Clays and Clay Minerals, Vol. 31, No. 4, 293–298, 1983.

MÖSSBAUER EFFECT STUDIES OF IRON IN KAOLIN. II. SURFACE IRON

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Abstract—^{57}Fe Mössbauer spectra have been used to interpret the effects of different cleaning processes on the iron mineralogy of a Weipa, Australia, kaolin. A magnetically separated fraction contained 28% of its iron as hematite likely of secondary origin. An initial centrifugal size separation was shown to give an improved final product, and oxalic acid was found to be more efficient at removing Fe from the kaolinite surface than dithionite bleach. The Mössbauer spectra clearly show that beneficiation steps which give a substantial increase in kaolin brightness result in only minor changes in the clay iron mineralogy. Similar results were also obtained for two commercially available kaolins.

Key Words—Beneficiation, Iron, Kaolin, Mössbauer effect, Surface.

INTRODUCTION

Recent developments in the processing of kaolins for a variety of end uses were discussed by Murray (1980). Both chemical bleaching (e.g., Bundy and Murray, 1973) and wet high-intensity magnetic separation (e.g., Lawver and Hopstock, 1974; Iannicelli, 1976; Schulze and Dixon, 1979) are currently employed to improve the color and brightness of kaolins for use in the paper industry. Application of these techniques to Weipa kaolins is currently under investigation by Comalco.

In the preceding paper, Fysh *et al.* (1983) identified from Mössbauer parameters structural and surface Fe in a kaolin from Weipa, Cape York Peninsula, Australia. In this paper the effects on the iron sites are examined at different stages of a kaolin clean-up procedure.

EXPERIMENTAL

All of the raw and beneficiated kaolin samples used in this study were provided by Comalco. The Weipa kaolin was cyclone-separated to remove coarse particles (predominantly quartz) and dried. A sample of the dried kaolin (K1) was retained, and the remainder subjected to iron removal treatments as depicted in Figure 1. The magnetic (K2) and non-magnetic (K3) fractions were obtained in the approximate mass ratio 1:100. Sample K3 was the principal material studied in the preceding paper. For comparison purposes specimens of commercially available kaolins (Ultrawhite 90 (UW90) and Amazon 88 (A88)) were also examined, in the as-purchased state.

Apart from the magnetic fraction, K2, which is quite pink, all of the Weipa kaolins examined are about the same color and brightness to the naked eye. However, precise measurements show a clear improvement in brightness at each beneficiation step, with the final products after the dithionite bleach (K4 and K5, see Figure 1), having a brightness comparable with that of commercially available paper coating kaolins.

Details of the absorber preparation, Mössbauer spectrometer, and analysis procedures used were listed in Fysh *et al.* (1983).

RESULTS

300°K spectra

The room temperature Mössbauer spectra of samples K1, K4, K5, and A88 are very similar to that of sample K3 described in the previous paper, and the fitted parameters of each are the same as those given there within experimental uncertainty. The spectrum of sample K2, the magnetic fraction of Weipa bauxite, is shown in Figure 2. This spectrum has been fitted in the same way as that of sample K3, etc., but with an additional magnetically split subspectrum. The parameters of the relaxed component and the central doublet are the same as for the other samples, and their relative contributions are in about the same ratio. The magnetic component has a hyperfine splitting of 504 ± 1 kOe, and isomer shift and quadrupole splitting of +0.38 ± 0.02 mm/sec and −0.20 + 0.02 mm/sec, respectively. It accounts for 34% of the total spectral area, and is most likely due to hematite. Its hyperfine field is too large to be due to goethite ($H_{300°K}$ = 383 kOe, Fysh and Clark, 1982a), and the negative quadrupole splitting eliminates the possibility of maghemite ($H_{300°K}$ = 500 kOe, Δ = +0.01 mm/sec, Longworth and Tite, 1977). The hyperfine field of hematite at 300°K is 517 kOe, and its quadrupole splitting is −0.21 mm/sec (Fysh and Clark, 1982b). Possible reasons for the observation

