

Visible and infrared reflectance spectroscopy for characterization of iron impurities in calcined kaolin clays

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Abstract Visible (VIS) and Short Wavelength Infrared (SWIR) Reflectance Spectroscopy are used to determine the presence of iron impurities on calcined kaolin. For industrial applications, primary kaolin is calcined by roasting at temperatures of greater than 1100 °C. The presence of iron impurities in the primary kaolin affects the optical properties of the processed calcined clay. Spectral analysis in the VIS and SWIR ranges allows the analysis of iron phases in kaolin. In the kaolin calcination sequence, features in the VIS range change as a consequence of the variations in iron oxidation. Some of these variations are related to iron released in the breakdown of the kaolinite crystal lattice, which is identified by the changes in the SWIR features. The spectral characterization of the calcination of kaolin contributes to the understanding of these processes. Its application would enable more precise control of calcined kaolin properties and help to optimise the calcination process.

1 Introduction

For industrial applications, primary kaolin is calcined by roasting at temperatures of greater than 1100 °C. The resulting calcined kaolin clays are widely used in the manufacture of pigments and coatings. For such applications the key parameters determining calcined product quality are colour and brightness. The latter is used as the industrial standard for measuring the optical properties of papers [1], and therefore it is of maximum importance in kaolin processing. Brightness is defined by

the norm ISO 2470 as a mathematical function having an effective wavelength of 457 nm and a bandwidth of 44 nm [2]. The presence of iron impurities in the primary kaolin prior to calcination affects visual colour and brightness in the processed calcined clay.

Kaolin is mainly composed of kaolinite; ancillary minerals such as feldspars, micas, oxides and hydroxides are also commonly present. Most of these minerals host iron either within the crystal lattice or as a surface element. Special interest in iron impurities in kaolin and calcined kaolin arises from its influence on the colour and brightness of the clay products [3]. Nevertheless, the close coexistence of the minerals in the kaolin clays hinders the evaluation on the nature of the iron [4].

The thermal treatment of kaolin aims to transform kaolinite into metakaolin. In this process, kaolin minerals are dehydrated and dehydroxylated, leading to modifications in the crystal lattice. During the transformation iron is released and oxidized. This residual iron in the form of hematite acts as a chromophore giving a yellow/pink shade to the calcined clay [5].

Usually X-ray diffraction (XRD) and X-ray Fluorescence (XRF) are used as preferred techniques for kaolin mineral and chemical characterization, respectively. However, they are sometimes constrained by parameters such as particle size or require extensive preparatory work. In the mineral processing industry there is a growing interest in real-time or near real-time techniques that can be easily implemented in a production environment. In this context, Visible and Infrared Reflectance Spectroscopy has the potential to be an adequate technique for characterisation of calcined kaolin processing. This technique is well known for requiring simple or no sample preparation and for the availability of instruments that can be used *in situ* and provide real time data.

The spectral features that describe the transformation of kaolinite into metakaolin have been identified in the short and mid infrared ranges by using FTIR spectroscopy [6, 7]. The breakdown of M-OH bonds (M=metal), especially those related to Al-containing phases are the main features in the kaolinite-metakaolin spectra. Distortions in the kaolinite crystal lattice due to impurities can be recognized in the spectral profile, for example, in cases where Fe replaces Al in the kaolinite structure [8–10]. In addition, iron in kaolin ancillary minerals such as goethite and hematite, and its influence on the optical properties of the kaolin industrial products have been mainly researched in the visible range of

the spectrum using diffuse reflectance spectroscopy [11].

In this study, Visible (VIS) and Short Wavelength Infrared (SWIR) Reflectance Spectroscopy are used to characterize the behaviour and influence of iron in three different calcined kaolin samples. Discrimination between kaolinite structural iron and other iron bearing minerals is done by identification of the main spectral features. These are compared at different calcination temperatures in order to determine how the iron impurities are affecting the kaolinite-metakaolin transformation process.

