

Quantitative thermogravimetric analysis of haematite, goethite and kaolinite in Western Australian iron ores

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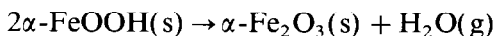
Abstract

A quantitative thermogravimetric method has been developed for the routine analysis of goethite and kaolinite in a Western Australian iron ore sample. Standards were used to construct calibration graphs based on the mass loss due to the dehydroxylation of goethite and kaolinite. The haematite content is calculated from the total soluble iron content in the sample. The method is precise (maximum relative standard deviation of 3.3%) and accurate (within $\pm 10\%$), provided the crystallinity and particle size of the minerals in the standards are matched to the minerals in the unknown samples. The method was applied to the characterisation of an iron ore tailing and used to assess the performance of a selective flocculation process for upgrading the tailing.

INTRODUCTION

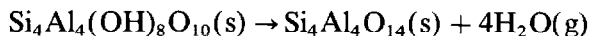
Minerals commonly associated with iron ores originating from the Pilbara district of Western Australia include haematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), silica (SiO_2) and kaolinite ($\text{Si}_4\text{Al}_4(\text{OH})_8\text{O}_{10}$). Kaolinite occurs as ultrafine ($< 10\ \mu\text{m}$) material and, after processing of the ore, is present in iron ore tailings along with non-recoverable ultrafine haematite and goethite. A selective flocculation process has been investigated for separating the ultrafine haematite and goethite from the kaolinite [1]. Assessment of the process relied on the quantitative analysis of haematite, goethite and kaolinite in the iron ore tailing and selective flocculation concentrates.

Preliminary investigations showed that thermogravimetry (TG) might be suitable for the quantitative analysis of goethite and kaolinite because both minerals lose mass over a defined temperature range. Goethite dehydroxylation results in a loss of water (mass) and the formation of haematite over the range 250–400°C according to the reaction



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The exact temperature range varies depending on the crystallinity, particle size and morphology of the goethite [2–4]. Stoch [5] lists a number of factors which can affect the dehydroxylation process. In goethite samples of low crystallinity, a two-stage dehydroxylation may be observed [6]. Particle size, in particular, has an influence on the formation of the haematite layer around goethite particles and as a consequence affects the rate of diffusion of water from inside the particle [3]. Kaolinite dehydroxylation occurs over the range 510–640°C via the reaction [7]



Again the exact range is primarily dependent on the crystallinity, particle size and morphology of the specimen [5]. Hence, goethite and kaolinite specimens may differ in the precise temperature range of dehydroxylation, and, as a consequence, the shape of the TG curve depends on their origin, history and/or preparation method. This suggests that TG calibration standards should consist of minerals of the same origin as those in the unknown samples.

If quantitative analysis of goethite and kaolinite could be proven, then haematite could be calculated by difference, assuming that the soluble iron content of the sample (as determined by wet chemical analysis) originated from goethite and haematite only. An extensive literature survey was therefore carried out, but failed to find any literature dealing specifically with quantitative analysis of goethite and kaolinite in the same sample using TG. The utilisation of differential thermal analysis (DTA) was demonstrated by Kerr and Kulp [8] for the determination of mixtures of goethite and kaolinite over the concentration range from 0 to 100%. In our case, the speed and convenience of the TG method was preferred.

EXPERIMENTAL

Materials

The iron ore tailings sample was obtained from the BHP Iron Ore (Goldsworthy) Limited beneficiation plant at Finucane Island. The ore originated from the Shay Gap/Nimingarra Hill minesite. Specimens rich in goethite or kaolinite were obtained from the same minesite. Goethite and kaolinite were purified by treatment with 5 mol l⁻¹ sodium hydroxide [9] and sodium dithionite/sodium citrate [10], respectively. Haematite originating from a neighbouring minesite (Mt. Goldsworthy) was supplied by Dr. R. Morris, CSIRO. The haematite and goethite samples were ground and wet-sieved to obtain size fractions of less than 20 μm. The kaolinite was supplied as less than 10 μm.

