissions [1], [2]. The increasing environment concerns from this industrial activity have driven research on the chemical nature of the pollution generation and its control and recycling during the iron ore processing.

Non-ferrous elements, such as magnesium (Mg), chromium (Cr), nickel (Ni), mercury (Hg) and lead (Pb) [3] are typically represented in trace concentrations in iron ores [4]. These elements can be released from the iron ores into the atmosphere during thermal processing causing environmental concerns. For example, mercury, a potential neurotoxin, is one of the most toxic trace metals with the possibility of entering human food chain [5]. Selenium, acting as an antioxidant, is one of the essential trace elements, which may become toxic, depending on its oxidation form and quantity [6]. Some elements may have existing or potential applications in other industries, hence their collection maybe economically attractive. Various types of techniques (e.g., gas phase extraction) have been developed to recover the metals from the ores and slags [7].

In this work, goethitic iron ore particles were subjected to thermal processing in a fixed bed reaction system under inert nitrogen atmosphere. The objective of this work was to give an insight into the types and concentrations of non-ferrous elements in the produced condensable vapour as well as the thermochemical behaviour of the iron ore during heating. This work provides reference for the processes of iron ore sintering and element recycling.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

A. Feedstock

The iron ore used in this work was goethite (FeOOH) from Western Australia. The iron ore particles were crushed, sieved, and then dried in a vacuum oven at 80 $^{\circ}$ C for 1.5h to remove the surface moisture.

B. Thermal Processing Experiments

The water condensate from the decomposition of goethite was conducted in a fixed bed reactor system. High-purity nitrogen with a flow rate of 50 ml/min swept through the quartz tube fixed bed where the dried goethite particles (0.85–2.8mm) were loaded. The sample was heated to 500 °C at a heating rate of 20 °C/min, and then kept at 500 °C for 2h. The hot effluent gas from the fixed bed passed through a glass U tube which was dipped into a cold trap with liquid nitrogen. The moisture and the condensable mass within the effluent were captured in the U tube and then sent for elemental analysis. Around 125 g of goethite particles were filled into the quartz tube, and about 62 g of liquid condensate was collected and removed for analysis.

In a paralleled blank experiment aiming at providing a basis for the elements contained in the water, clean quartz fragments were installed to replace the goethite sample. The same amount of deionised water (MilliQ water) as the collected condensate from goethite was injected into the fixed bed at the inlet of the quartz tube, and then carried by the sweeping nitrogen gas.

C. Elemental Analyses of Goethite and Collected Condensates

The elemental content of iron ores was analysed using X-Ray fluorescence (XRF) method according to the ISO 9516 standard. Most elements in the condensates were detected according to USEPA 200.8 ICPMS, and the mercury was measured in a standard procedure defined by USEPA245.1 CVAAS.

D. Thermogravimetric Analysis of Goethite

Thermogravimetric analysis (TG, model: TGA/DSC 1 STARe System, Mettler Toledo Ltd.) was applied to measure the mass loss of the raw goethite during heating. The sample was continuously heated from room temperature to 1000 $^{\circ}$ C under a heating rate of 20 $^{\circ}$ C/min, using high-purity nitrogen

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(20 ml/min) as the carrier gas. The obtained TG curve was processed to produce a differential thermogravimetric (DTG, in units of wt%/ $^{\circ}$) curve.

attenuated total reflectance (ATR) accessory with a diamond crystal was used for sample analysis.

E. Computer Aided Thermal Analysis (CATA) of Goethite

Specific heat of the goethite during heating was measured by a CATA apparatus. It was comprised of an infrared image gold furnace and specially designed internal arrangements as described previously [8]-[10]. Two coaxial quartz tubes with respective diameters of 50 mm and 13 mm were installed in the furnace and a graphite tube was placed between the above two quartz tubes. Ultra high-purity argon (Ar) at 5 ml/min continuously passed through the smaller quartz tube wherein 2.4 cm³ of the goethite was packed. The graphite tube was also flowed by inert Ar gas at 50 ml/min. The furnace was heated from room temperature to $1000 \ C$ at a heating rate of 20 °C/min. Three thermocouples were used to log the data of temperatures of the graphite (control temperature) as well as the surface and centre of the goethite sample. The principle and procedure for specific heat calculation was described previously [8].

F. Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Goethite

The FTIR spectra of goethite and the samples after heating at 500 $^{\circ}$ C and 900 $^{\circ}$ C were acquired by a FT-IR spectrometer (Model: Nicolet 6700, Thermo Fisher Scientific, Inc.). An

III. RESULTS AND DISCUSSION

The results of elemental analyses of the iron ore, the background test, and the chemically produced water from the decomposition of the goethite iron ore are presented in Table I. All the elements are divided into four groups and listed in order of the atomic weight. For the raw goethite, Al, Si, and Fe were the main elements with contents of 0.76, 2.07, and 58.85 wt%, respectively. The other elements were identified in the raw goethite in very small or trace concentrations.