2 Materials and Methods

Three kaolin samples with different iron content were prepared for spectral analysis. They were named Feed 1, Feed 2 and Feed 3 and represent low, medium and high Fe content, respectively. These samples were calcined at various temperatures using a muffle furnace. They were calcined at temperatures from 500 to 1200°C at 100°C intervals. Each feed was split into 6 subsamples and placed in the calciner and heated from ambient to the specified temperature at a rate of 15°C per minute. The resulting powders were measured for ISO brightness, XRD and XRF. The XRF measurements for Fe₂O₃ are indicated in Figure 18.1.

Visible and short wavelength infrared spectra were collected with an ASD FieldSpec spectrometer, using the contact probe and the internal light source. Measurements were completed over compacted powders with a flat surface for oriented kaolinite crystals. Analyses of the resulting spectra were undertaken using the Hyperspectral Python software, always over convex hull removed spectra (CR).

3 Spectral identification of Fe in Kaolin

3.1 VNIR spectrum: Fe compounds in kaolin

Spectral features typical of iron compounds in the visible and near infrared (VNIR) are present near 430, 520 and 870-960 nm (Figure 18.2). These absorptions are characteristic of Fe³⁺ present in hematite. The wavelength position and depth of these features varies in relation to the initial feed composition and calcination temperature. However, they are

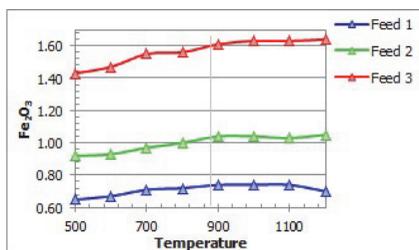


Figure 18.1: Fe₂O₃ content measured by XRF. Vertical line before 900°C represents a point where the iron oxide increasing rate decreases

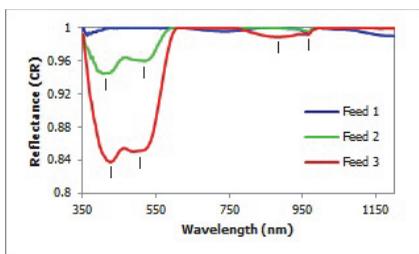


Figure 18.2: Main spectral features detected in the VNIR spectra. Absorptions at 430, 520 and 870 nm are due to Fe oxides. The small feature at 966 nm belongs to kaolinite

more clearly present along the calcination sequence in Feed 3. Absorptions nearby 670 nm, as an indicator of Fe³⁺ in goethite, are not detected in any of the samples. In Feeds 1 and 2 a broad absorption at 740 nm and a sharp one 966 nm are present in the lowest temperatures (Figure 18.2), and might belong to kaolinite instead of hematite. The intensity of the 870 absorption in Feed 3 would mask these kaolinite features.

Features in the visible range are used to explain the brightness and colour variations in the samples. Hematite absorptions in this range affect the reflectivity ratio, measured as the ratio of the reflectance values at 450 and 600 nm in not continuum removed spectra [12], which is likely related to the ISO brightness standard (Figure 18.3). Therefore, hematite content can be taken as the main parameter that affects the visible characteristics of the samples.

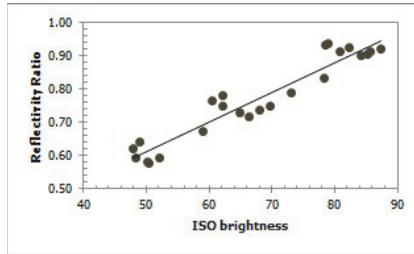


Figure 18.3: Correlation between Reflectivity Ratio and ISO brightness as mean for describing the optical properties of the samples

3.2 SWIR spectrum: Kaolinite structure

The SWIR spectra of the 3 feeds at the lowest temperature are very similar. As expected, the characteristic kaolinite features dominate the spectral profile with only small differences in some of the absorptions (Figure 18.4). Well-developed features that characterize the strength of OH bonds, as well as the Kaolinite Crystallinity Index (KX) demonstrates that kaolinite in these samples has highly ordered structure. However, these same parameters suggest that kaolinite in Feed 1 has a higher order of crystallinity than Feed 2 and Feed 3.

Studies developed by [8] indicate that $\text{Fe}^{3+} - \text{Al}^{3+}$ substitution in kaolinite causes an absorption band at 2240nm. Nevertheless, this absorption is not clear in any of the feeds. Absorptions due to Fe replacement within the kaolinite structure are not evident in this part of the spectra.