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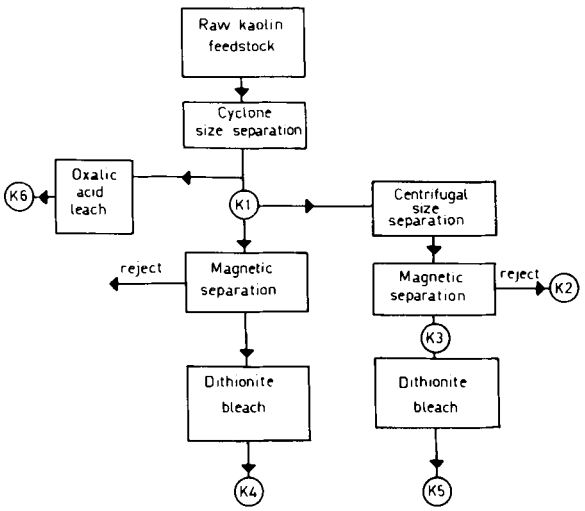

Figure 1. Beneficiation process for the Weipa kaolin, showing origin of the samples studied.

of a decreased hyperfine field for hematite at 300°K have been discussed elsewhere (Fysh and Clark, 1983). The most probable cause, bearing in mind the relaxed nature of the spectrum, is the small size of the hematite particles present. Reduced hyperfine splittings for microcrystalline hematite have been observed to persist even at 4.2°K (Fysh and Clark, 1982b), and are probably due to the reduced hyperfine field experienced by the nuclei near the surface of particles, and small fluctuations in the magnetization of the particles about the easy direction.

The spectrum of sample UW90 at 300°K (see Figure 3) is quite different to those of the other kaolins. The poor definition of the spectral lines is due to the low concentration of Fe in the absorber, and in fact the spectrum contains $\sim 3 \times 10^6$ counts/channel, compared with $\sim 2 \times 10^6$ counts/channel for that of sample K2. The spectrum has negligible baseline curvature,

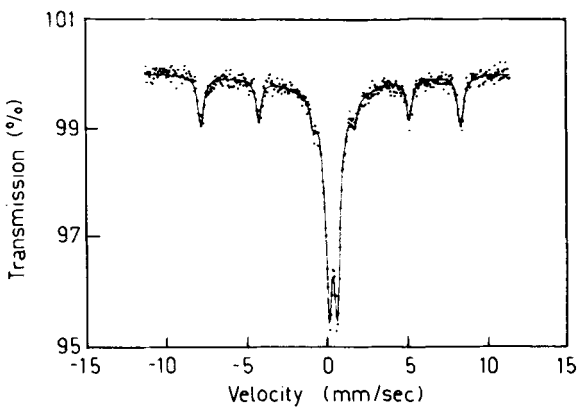

Figure 2. Mössbauer spectrum of sample K2 at room temperature.

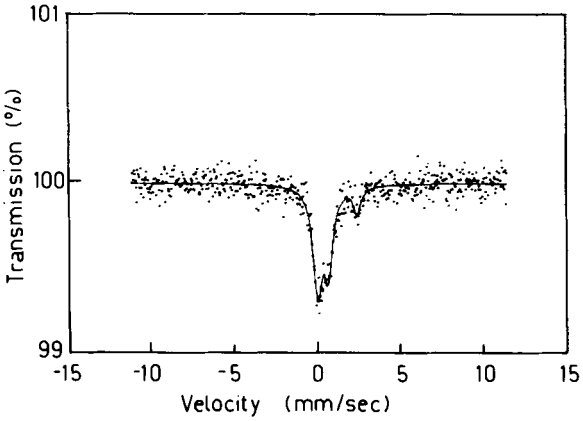

Figure 3. Mössbauer spectrum of specimen UW90 at room temperature, showing the absence of any relaxation or magnetic ordering effects in this sample.

and has been fitted with two doublets. These have isomer shifts of $+0.28 \pm 0.05$ mm/sec and $+1.1 \pm 0.1$ mm/sec and quadrupole splittings of 0.63 ± 0.05 mm/sec and 2.5 ± 0.1 mm/sec, respectively. The more intense (75% of spectral area) doublet, having the smaller quadrupole splitting, is presumably due to Fe^{3+} in the kaolin lattice, although its parameters are different to those reported by Fysh *et al.* (1983). They observed quadrupole splittings as large as 0.75 mm/sec for kaolin from the bauxitic zone at Weipa, and, considering both X-ray powder diffraction analysis of these specimens and the variation in Δ values reported in the literature, concluded that this parameter may increase significantly with decreasing kaolinite crystallinity. The isomer shift and quadrupole splitting of the less intense doublet agree well with values reported for Fe^{2+} in the kaolinite structure (Malden and Meads, 1967; Jefferson *et al.*, 1975).