The purities of goethite and haematite, as determined by wet chemical analysis for iron, were 93 ± 1% and 97 ± 1%, respectively. Analysis of

goethite by TG gave a purity of $93 \pm 4\%$, assuming it had the stoichiometric formula FeOOH . XRD analysis showed the goethite to be slightly contaminated with haematite. The purity of kaolinite was measured by TG to be $94 \pm 4\%$ using the method of Earnest [11].

Standard mixtures containing goethite, kaolinite and haematite (used as the diluent) were prepared and homogenised by mixing in a 5 ml glass vial with a spatula. The standards contained a range of 10–20% w/w goethite and 5–20% w/w kaolinite. The w/w concentrations of goethite and kaolinite were adjusted for their actual purities quoted above.

Methods

TG curves for each standard mixture were obtained in triplicate using a Stanton Redcroft TG-750 thermobalance linked to an $X-Y$ chart recorder. The analysis conditions were: sample weight, 10–20 mg; gas, nitrogen; gas flow rate, 25 ml min^{-1} ; temperature range, 20–800°C; heating rate, $20^\circ\text{C min}^{-1}$; crucible type, platinum.

The mass loss for goethite and kaolinite dehydroxylation was measured from each TG curve. Triplicate analyses were averaged and calibration graphs of mass loss versus goethite and kaolinite content were constructed.

TG curves for the iron ore tailing and selective flocculation concentrates were obtained using the same conditions as for the standards. In addition, the haematite, goethite and kaolinite contents of the tailing were measured as a function of particle size by separating it into four size fractions. The beaker decantation procedure of Pryor [12] was used to fractionate the sample and a Malvern MasterSizer MS20 was used to measure the particle size distribution of each fraction. Mass losses for goethite and kaolinite dehydroxylation were converted to goethite and kaolinite contents using the calibration graphs. Analysis time per sample was approximately 45 min, of which 10 min was operator time.

Wet chemical analysis for soluble iron was carried out using the standard hydrochloric acid digest, stannous chloride reduction, potassium dichromate method described by Basset et al. [13].

RESULTS

Method development and performance

Standards were prepared initially using high-purity goethite and kaolinite specimens not originating from the Shay Gap/Nimingarra Hill minesite. The shapes of the TG curves for these standards were significantly different from the TG curves produced by the tailing and selective flocculation concentrates. Such differences may have resulted in either high or low values of goethite and kaolinite with respect to the actual amount in the sample.

Calculating the goethite and kaolinite content from the mass loss and stoichiometric formula gave equally uncertain results. To overcome these uncertainties it was necessary to prepare standards using haematite, goethite and kaolinite originating from the same location as the tailing.

Figures 1–4 show the TG curves of the three pure components of the standards, a standard mixture and an unknown typical selective flocculation concentrate. All samples have an initial mass loss occurring below 100°C due to surface moisture. This mass loss is dependent on the surface area of the sample. The standard mixture (Fig. 4) had two mass losses, due to dehydroxylation of goethite over the range 275–355°C and of kaolinite over the temperature range 495–645°C. The temperatures corresponded with

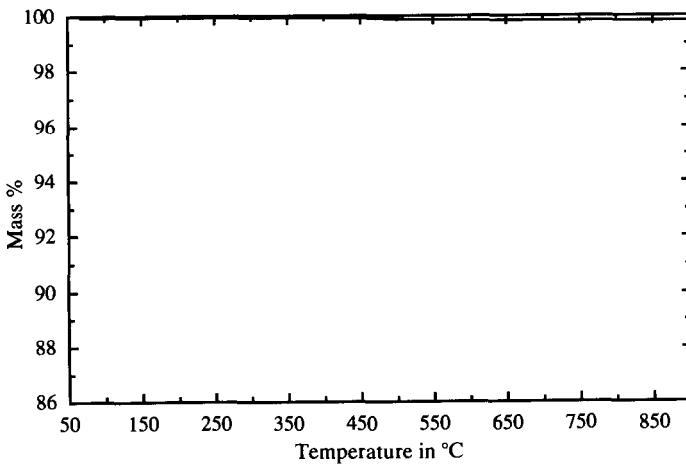


Fig. 1. TG curve for Mt. Goldsworthy haematite standard.