4 Kaolin calcination and spectral changes

Calcination of kaolin affects the entire spectral profile, demonstrating that the thermal treatment affects both the optical and physical parameters of the calcined clay. As remarked previously, features in the VNIR spectra are mainly related to iron hosted in kaolin ancillary minerals, whereas features in the SWIR range are closely related to the kaolinite crystal structure.

Kaolinite, as the main kaolin component, dominates the processes oc-

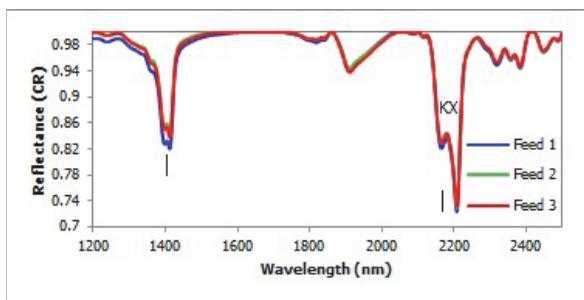


Figure 18.4: Characteristic kaolinite absorptions in the SWIR spectra. The doublet at 2200 nm is diagnostic for kaolinite identification and is used to measure the Kaolinite Crystallinity Index (KX)

curing during calcination. The main process is driven by the kaolinite – metakaolin transformation, and therefore affects the OH-related features measured in the SWIR range. The dehydroxylation process can be illustrated by the flattening of the 1400 and 2200 absorptions with increasing temperature (Figure 18.5). The transformation of these features is similar for the three feeds, although there are subtle differences at specific calcination stages. From 500 to 700°C OH features are weakened, but they still preserve the characteristic kaolinite doublets. Spectra at 800°C represent the most distinctive differences for the 3 feeds. The KX, calculated for the whole calcination sequence, shows that Feed 3 has a faster dehydroxylation rate, whereas Feed 2 seems to have a more stable structure than Feed 1 (Figure 18.6). After 900°C none of the kaolinite distinctive features are recognized, although weak OH absorptions are still present. After this point, the most prominent feature occurs at 1900nm, which corresponds to the water feature (Figure 18.5).

Changes in the VNIR spectra along the calcination sequence differ between feed types due to the compositional differences. However, as shown in Figure 18.7, some points are comparable. At lower temperatures, hematite features are clearly dominant in Feed 2 and 3. They are always deeper in Feed 3. They are absent in Feed 1. Instead in Feed 1 most of this part of the spectrum is dominated by kaolinite, with some small features. Up to 700°C the maximum absorption in Feeds 2 and 3 is at 430nm. Above 800°C this absorption weakens and the 520nm fea-

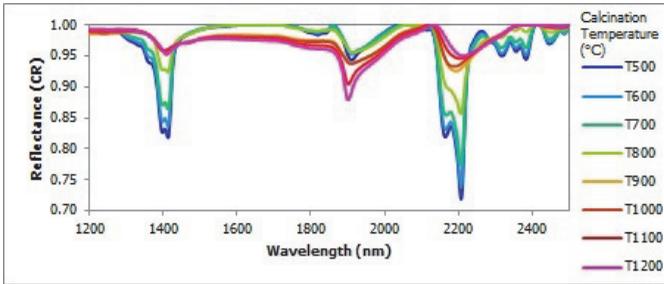


Figure 18.5: Changes in the SWIR spectra due to dehydroxylation with increasing the calcination temperature. OH-related features at 1400, 2200 and 2250-2400 nm become shallower and smoother at higher temperatures

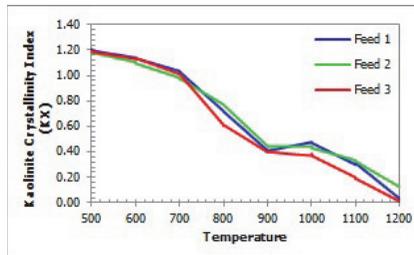


Figure 18.6: Variations in kaolinite crystallinity along the calcination sequence, as a measure of dehydroxylation degree

ture is the deepest one. It disappears in Feed 2 at 1000°C and in Feed 3 at 1100°C. After 800°C the 520nm absorption becomes the most relevant absorption, not only for Feeds 2 and 3, but also for Feed 1, where an incipient Fe-feature appears and remains present until 1100°C. At this temperature the same feature is also weaker for the other feeds. In contrast, the broad feature nearby 870nm gets deeper along the whole sequence for Feeds 2 and 3. This feature is not present in Feed 1. At 1200°C a goethite absorption feature is apparently present in Feed 3.

