Kaolin mining and beneficiation: the role of iron

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Abstract. Mössbauer spectra of raw kaolins generally comprise components from iron bound in the structures of kaolinite minerals and iron in ancillary minerals. Of the latter, iron oxides are among the most detrimental to industrial uses. Although a distinction of structural and oxidic iron is generally possible if the oxides are magnetically ordered, Mössbauer spectra of kaolins are generally complicated as a result of slow paramagnetic relaxation of iron bound in the kaolinite structure. A distinction of iron bound in oxides and the kaolinite structure may therefore require the application of selective dissolution procedures in addition to Mössbauer spectroscopy.

Thus Mössbauer spectroscopy, where necessary in conjunction with chemical analyses, enables a quantitative assessment of the iron mineralogy of kaolins to be made at all stages of industrial beneficiation. This allows the efficiency of individual stages of processing and the quality of the final product to be monitored, problems during processing to be identified, and individual processing stages to be fine-tuned.

1. Introduction
Kaolinite is a layer silicate with a structure that consists of two-dimensional tetrahedral silica (SiO$_4$) sheets linked to octahedral alumina (Al(O,H)$_6$) sheets to form 1:1 layers (figure 1). The formula of kaolinite is Al$_2$Si$_2$O$_5$(OH)$_4$, generally with little to no cation substitution. Dickite, nacrite and halloysite...
are polymorphs of kaolinite, i.e. they have the same chemistry (halloysite contains additional interlayer water) but different structures.

The kaolinite structure can accommodate moderate amounts of iron that substitute for Al$^{3+}$ on the octahedral sites. Such substitutional iron allows an assessment of the octahedral site geometry to be made using $^{57}$Fe Mössbauer spectroscopy. The Mössbauer parameters given by [2] and [3] probably constitute the most reliable data on a wide range of kaolinites to date. The average Fe$^{3+}$ isomer shift $\delta$/Fe of 0.35 mm/s confirms the octahedral coordination of iron. The relatively low, temperature-independent “best” value for the Fe$^{3+}$ quadrupole splitting of Fe$^{2+}$-free kaolinite of about 0.51 mm/s is in good agreement with the moderate octahedral flattening angle $\Psi_{oct}$ of 57.5° (ideally 54.73° for undistorted octahedral sites) observed by X-ray and neutron diffraction [4]. The Fe$^{3+}$ quadrupole splitting increases from the value given above with the Fe$^{2+}$/Fe$^{3+}$ ratio, indicating the incorporation of a relatively large ion such as Fe$^{2+}$ in the kaolinite structure to increase the average octahedral site distortion.

Kaolin, as opposed to kaolinite, is a kaolinite-rich product of intense weathering or hydrothermal alteration of aluminosilicate minerals such as feldspar and mica. The Glossary of Geology [5] defines kaolin as “A soft, relatively nonplastic but dispersible, usually white or nearly white claystone comprised mainly of minerals of the kaolin group, principally kaolinite …”. In reference to porcelain that originated in China, “China Clay” is a common synonym for high-grade white (i.e. iron-poor) kaolin.

Kaolin has a variety of industrial uses, the most important of which is the production of paper, where it is used as a filler and coating (requiring the kaolin to have a high whiteness). Other major uses of kaolin include the production of ceramic products such as porcelain and refractories, of rubbers, to which it adds strength, abrasion resistance and rigidity, and of paints and inks, in which it can act as a filler and thickening agent or substitute for titanium-based pigments. More exotic uses include cosmetics, soaps, toothpastes and medicines (for example as antidiarrheal adsorbents or inactive excipients).

Genetically, there is a twofold classification of kaolin deposits: those that have formed in situ (“primary” deposits) and others that have been eroded, transported and redepósited after formation (“secondary” or “sedimentary” deposits). Although numerous kaolin deposits exist worldwide, the market is currently dominated by three regions: the southeastern U.S.A., the lower Amazon Basin in Brazil and the Cornwall area of southwestern England [6]. Current mining is almost exclusively performed in open pits. Besides kaolinite, kaolins often contain other mineral alteration products, the most deleterious of which for industrial uses are iron oxides and oxyhydroxides (here generically termed “iron oxides”), quartz, and the TiO$_2$ polymorphs anatase and rutile. Raw kaolin ores must therefore be subjected to processing (“beneficiation”) following mining to remove associated minerals that would decrease the commercial value of the final product or even render it unsuitable for specific uses. Kaolin processing involves a variety of stages to homogenize the raw ore and concentrate desired particle size fractions while removing unwanted ancillary components. Depending on the properties of the raw material and the desired properties of the final product, the individual steps and their sequence can vary significantly.