4.2°K spectra

To determine the effects of the magnetic and chemical treatments on the impurity iron associated with the Weipa kaolin, and whether or not such iron is associated with the samples A88 and UW90, spectra of all of these specimens were taken at 4.2°K.

The 4.2°K spectrum of sample K1, the initial kaolin, is indistinguishable from that of sample K3. Thus, it appears that the hematite detected in the 300°K spectrum of sample K2, the magnetic fraction, is only present at very low levels in the initial kaolin, and has been very effectively concentrated by the magnetic separation process. In the 4.2°K spectrum of sample K2 (Figure 4) the separate, magnetically split spectral contributions arising from the hematite and kaolinite structural and surface iron are well resolved. The contributions of the magnetically split and relaxed spectral components arising from the kaolinite structural Fe relative to that of the central kaolinite doublet are

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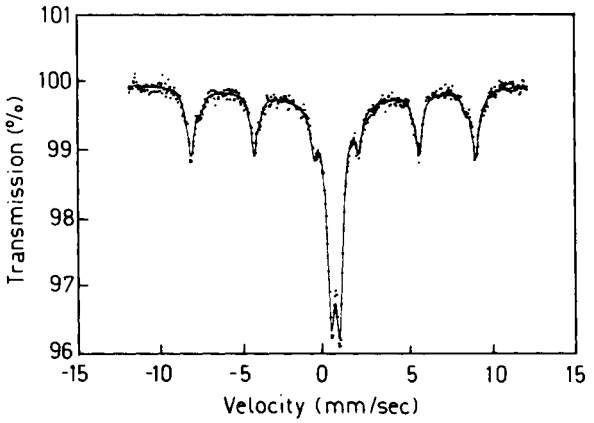

Figure 4. Mössbauer spectrum of sample K2 at 4.2°K.

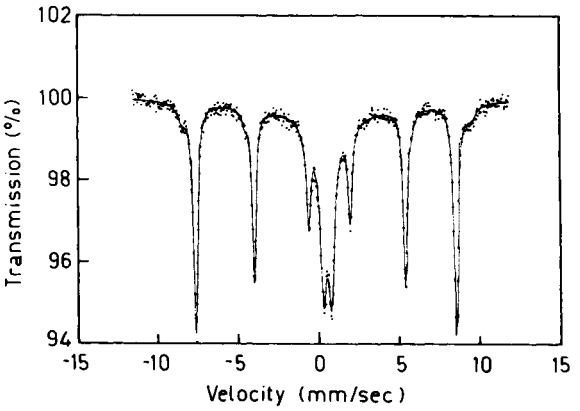

Figure 5. Mössbauer spectrum of a mixture of sample K3 and pure goethite used to determine the recoilless fraction of kaolinite structural iron at 4.2°K.

somewhat smaller than in sample K3, probably reflecting the difficulty in resolving them from the hematite subspectrum. The relative surface iron contribution has increased to 8% of the spectral area compared with 4% for sample K3. This is unlikely to be a direct result of the magnetic concentration, but may reflect a greater surface iron content of kaolinite particles intimately associated with the hematite present. This would be expected if, as suggested by Fysh *et al.* (1983), the surface iron and hematite are both the result of a secondary Fe precipitation. The hyperfine splitting of the surface iron phase is the same as for sample K3, while that of the hematite (533 ± 1 kOe) indicates an Al substitution of ~7 mole % (Fysh and Clark, 1982b). Some of the reduction in hematite hyperfine splitting from the value for pure hematite may be due to particle size effects, but this seems unlikely considering the well-resolved hematite subspectrum at 300°K.