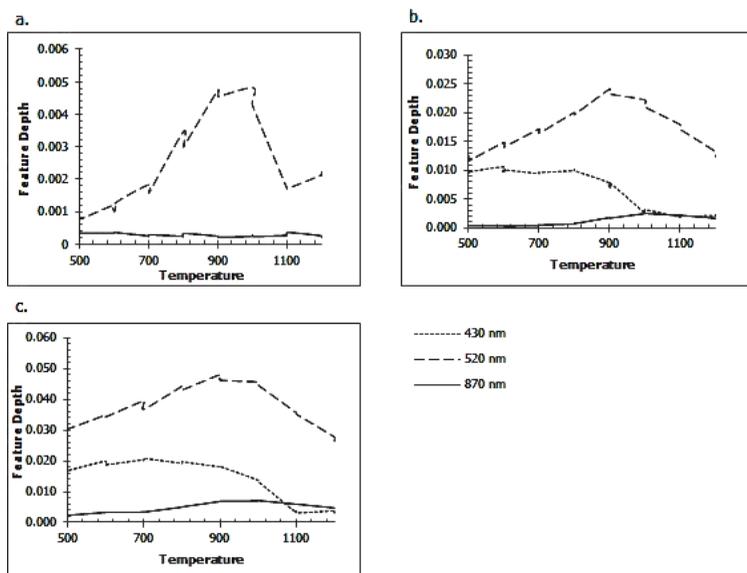


Figure 18.7: Variations in the VNIR absorptions along de calcination sequence, represented as the depth of the feature at a given wavelength. **a. Feed 1, b. Feed 2, c. Feed 3.** The 430nm feature becomes shallower until almost vanishing at higher temperatures. No data is shown for Feed 1 since feature is not present. The 520 nm absorption reaches its maximum depth at 900°C in all the feed types. Broad absorption in the 870 nm region gets deeper with increasing temperature, although its intensity is very low in relation to the other features. This feature is not developed in Feed 1

5 Discussion

Kaolinite-metakaolin transformation

The transformation of kaolinite into metakaolin is clearly recorded in the variations of the SWIR spectral profile. As the lowest temperature measured is 500°C it is assumed that dehydration has taken place already. Therefore the main process occurring is dehydroxylation. The flattening of the spectral features at 1400 and 2200nm, representing OH bonds and Al-OH stretching respectively, indicates that the attractive forces among atoms weaken when temperature increases. This leads

to distortions in the kaolinite crystal structure. It becomes an amorphous compound referred to as metakaolin. This stage is reached between 800°C and 900°C for the given set of samples. However, the rate of this process is not the same for the three different kaolinites. With Fe^{3+} replacing Al^{3+} in the kaolinite octahedral spaces, the crystal lattice becomes more unstable, and therefore prone to quicker dehydroxylation. It is expected that high iron content and low crystallinity values in the samples correspond to a larger amounts of structural Fe. This is true for Feed 3, which initially has the lowest KX values, and becomes dehydroxylated more rapidly than the other feeds (Figure 18.4). However, this situation is not that clear for Feeds 1 and 2. Even though initially Feed 2 is less crystalline than Feed 1, its dehydroxylation rate is slower. This might indicate that the distortions in its crystal lattice are not necessarily caused only by Fe replacement, but also by other factors that do not destabilize the structure to the same extent as Fe does. It might also be possible that the crystallinity measurement has been affected by factors such as mineral mixtures. XRD analysis revealed the presence of muscovite in these samples. Nevertheless, due to the invariability on the wavelength position of the Al-OH feature (2207nm) it was assumed that the influence of muscovite in the kaolinite spectra is very small. Despite the fact that muscovite might also host iron in its structure, it reacts similarly to kaolinite. Therefore, it does not have any significant impact on the Fe-related observations.