The elements in the condensate from thermal processing of raw goethite at 500 $^{\circ}$ C showed that in the group of alkali and alkali earth metals, K and Ba were the two outstanding elements. Among the group of heavy metals, Mn, Ni, Cu, Zn, and Hg were the most dominant elements identified in the condensate. the non-metal Among elements, the concentrations of P and S were significant. The mechanism of deportment of the trace elements from the ore to the condensate during heating could occur via iron ore particle cracking accompanied by the breakage of bonds and functional groups within the particles, releasing moisture, inorganic (e.g., Hg), and organic (which probably contains P or S) vapours.

ABLE I: ELEMENTAL COMPOSITION OF RAW	GOETHITE AND CONDENSATES
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Elements		Goethite (wt%.)	Condensate from blank experiment (ug/L)	Condensate from 500 ${}^{\circ}\!C$ heating of goethite (ug/L)	
Main elements	Al	0.7571	48	120	
	Si	2.072	2900	2100	
	Fe	58.85	43	59	
Alkali and alkali	Na	< 0.01	5.4	6.9	
earth metals	Mg	0.042	0.13	0.3	
	Κ	0.0042	0.058	0.37	
	Ca	0.0786	0.48	1.1	
	Sr	< 0.001	<1	1.3	
	Ba	< 0.01	<1	14	
Heavy metals	Cr	< 0.001	<1	2.9	
	Mn	0.04	1.5	24	
	Ni	0.003	1.3	29	
	Cu	0.003	8.5	95	
	Zn	< 0.001	9.2	91	
	Cd	/	<0.1	0.48	
	Hg	/	3	120	
	Pb	< 0.001	<1	3.6	
Non-metal	В	/	1100	980	
elements	Р	0.053	0.096	0.14	
	S	0.011	0.76	1.8	
	As	0.001	24	23	



Fig. 1. TG and DTG curves of raw iron ore at the heating rate of 20 $\,$ C/min.

The superimposed mass (TG) and mass loss rate (DTG) data for the raw goethite at the heating rate of 20 °C/min are shown in Fig. 1.

According to the TG curve, 90.1 wt% of the initial mass remanied at the final temperature of 1000 °C. The iron ore mass loss went through three main discrete stages of decomposition. During the first stage (room temperature to 150 °C), a small peak centring at around 70–80 °C indicates the evaporation of the bound water.

The second stage ranging from $150 \,^{\circ}{\rm C}$ to $500 \,^{\circ}{\rm C}$ is responsible for the main mass loss of the sample. The sharp peak centring at $310 \,^{\circ}{\rm C}$ was associated with the

decomposition of the goethite during heating, with a maximum mass change rate of 0.12 wt%/°C. The main contributor to the loss of weight during heating, as shown in Fig. 1 was the production of water as a product of decomposition, which was analysed in this research. The water is produced with dehydroxylation of the goethite expressed with equation 2FeOOH \rightarrow Fe₂O₃ + H₂O. During the third stage (after 500 °C), the mass of residual solid continuously decreased at a very slow rate.

The change in specific heat (C_p) of the goethite with temperature at a heating rate of 20 °C/min is shown in Fig. 2.



Fig. 2. Specific heat during thermal processing of iron ore at the heating rate of 20 $^{\circ}$ C/min.

Three positive peaks were identified. Each peak on the Cp curve was then integrated by connecting the peak start temperature (Ts) and the end temperature (Te) of and the volumetric heat of reaction (Δ Hv) was thus determined. The integration results are shown in Table II.

The specific heat of the goethite at room temperature was 1.5 MJ/m³K. The initial small endothermic peak between 96 and 174 °C corresponded to the peak No.1 of dehydration in Table II with a mass loss percent of 1.08 wt%. The most outstanding and sharp endothermic peak (peak No.2) between 212 and 424 °C centring at 310.2 °C was ascribed to the dehydroxylation reaction with a reaction heat of 258.41 MJ/m³. This reaction corresponded to the main sharp peak centring at 310 ℃ in the DTG curve in Fig. 1, and was responsible for the main mass loss percent of 8.38 wt%. The 3rd endothermic peak followed in the temperature range of 532–618 $^{\circ}$ C and was the indication of reaction of clay decomposition. This resulted in a minor mass loss of only 0.41 wt%. After 620 °C, as shown in Fig. 2, no obvious peaks appeared. Mass loss in Table II was calculated from the TG data and based on the mass of raw goethite.

TABLE II: REACTION HEATS DURING THERMAL PROCESSING OF GOETHITE AT THE HEATING RATE OF 20 $\,^{\circ}C/MIN$

Peak No.	Reaction type	Ts (°C)	Te (°C)	ΔHv (MJ/m ³)	Mass loss (wt%)
1	Dehydration	96	174	7.91	1.08
2	Dehydroxylation	212	424	258.41	8.38
3	Clay decomposition	532	618	15.39	0.41

FT-IR analysis (see Fig. 3) was used to investigate the chemical functional groups existing in the raw goethite (curve A) as well as the produced solid after heating to 500 $^{\circ}$ C (curve B).