Recoil-free fraction determination

To calculate more accurately the relative proportions of Fe present in the various phases, allowance must be made for the different temperature-dependent recoil-free fractions (f values) of each. The 4.2°K recoil-free fractions of aluminous goethites and hematites were determined by Fysh and Clark (1982a, 1982b) by measuring the dependence of the Mössbauer line-width on absorber thickness. Such an approach is not practical for the Fe in kaolin because of the complicated nature of the spectrum. A value for f may be obtained by measuring the relative spectral areas of a specimen consisting of two or more Fe phases if the f of one phase and the relative Fe content of each of the phases is known. Unfortunately, an accurate chemical analysis was not available for the hand-picked kaolin specimen containing only structural Fe examined by Fysh *et al.* (1983), so that one of the cleaned kaolins, sample K3, was used to make the f measurement.

Known masses of the cleaned kaolin (sample K3) and pure goethite ($f_{4.2°K} = 0.69 \pm 0.02$, Fysh and Clark, 1982a) of known Fe content were mixed, and the 4.2°K spectrum of this absorber is shown in Figure 5. The hyperfine splitting of the pure goethite is 505 kOe, so that the small spectral contribution arising from the surface iron could not be resolved from that of the goethite. However, on the basis of the fit to the spectrum of sample K3 (see previous paper), the area of this subspectrum relative to that of the outer magnetically split subspectrum of the kaolin was calculated for the present absorber. The recoil-free fraction of the surface iron was assumed to be 0.89, the recoil-free fraction of aluminous goethite having the same hyperfine splitting (and probably a fairly similar structure) as the surface iron. Yassoglou and Peterson (1969) found that the room temperature recoilless fraction of iron hydroxide precipitated on the surface of kaolin is substantially greater than that of the pure hydroxide, but did not give a value for it. Whereas the higher f value of *aluminous* goethite compared to the pure mineral may be explained in terms of decreasing bond length (Fysh and Clark, 1982a), no reason for an increase in the f of a surface-deposited phase is immediately apparent. In the present investigation the surface iron represents less than 2% of the spectral area, so that the error in the calculation of the kaolinite

Table 1. Relative contents of hematite and structural and surface iron calculated from fits of 4.2°K Mössbauer spectra.

Kaolin sample	Hematite (%)	Kaolin structural Fe (%)	Surface iron (%)
K1		98	2
K2	28	67	5
K3		98	2
K4		96	4
K5		98	2
K6		99	1

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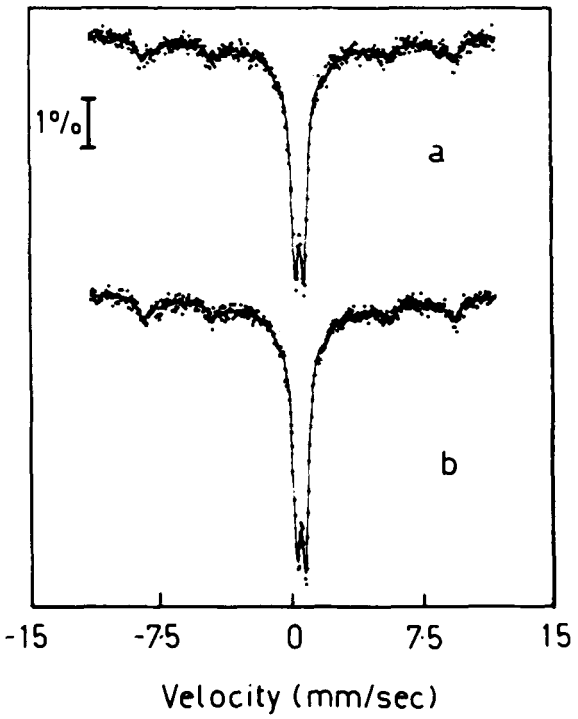

Figure 6. Mössbauer spectra of the two dithionite-bleached clays (a) sample K4 and (b) sample K5 taken at 4.2°K.

structural Fe content is only about 5% for a 20% error in the f value used. Nevertheless, an exact determination of the f of kaolin surface iron is desirable. The value of $f_{4.2°K}$ calculated for kaolinite structural Fe is 0.52 ± 0.06. This is considerably less than the f values measured for iron oxides/oxyhydroxides (Fysh and Clark, 1982a, 1982b), reflecting the comparatively weaker bonding of Fe in the kaolinite structure.

Using an f value of 0.7 for 7% Al-substituted hematite (Fysh and Clark, 1982b) and the value previously assumed for the surface iron, the *relative* concentrations of the Fe phases at the various stages of magnetic cleaning can be calculated (see Table 1). It is difficult to estimate the error associated with the determination of these values, particularly because of the uncertainty in the recoil-free fraction of the surface iron phase, but a *relative* accuracy of $\pm 2\%$ appears reasonable.