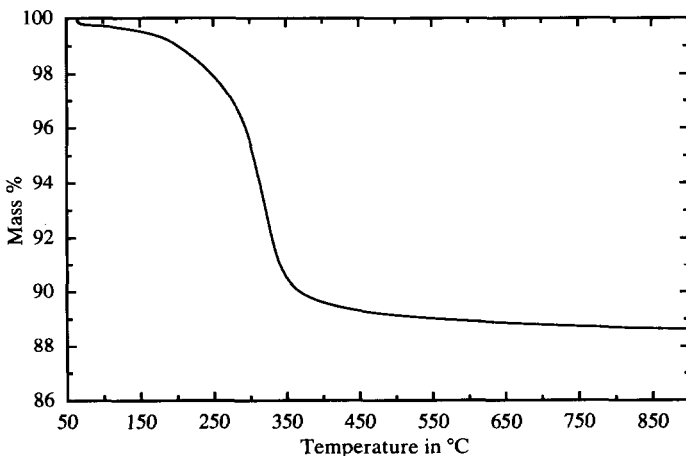


Fig. 2. TG curve showing the dehydroxylation mass loss for the Shay Gap/Nimingarra Hill goethite standard.

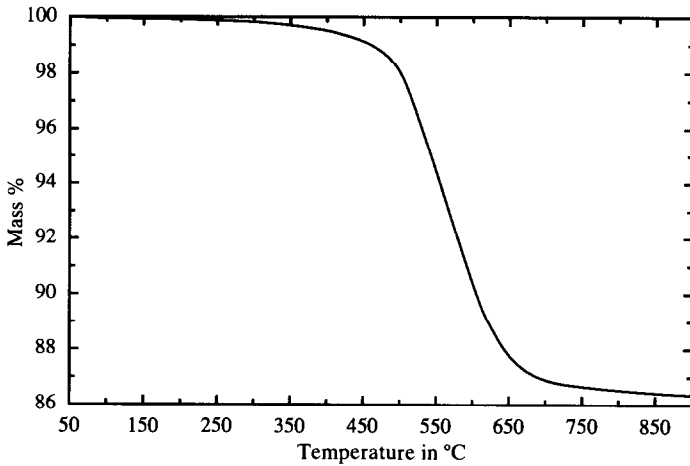


Fig. 3. TG curve showing the dehydroxylation mass loss for the Shay Gap/Nimingarra Hill kaolinite standard.

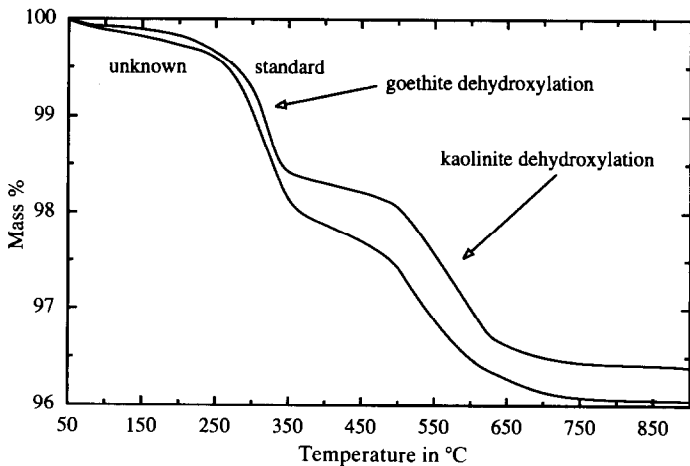


Fig. 4. TG curves for a known mixture of Shay Gap/Nimingarra Hill goethite and kaolinite standards compared to a selective flocculation concentrate of unknown composition.

those of pure goethite (Fig. 2) and pure kaolinite (Fig. 3). Haematite (Fig. 1) had an insignificant continual mass loss above 100°C. The unknown sample (Fig. 4) had mass losses for goethite and kaolinite dehydroxylation over the temperature ranges 285–365°C and 480–625°C respectively. The major difference between the standard mixture and the unknown is the resolution between the end of the goethite dehydroxylation and the start of the kaolinite dehydroxylation, and the slope of the baseline. An estimate of the error due to differences in resolution and baseline slope of the standards and unknowns gave a value of approximately $\pm 10\%$.