Like kaolinite, hematite ($\alpha$-Fe$_2$O$_3$) and goethite ($\alpha$-FeOOH) are common products of intense weathering and therefore also frequent constituents of kaolins. Because of their intense colour, iron oxides (in particular hematite) must be removed from kaolins for most industrial applications. The removal of iron oxides is generally effected by either physical (magnetic separation, flotation) or chemical (selective dissolution) means, or both. A more modern approach involves biological leaching using Fe$^{3+}$-reducing bacteria or fungi. The particular value of Mössbauer spectroscopy for the current issue lies in the possibility of enabling a distinction to be made between iron in ancillary iron oxides and iron that is bound in the kaolinite structure, and to quantify these forms of iron.

2. Mössbauer spectroscopy

Iron oxides formed in the weathering environment are generally of small particle size, and thus often superparamagnetic at room temperature, and furthermore generally aluminium substituted. Thus,
rather than being pure iron oxides, natural hematites and goethites have compositions given by $\alpha-(\text{Al}_{x}\text{Fe}_{1-x})_2\text{O}_3$ and $\alpha-(\text{Al}_{x}\text{Fe}_{1-x})\text{OOH}$, where $x$ can amount to as much as 0.16 and 0.36, respectively [7]. In the (super)paramagnetic state, the Mössbauer parameters of these iron oxides resemble those of Fe$^{3+}$ in kaolinite and cannot be distinguished from these. A discrimination between iron bound in the kaolinite structure and associated iron oxides therefore requires Mössbauer spectra to be taken at low temperatures, usually in the liquid-nitrogen range (~ 77 K). A further complication can arise because the generally low structural iron content of kaolinite may result in slow paramagnetic relaxation. For Fe$^{3+}$, this leads to a six-line spectrum with a magnetic field of ~ 55 T at low temperatures. Although the lines are considerably broader than for a typical magnetically ordered hematite, the spectrum “mimics” a magnetically ordered iron oxide. Such a component therefore may be (and has been) mistaken for hematite. The lower magnetic field that is developed at room temperature, in contrast, is more suggestive of a non-Lorentzian broadening of the paramagnetic doublet. As an example, figure 2 shows Mössbauer spectra of an iron oxide-free kaolin from Brazil at room temperature and 4.2 K. The broken subspectra show Lorentzian doublet fits to both spectra. Note the broadening of the observed Fe$^{3+}$ doublet relative to the Lorentzian fit at room temperature and the sextet component at 4.2 K. Both result from slow paramagnetic relaxation and not from the presence of associated iron oxides [2].

![Mössbauer spectra of an iron-oxide free kaolin from Brazil taken at room temperature and 4.2 K.](Figure 2)

Figure 2. Mössbauer spectra of an iron-oxide free kaolin from Brazil taken at room temperature and 4.2 K. The broken subspectra indicate Lorentzian Fe$^{3+}$ doublets that were fit to the spectra. Modified from [2].

![Mössbauer spectra of a kaolin taken at 4.2 K before (top) and after (bottom) iron oxide removal with Na dithionite (“DCB”).](Figure 3)

Figure 3. Mössbauer spectra of a kaolin taken at 4.2 K before (top) and after (bottom) iron oxide removal with Na dithionite (“DCB”). The dotted subspectrum indicates a sextet fit to the iron oxide (here goethite) component of the original sample. Modified from [2].

Figure 3 shows Mössbauer spectra of a commercial kaolin from Germany taken at 4.2 K before and after selective iron oxide removal with Na dithionite [2]. The parameters of the inner sextet in the spectrum of the original sample show this to result from goethite. The slight amount of iron dissolved by the dithionite treatment (0.07 mass %), corresponding to a mere 0.11 % goethite in the original kaolin, attests to the sensitivity of Mössbauer spectroscopy towards magnetically ordered phases. The magnetic component remaining after goethite removal (bottom spectrum) can again be attributed to paramagnetic relaxation of iron in the kaolinite structure. It must, however, be pointed out that the significant difference in magnetic fields between that generated by paramagnetic relaxation (~ 56 T)
and goethite (~50 T) renders this case particularly favourable for a direct observation of the two magnetic components in the untreated sample. A distinction of the magnetic field due to paramagnetic relaxation in kaolinite from the hyperfine field of hematite at 4.2 K (≤54.2 T or ≤53.5 T for hematite that has and has not passed through a Morin transition, respectively [8]), in contrast, would hardly be possible, and such a case would require spectra to be taken before and after the selective removal of hematite for a definitive discrimination of the two contributions.

3. Mining and beneficiation: an example
The possibilities of Mössbauer spectroscopy as a probe for the physical and chemical changes of iron during the industrial production of kaolin are best exemplified by presenting a specific example. For this purpose we select here the raw ore and beneficiated products of a kaolin mined by Pará Pigmentos S.A. in the Ipixuna area of the State of Pará, Brazil. A detailed description of the deposit, its mineralogy and the mining process has been recently published [9] and the constitutions and selected properties of the raw ore and the intermediate and final products of the industrial beneficiation have been described by [10]. Here we restrict ourselves to the original (raw) product extracted from the deposit, the reject of magnetic separation in the course of beneficiation, and the final product.