Analysis of bleached clays

The spectra of the two dithionite bleached clays, samples K4 and K5, are shown in Figure 6 and are qualitatively very similar to those of samples K1 and K3. The greater intensity of the magnetically split subspectrum due to the surface iron for specimen K4 can be clearly seen, although it only represents a small fraction of the total Fe present (see Table 1). No hematite was detected in any of these four clays, but it

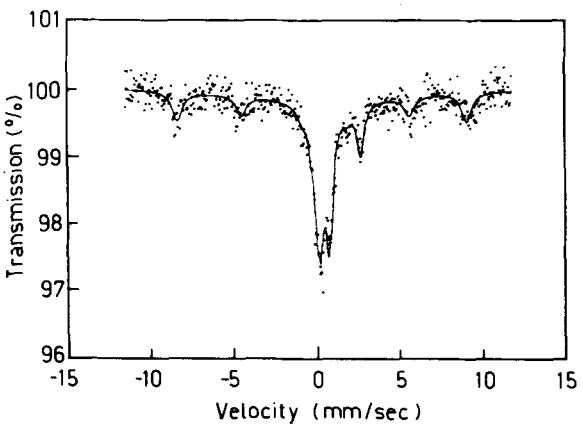

Figure 7. Mössbauer spectrum of sample UW90 at 4.2°K.

can be seen from Figure 6 that the spectral lines of the surface iron are much broader for sample K4, and fitting reveals that the hyperfine splitting of this subspectrum has increased to 501 kOe. The spectral lines of hematite lie between those of the kaolin surface and structural Fe (see Figure 4). While the scatter in the data means that reliable fitting of a third subspectrum corresponding to hematite is not justified for sample K4, the increase in the hyperfine splitting of the surface iron is probably due to the presence of hematite in this specimen, resulting in broad resonance lines.

The centrifugal size separation before magnetic separation and bleaching resulted in a brightness increase of 1 point in the final product, and it appears that the size fraction of kaolin removed in this separation has a higher hematite content than that which remains.

The brightness of the oxalic-acid bleached clay (sample K6) was not determined, but the 4.2°K Mössbauer spectrum of this specimen shows a decrease of about 50% in the surface iron content compared to sample K5 (see Table 1). The other parameters describing the spectrum are very similar to those of sample K5, and the presence of hematite is not indicated. The decreased surface iron content shows that the oxalic acid is more effective in removing the surface iron contaminant than the dithionite bleach step, although the latter method is that which is most commonly employed for kaolin cleaning.

Analysis of samples A88 and UW90 at 4.2°K

The 4.2°K spectrum of sample A88 is very similar to that shown in Figure 6 for sample K4, the dithionite-bleached Weipa kaolin not subjected to centrifugal size separation. Both the relative area and hyperfine splitting of the impurity Fe subspectrum are equal to those of K4, indicating that this clay also contains a small amount of hematite besides the Fe present on the kaolin surface.

The 4.2°K spectrum of sample UW90 is shown in

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Figure 7, and, as at room temperature, the scatter of the data is much greater than for any of the other 4.2°K spectra. The fit to the data consists of a magnetically split subspectrum (545 ± 10 kOe), a relaxed subspectrum to account for the baseline curvature, and two doublets. As was mentioned in the previous paper, the spin-spin relaxation rate for Fe^{2+} is fast enough to preclude the observation of Fe^{2+} paramagnetic hyperfine split spectra. Despite the considerable error associated with fitting the magnetically split subspectrum, this contribution likely arises from paramagnetic ions rather than from hematite (the only iron oxide with a hyperfine splitting in the range quoted). Because of its low Fe concentration, this kaolin should exhibit paramagnetic hyperfine splitting. Also, it has a very high brightness, and is thus unlikely to contain a significant quantity of hematite. No other conclusions regarding possible Fe contaminants can be drawn because of the poor resolution of the magnetic part of the spectrum. The respective isomer shifts (+0.47 ± 0.05 mm/sec and +1.27 ± 0.05 mm/sec) and quadrupole splittings (0.59 ± 0.05 mm/sec and 2.78 ± 0.05 mm/sec) of the Fe^{3+} and Fe^{2+} doublets only exhibit changes from the room temperature values which are consistent with the decrease in measurement temperature.