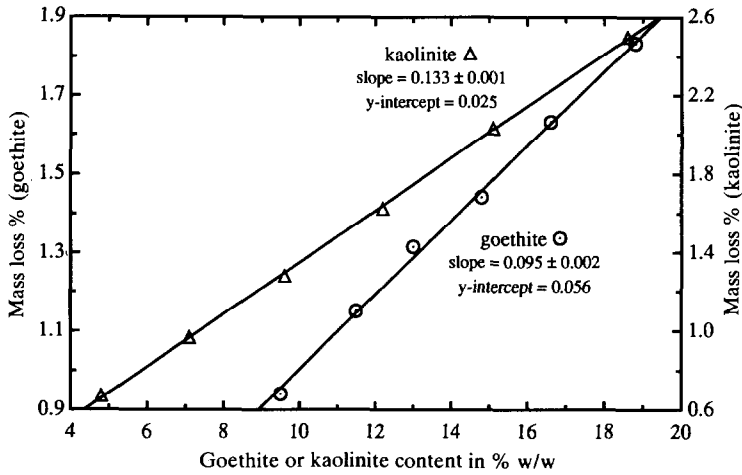


Fig. 5. Calibration curves for the quantitative analysis of goethite and kaolinite.

The calibration graphs for goethite and kaolinite in the standard mixtures are shown in Fig. 5. The line of best fit and the standard deviation of the data from the slope were calculated using the method of least squares and the statistical formulae of Kolthoff et al. [14]. Note that the *y*-intercept for both graphs is slightly greater than zero owing to the slight mass loss from the haematite. The detection limit was estimated to be 2% for both minerals.

The precision (reproducibility) of the thermogravimetric procedure was determined by measuring the goethite and kaolinite content in the iron ore tailing seven times. The soluble iron content was also measured seven times. The mean soluble iron value was used to calculate the haematite content. The range, mean and standard deviation of all the analyses are shown in Table 1. The accuracy of the procedure was measured by analysing a standard containing 69.2% haematite by weight. Calculation of the haematite content from analysis results for goethite and total soluble iron gave 69.4%.

TABLE 1

Precision of the thermogravimetric procedure for the determination of haematite, goethite and kaolinite in the iron ore tailing; soluble iron measured by wet chemical analysis

	Soluble iron	Haematite	Goethite	Kaolinite
Range	46.4–46.7	52.8–53.7	14.5–15.1	20.3–22.2
Mcan	46.6	53.2	14.8	21.3
Standard deviation	0.1	0.4	0.3	0.7
% Relative standard deviation	0.2	0.8	2.0	3.3

TABLE 2

Mineralogical analysis of the iron ore tailing. All phases identified by XRD analysis; total silica analysis performed by XRF

Mineral	Content (%)	Analysis technique
Goethite (α -FeOOH)	14.8	Thermogravimetry
Kaolinite ($\text{Si}_4\text{Al}_4(\text{OH})_8\text{O}_{10}$)	21.3	Thermogravimetry
Haematite (α -Fe ₂ O ₃)	53.2	Wet chemical/calculated ^a
Silica (SiO ₂)	≈ 5	Calculated ^b
Others (?)	≈ 6	Calculated ^c

^a % haematite = [%Fe(soluble) - (A_r(Fe)/M_r(FeOOH)) × %(FeOOH)]/[2A_r(Fe)/M_r(Fe₂O₃)]. ^b % silica = %SiO₂(total) - [2M_r(SiO₂)/M_r(Si₄Al₄(OH)₈O₁₀)] × %(Si₄Al₄(OH)₈O₁₀). ^c Balance to give 100%.

Composition of the iron ore tailing

Mineralogical analysis results for the ultrafine iron ore tailing are shown in Table 2. The calculated value of silica is only an approximation and represents the amount of SiO₂ not accounted for by the kaolinite. Elenor [15] has identified these sources of silica as quartz, chert and jasper. The calculated value of silica will also include the contribution from other aluminosilicates present in the sample such as beryl, muscovite and tourmaline. Other minerals in the sample have not been identified but possibilities include apatite, ilmenite/rutile and pyrolusite, which account for phosphorus, titanium and manganese in the sample [15].