Figure 4. Room-temperature Mössbauer spectra of the raw ore and the reject of magnetic separation of kaolin mined at the Ipixuna deposit of Pará Pigmenos S.A., Brazil. The broken subspectrum in the bottom diagram indicates a Lorentzian Fe$^{3+}$ doublet that was fit to spectrum. Modified from [10].

Figure 4 shows room-temperature Mössbauer spectra of the raw product and the magnetic reject. The spectrum of the raw ore shows – in spite of considerable data scatter because of the low iron content of the sample – the already familiar discrepancy between an Fe$^{3+}$ doublet fitted to the spectrum and the actual data. In contrast to Mössbauer spectra of other samples from the same region [11,12], the sample we studied showed no evidence of iron oxides that are magnetically ordered at room temperature, indicating at most very low iron oxide contents. The spectrum of the magnetic reject, in contrast, displayed a well-developed sextet in addition to the paramagnetic components, and could be fit with four components: a major Fe$^{3+}$ doublet, a subordinate Fe$^{2+}$ doublet, and two sextets. The magnetic hyperfine fields of 51.1 and 49.5 T of the two sextets that were fit to the magnetic component (at an average quadrupole shift of ~0.18 mm/s) can, rather than indicating two discrete mineral components, be taken as ensuing from a distribution of hyperfine fields in hematite of
moderate crystallinity and/or significant Al substitution. A Mössbauer spectrum of this sample taken at 110 K could be fit with a major Fe$^{3+}$ doublet, a subordinate Fe$^{2+}$ doublet, and three sextets (figure 5). In addition to hematite, the two other sextets evidence the presence of goethite and (tentatively) indicate maghemite. The latter can also be observed (though not quantified) in the magnetic reject by X-ray diffraction, thereby validating this assignment in the Mössbauer spectrum, whereas overlap of the most intense X-ray peaks of goethite with peaks of kaolinite prevents a definitive identification of goethite by X-ray diffraction.

*Figure 5.* Mössbauer spectrum at 110 K of the magnetic reject of the Pará Pigmentos kaolin. Modified from [10].

The iron mineralogy of the magnetic reject deduced from the spectrum taken at 110 K is summed up in table 1. Chemical analysis shows this sample to have a total iron content of 10.89 % Fe$_2$O$_3$ [10]. Breaking this up into the components indicated by the Mössbauer spectrum at 110 K allows an assessment of the relative amounts of iron oxides to be made. The Fe$^{3+}$ doublet is attributed to iron that is bound in the structure of the final kaolin (0.69 mass %), although contributions from iron oxides that are still superparamagnetic at 110 K cannot be excluded.

*Table 1.* Iron mineralogy of the magnetic reject of the Pará Pigmentos kaolin derived from the Mössbauer spectrum at 110 K (Figure 5).

| Mineral              | Relative area | Mass %$^a$ |
|----------------------|---------------|------------|
| Hematite             | 0.29          | 3.74       |
| Maghemite            | 0.04          | 0.59       |
| Goethite             | 0.28          | 4.22       |
| Fe$^{2+}$ [paramagnetic]$^b$ | 0.02        |            |
| Fe$^{3+}$ [paramagnetic]$^c$ | 0.38        |            |

$^a$Corrected for recoil-free fractions [13,14].

$^b$Paramagnetic Fe$^{2+}$ in kaolin and ancillary minerals.

$^c$Includes contributions from paramagnetic Fe$^{3+}$ in kaolin and ancillary minerals and possibly superparamagnetic Fe$^{3+}$ oxides.
4. Conclusions

$^{57}$Fe Mössbauer spectra of kaolinite are generally complicated by slow paramagnetic relaxation of iron bound in the kaolinite structure. Because kaolins tend to be mixtures of minerals of the kaolin group (kaolinite with possible admixtures with dickite, nacrite and/or halloysite) and other minerals formed during intense weathering, their Mössbauer spectra are correspondingly complex, comprising components from iron bound in the structures of the kaolinite minerals and iron in ancillary minerals. During industrial processing the proportions of kaolinite and other kaolin minerals are increased relative to those of the ancillary minerals, and the resultant changes in iron mineralogy can be monitored by Mössbauer spectroscopy. A comprehensive characterization of the kaolin and ancillary mineral mineralogy will nevertheless usually require a combination of Mössbauer spectroscopy with other analytical procedures such as X-ray diffraction, Raman spectroscopy and selective chemical dissolution.

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