For the IR spectrum of the raw goethite, the minor peaks between 3560 and 3750 cm⁻¹ (such as 3694 cm⁻¹) and the

obvious peaks in the range of 950-1200 cm⁻¹ (1095, 1033, and 1007 cm⁻¹) correspond to the aluminosilicate clays such as kaolinite [11]. The broad band at 3097 cm⁻¹ is due to the stretching vibration of the OH group and the bonded water [12]. The small peak at 1633 cm⁻¹ is associated to the bending of –OH [13], [14]. The two sharp peaks at 885 and 796 cm⁻¹ correspond to the vibrations of O=Fe–O–H [12], [14]. The small peak at 526 cm⁻¹ should be ascribed to the presence of small amount of hematite (Fe₂O₃).



Fig. 3. FTIR spectra of raw goethite and thermally processed goethite at 500 $\,$ C.

The FTIR spectra of the sample heated to $500 \,^{\circ}\mathrm{C}$ (curve B in Fig. 4) exhibited broad absorption band between 2900 and 3700 cm⁻¹ indicating presence of small amount of OH group and bonded water, which is much lower than the corresponding broad band for the raw goethite. After heating at 500 °C, the appearance of single peak at 1042 cm⁻¹ relates to the asymmetric stretch of the Si–O–Al framework, which is accompanied by the disappearance of the peaks at 1095, 1033, and 1007 cm⁻¹. This is due to the decomposition of aluminosilicate clays. The appearance of two sharp peaks at 519 and 432 cm⁻¹ are associated with the formation of hematite (Fe₂O₃) [12].

IV. CONCLUSIONS

In this study, a typical goethitic iron ore was heated under inert nitrogen atmosphere to collect the released vapour, which was then condensed by liquid nitrogen trap and elemental analysis. Thermochemical subjected to characteristics of goethite during its thermal processing were also investigated by various technologies. Results indicated that Ba, Mn, Ni, Cu, Zn, Hg, P, and S were the most represented elements with higher concentrations in the condensate. Three main reactions occurred during the heating of goethite with the volumetric reaction heats of 7.91, 258.41, and 15.39 MJ/m³. The decomposition of goethite occurred in the temperature range of 212-424 $^{\circ}$ C (peak T at 310 $^{\circ}$ C) and was responsible for the maximum sample mass loss rate of 0.12 wt%/°C. Results of Fourier transform infrared spectroscopy also reflect the changes of functional groups during the heating of goethite.

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REFERENCES

- T. E. Norgate, S. Jahanshahi, and W. J. Rankin, *J Clean Prod*, vol. 15, p. 838, 2007.
- [2] D. B. Korol, J Clean Prod, vol. 54, p. 235, 2013.
- [3] K. A. Akinade, R. M. Campbell, and D. A. C. Compton, *J Mater Sci*, vol. 29, p. 3802, 1994.
- [4] M. Alvarez, E. E. Sileo, and E. H. Rueda, *Chem Geol*, 2005, vol. 216, p. 89, 1994.
- [5] P. Shah, V. Strezov, K. Prince, and P. F. Nelson, *Fuel*, vol. 87, p. 1859, 2008.
- [6] P. F. Nelson, P. Shah, V. Strezov, B. Halliburton, and J. N. Carras, *Fuel*, vol. 89, p. 810, 2010.
- [7] Y. Chen, E. R. M. Mariba, L. V. Dyk, and J. H. Potgieter, *Int J Min Process*, vol. 98, p. 1, 2011.
- [8] V. Strezov, J. A. Lucas, and L. Strezov, J. Therm. Anal. Calorim., vol. 72, p. 907, 2003.
- [9] V. Strezov and T. J. Evans, Int. J. Food Prop., vol. 8, p. 101, 2005.
- [10] V. Strezov, B. Moghtaderi, and J. A. Lucas, J. Therm. Anal. Calorim., vol. 72, p. 1041, 2003.
- [11] J. Kristof, R. L. Frost, A. Felinger, and J. Mink, *J Mol Struct*, vol. 410, p. 119, 1997.
- [12] V. Strezov, A. Ziolkowski, T. J. Evans, and P. F. Nelson, J Therm Anal Calorim, vol. 100, p. 901, 2010.
- [13] P. S. R. Prasad, K. S. Prasad, V. K. Chaitanya, E. V. S. S. K. Babu, B. Sreedhar, and S. R. Murthy, *J Asian Earth Sci*, vol. 27, p. 503, 2006.
- [14] X. M. Rong, W. L. Chen, Q. Y. Huang, P. Cai, and W. Liang, *Colloid Surface B*, vol. 80, p. 79, 2010.



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