Composition as a function of particle size

The iron ore tailing was separated by beaker decantation into the four size fractions shown in Table 3. The significant overlap between the d_{10} and d_{90} particle sizes of any two adjacent fractions was unavoidable due to difficulties in keeping all particles dispersed during settling. TG analysis of each fraction revealed kaolinite to be the major constituent below approximately 1 μm and haematite to be the major constituent above approximately 2.5 μm (Table 3). The majority of the goethite was found in the range 1–6 μm. A portion of very fine particles was lost during the beaker decantation procedure and accounts for the low total mineral content of the two finest size fractions.

DISCUSSION

Shape of goethite and kaolinite TG curves

Even though the goethite and kaolinite in the standards and unknowns were of similar origin and geological history, differences in the TG curves still occurred (Fig. 4).

TABLE 3
Analysis results for the particle size fractions separated from the iron ore tailing

Size fraction (μm) d_{10} – d_{50} – d_{90} ^a	Surface area/ (m^2g^{-1})	Proportion of total sample/(weight %)	Soluble iron/ %	Haematite/ %	Goethite/ %	Kaolinite/ %	Total (%) = haematite + goethite + kaolinite
0.3–0.9–4.7	23.9	37.7	20.7	14.9	16.4	52.0	83.3
1.0–2.4–6.1	13.5	17.6	47.5	46.7	23.6	19.0	89.3
2.0–5.2–11.6	6.0	26.3	59.4	72.0	14.5	5.8	92.3
5.3–11.8–25.4	2.8	18.8	64.2	84.6	8.1	1.8	94.5
Composite of size fractions	13.4	100	43.8	48.6	15.6	24.6	88.8
Bulk sample	17.7	–	46.6	53.2	14.8	21.3	89.3
Discrepancy (%)	–24	–	–6	–9	+5	+16	–0.6

^a d_{10} = 10% by volume of particles less than equivalent spherical diameter, d ; d_{50} = 50% by volume of particles less than d ; d_{90} = 90% by volume of particles less than d .

The differences are attributed to differences between the crystallinity, particle size and morphology of the goethite and kaolinite minerals in the standards compared to the unknowns. These affected the accuracy of the method (estimated to be $\pm 10\%$), but not the precision (maximum relative standard deviation was 3.3%). The purification of the goethite and kaolinite standards and the crushing and grinding of the goethite and haematite standards would have contributed to the differences.

Application of results to upgrading the iron ore tailing

Table 2 showed the iron-bearing minerals in the iron ore tailing to be haematite (53.2%) and goethite (14.8%). Kaolinite was the major gangue mineral (21.3%) and was present mainly in the finest size fraction (Table 3). Based on these results a significant upgrading of the iron ore tailing was predicted by desliming the sample at approximately $2\ \mu\text{m}$ prior to selective flocculation. Laboratory scale beaker decantation followed by selective flocculation produced a concentrate containing 78.6% haematite, 14.0% goethite (total soluble iron was 63.8%) and 2.0% kaolinite, with a 58% iron recovery [1].

Applications to analysis of iron ores

In addition to haematite, goethite and kaolinite, iron ores may also contain magnetite (Fe_3O_4), siderite (FeCO_3), silica (as quartz or chert) and clay minerals (such as montmorillonite, illite, muscovite and orthoclase) as major minerals [16–18]. Of these minerals, goethite, siderite and some clay minerals lose mass over a defined temperature range. Provided the mass loss for each mineral does not overlap with that of the other minerals, the iron ore is amenable to quantitative analysis by TG.

SUMMARY AND CONCLUSIONS

The thermogravimetric method allows quick, simple and accurate analysis of goethite and kaolinite in an iron ore, although the method suffers in accuracy if the compatibility between the crystallinity and particle size of the standards and unknowns is poor.

The iron ore tailing was found to contain 53.2% haematite, 14.8% goethite and 21.3% kaolinite. The majority of kaolinite occurred as particles less than $1\ \mu\text{m}$ in size. The application of the TG method was essential for optimising the performance of the selective flocculation process.

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