Even though the absorptions bands that represent $\text{Fe}^{3+} - \text{Al}^{3+}$ replacement in kaolinite were not identified, other factors suggest the presence of structural iron in the analysed samples. The 800-900°C temperature window, where it is considered that metakaolin formation is taking place, coincides with the peak of energy absorption of iron in the VNIR range. Similarly, the iron content as measured by XRF increases up to 800°C and becomes less variable after this temperature (Figure 18.1). It is interpreted that during dehydroxylation iron has been released from the kaolinite structure. In oxidizing conditions it reacts to form Fe_2O_3 , and therefore hematite absorptions are enhanced. A decrease in the intensity of these absorptions at the highest temperatures might be explained by particle size effects, as it will be further explained, or by reincorporation of Fe in the structure during the next step of the calcination sequence that results in mullite crystallization. However, the shape of the spectral features at high temperatures suggests that recrystalliza-

tion has not yet taken place. Spectral features in the Mid Infrared range (MIR) may give more complete information about the possible crystallization of mullite. Moreover, the fundamental absorptions in that part of the spectrum should exhibit clearer absorption bands related to structural iron in kaolinite. This could therefore validate the observations herein presented.

Influence of Fe in the calcined kaolin optical properties

In the VNIR range the spectral features are caused by electronic processes, generated in this case by the iron content. Its presence in calcined kaolin clays has a remarkable influence on the optical properties. This influence is conditioned by the amount and the source of iron in the samples. In Feeds 2 and 3 it is clear that most of the initial iron content is derived from hematite as an ancillary mineral, whereas in Feed 1 it might come only from structural iron.

As for the SWIR spectra, features in the VNIR are affected by the calcination process. Higher calcination temperatures increase the energy of the Fe ions, intensifying the ferric charge transfer transitions from 500 to 800°C [12] in feeds 2 and 3. Because of this, features at 430 and 520 nm deepen, which is therefore shown in the colour/brightness of the samples. From 900-to 1200°C reflectivity is mostly driven by the particle size. Small particles interfere with charge transfer and ease energy scattering, resulting in weaker absorptions and increased brightness. In contrast, crystal field effects get stronger at the highest temperature, but because of the wavelength position of its feature, they do not have any effect on the visual colour of the samples.

As previously mentioned, Feed 1 initially does not show Fe-related features at low temperatures. A charge transfer absorption at 507nm appears at 800°C, as a consequence of the release of Fe from the kaolinite structure and its subsequent oxidation. This feature persists until 1000°C after which it vanishes due to particle size effects. It is possible that the enhancement of the 520nm feature in Feeds 2 and 3 at 800°C is reinforced by the increase in hematite amount that comes from structural iron, likewise in Feed 1. However, it is not possible to estimate the magnitude of this contribution.

6 Conclusions

Visible and Infrared reflectance spectroscopy has been shown to be a valuable technique for characterization of calcined kaolin clays. The focus of this study has been on the iron impurities hosted in the kaolinite structure as well as in ancillary minerals. The dehydroxylation process that drives the transformation of kaolinite into metakaolin is illustrated by the smoothening of the characteristic kaolinite spectral features in the SWIR range. In this process, 800-900°C is taken as the temperature range where the largest changes occur in the kaolinite structure. At this temperature iron is released from kaolinite as a consequence of the crystal lattice breakdown. The amount of hosted iron would speed up the dehydroxylation rate.

Spectral features characteristic of iron contained in ancillary minerals are present in the VNIR range. Iron is present as hematite. In Fe-rich samples hematite occurs naturally, whereas in iron - poor samples hematite is derived from iron released from kaolinite. The presence of iron oxides affects the optical properties of the calcined clay up to 800°C. Until this point, the increasing temperature enhances iron absorptions, controlling the shading of the samples. In addition, Fe enrichment from kaolinite contributes to intensify these features. At the highest temperatures the optical properties are influenced mostly by particle size.

Acknowledgments

This work was facilitated by Imerys Minerals Ltd and the STOICISM research project. It has been supported by the European Commission under the 7th Framework Programme through the grant number 310645.

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