CONCLUSIONS

The present data indicate that beneficiation of the Weipa kaolin results in substantial brightness increases but produces only minor effects on the clay iron mineralogy. They show also that Mössbauer spectroscopy is particularly suitable for the microscopic study of such effects. Also, the Mössbauer technique has been shown to be capable of comparing the iron mineralogies of various kaolins. Apart from possible studies of the structural role of Fe in kaolinite, it is likely that low temperature Mössbauer measurements may be of considerable value to the optimization of commercial kaolin processing. For example, Bundy and Murray (1973) indicated that maintaining a high Al^{3+} concentration during the washing of kaolin subsequent to chemical bleaching increases the amount of iron removed. They proposed that this effect is due to the fact that Al^{3+} fills the chemically active sites vacated by the Fe, thus preventing recombination with Fe during washing. In the light of the results obtained in the present study concerning the variation of the surface iron content with chemical bleaching it is clear that low temperature Mössbauer measurements would be of great value to the study and optimisation of this sort of iron-removal technology.

ACKNOWLEDGMENTS

This research has been supported by a grant from Comalco Ltd. The advice and assistance of Mr. W. H. Andrews, Mr. R. W. Moyle, and Mr. D. J. Fisher of Comalco are acknowledged. We would also like to thank the Comalco Research Centre for providing the chemical analyses.

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(Received 22 May 1982; accepted 27 January 1983)

Резюме—Мессбауеровские спектры ^{57}Fe исследовались для интерпретации эффектов различных процессов очистки на минералогию каолина из Вайпа в Австралии по содержанию железа. Магнитно отделенная фракция водержала 28% железа в виде гематита, вероятно, вторичного происхождения. Было показано, что начальная центробежна сепарация по размеру дала луьший конечный продукт, а щавелевая кислота была найдена более эффективной для удаления Fe из каолинитовых поверхностей, чем дитионитовый отбеливающий реагент. Мессбауеровские спектры ясно указывают на то, что результатом этих усовершенствований, которые дают значительное увеличение яркости каолинита, являются только незначительные изменения в минералогии глины по содержанию железа. Похожие результаты были получены для двух общедоступных каолинов. [E.G.]

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Resümee—^{57}Eisen-Mössbauerspektren wurden verwendet, um die Auswirkungen unterschiedlicher Reinigungsverfahren auf die Eisen-Mineralogie am Beispiel des Kaolin von Weipa, Australien, zu deuten. Eine magnetisch abgetrennte Fraktion enthielt 28% des Eisens in Form von Hämatit, der wahrscheinlich sekundär entstanden ist. Es zeigte sich, daß eine ursprüngliche Trennung mittels Zentrifuge ein verbessertes Endprodukt liefert. Außerdem ergab sich, daß Fe durch Oxalsäure von der Kaolinitoberfläche besser entfernt werden kann als durch Auslaugung mittels Dithionit. Die Mössbauerspektren zeigten ganz deutlich, daß Maßnahmen, die eine erhebliche Verbesserung des Kaolinglanzes bringen, nur zu geringen Veränderungen bei der Mineralogie des Eisens in den Tonen führen. Ähnliche Ergebnisse wurden für zwei käuflich erhältliche Kaoline erzielt. [U.W.]

Résumé—Des spectres de Mössbauer ^{57}Fe ont été utilisés pour interpréter les effets de différents procédés de nettoyage de la minéralogie du fer d'un kaolin de Weipa, Australie. Une fraction separée magnétiquement contenait 28% de son fer sous forme d'hématite, vraisemblablement d'origine secondaire. On a montré qu'une séparation initiale de taille centrifuge fournissait un produit final amelioré, et l'acide oxalique a été trouvée plus efficace pour enlever Fe de la surface kaolinite que du bleach dithionite. Les spectres Mössbauer montrent clairement que les étapes de bénéficiation qui donnent un accroissement appréciable de la clarté du kaolin ne résultent qu'en des changements mineurs dans la minéralogie de l'argile ferreux. Des résultats semblables ont aussi été obtenus pour deux kaolins disponibles commercialement. [D.J.]

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