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ESR investigation of deferration treatment of iron-rich kaolinite clay from Deopani, Assam, India

P. Sengupta*, N. J. Saikia, D. J. Bharali, P. C. Saikia and P. C. Borthakur

Regional Research Laboratory (CSIR), Jorhat 785 006, India

Kaolin, available at Deopani, Assam, India, is yet to be commercially exploited due to lack of detailed characteristics and appropriate process for beneficiation. The characteristics of the clay, as revealed by chemical, XRD, FTIR and SEM–EDX analyses and beneficiation by physico-chemical methods were reported earlier. The Fe content of the clay could be reduced consid-

erably from a high value of 9.48 to 1.0% by adopting simple beneficiation techniques due to favourable Fe-mineralogical form, but it is difficult to remove the impurities completely. This communication reports the characteristics of the clay and its beneficiated products, as revealed by ESR investigation. The clay contains relatively high amounts of both structural and non-structural iron and minor amount of Mn. The g factors calculated from the ESR signals are used to investigate the effect of the beneficiation techniques employed on structural and non-structural Fe. Magnetic separation and size fractionation yield products with high amount of structural iron. Oxalic acid that acts both as a complexing and leaching agent at relatively low concentration preferentially leaches structural iron, and at higher concentration removal of non-structural iron is enhanced. Increase in temperature initially from ambient condition results in preferential removal of the non-structural iron and thereafter it becomes the same for both forms of iron.

Keywords: Beneficiation, deferration, ESR spectra, kaolinite, structural and non-structural iron.

Many of the physical, chemical and thermal properties of clays are influenced by the presence and nature of impurities¹. Iron, one of the most common impurities in kaolinite clays, may occur as part of the clay structure or as separate Fe-bearing phases. Both the types, termed as ‘structural’ and ‘non-structural’ iron respectively, usually coexist in kaolinite. Structural irons result from isomorphous substitution of both octahedral-Al and tetrahedral-Si in the kaolinite structure, whereas non-structural iron is due to the coatings and discrete iron-bearing phases present in clay^{2,3}.

Industries like ceramic, paper, paint, rubber, plastic, polymer, cosmetics, medicine, insecticide, pesticide, etc. widely use kaolinite clay for various purposes. Presence of iron-bearing impurities in kaolinite is detrimental to its use¹. Several physical and chemical processes like sieving, magnetic separation⁴, selective flocculation⁵, ultrasound cleaning⁶, leaching with chemicals like oxalic and other organic acids^{7,8}, organic acids in the presence of a fermented medium⁹, lixiviant containing microbially-produced oxalic and hydrochloric acid¹⁰, carbohydrates¹¹, EDTA¹², sodium dithionate–H₂SO₄ mixtures^{13,14}, etc. have been employed to lower the iron content of clay. The residual iron after the deferrating treatments may exist either as structural and/or non-structural type^{3,15,16}.

Several kaolin (china clay) deposits have been located in Northeast India, including the one at Deopani, Karbi Anglong district, Assam. None of these deposits have been commercially exploited due to lack of detailed characteristics and appropriate processes for beneficiation. We had earlier reported the location and content of the deposit, characteristics of the clay as revealed by chemical, XRD, FTIR and SEM–EDX analyses and beneficiation

*For correspondence. (e-mail: pinakiajitsengupta@yahoo.com)

by physico-chemical methods to obtain various grades of the clay¹⁷⁻²⁰. The Fe content of clay could be reduced from a high value of 9.48 to 1.0% by adopting simple beneficiation techniques like size separation and oxalic acid leaching due to favourable Fe-mineralogical forms^{17,18}. SEM-EDX analysis revealed that most of the clay particles are coated with white patches containing iron and titanium, and these are not completely removed by oxalic-acid leaching^{19,20}.

ESR spectroscopic technique provides information on the local chemical and crystalline environment of unpaired electrons in the atoms and therefore, can be conveniently employed to detect the structural and non-structural Fe in kaolinite^{3,21}. This communication reports the characteristics of Deopani clay, as such and after beneficiation, as revealed by ESR spectroscopic technique. The g factors calculated from ESR signals are used to investigate the effect of deferration techniques employed on removal of structural and non-structural Fe of the iron-rich kaolinite clay.

Kaolin was collected from the Deopani deposit (lat. 26°14'27" to 26°14'39"N; long. 93°45'54" to 93°46'05"E), Karbi Anglong district, Assam. Representative clay samples were prepared from the bulk clay following the Indian standard method of mixing²². The clay was suspended in water and stirred. The -53 μm fraction was separated by wet-sieving and beneficiated, involving size separation, oxalic acid leaching, etc. A Wet High Intensity Magnetic Separator (WHIMS) was used to separate the nonmagnetic and magnetic fractions of the clay. Details of the methods adopted for beneficiation and characterization of the clay by wet chemical, XRF, XRD and FTIR analysis, SEM-EDX analysis are available in the literature¹⁷⁻²⁰. ESR spectra were recorded by a Varian E-line Century series E-112 X-band EPR spectrometer at room temperature using a microwave frequency of 9.1 GHz, microwave power of 5 mW, field set at 2000 G, scan range 4000 G and modulation frequency of 100 kHz. TCNE marker was used for the determination of g factors. The g_1/g_2 values that are indicative of relative presence respectively, of structural and non-structural iron were calculated by determining the ratio of the amplitudes (in cm) of $g_1 \approx 4.3$ and $g_2 \approx 2$ peaks^{23,24}.

Chemical analysis of the raw clay sample, the -53 μm fraction separated from it and the iron content of some of the fractions, obtained by processing the clay following various methods¹⁸, are presented in Tables 1 and 2. The amplitude ratio of the $g_1 \approx 4.3$ and $g_2 \approx 2$ peaks for structural and non-structural iron respectively, as determined from the ESR spectra, are also included.

Figure 1 shows the ESR spectra of the -53 μm fraction of clay. Two distinct signals in the regions of $g \approx 4.3$ and $g \approx 4.9$, corresponding respectively, to centres I and II in the kaolinite structures are observed. These can be interpreted as Fe^{3+} ions, occupying sites of complete and partial orthorhombic symmetry^{21,23}. The enhanced intensity of

the peak at $g \approx 4.3$, due to the centre I, may be attributed to the low crystallinity of kaolinite²¹. The spectra also show two distinct peaks in the regions of $g \approx 2$ and $g \approx 2.06$, assigned respectively to clusters of Fe^{3+} ions that are present as non-structural Fe-rich phases of the oxide-oxyhydroxy-type coats on the kaolinite surfaces or small heterogeneous inclusions within the framework and to lattice defects within the kaolinite structure³. The peaks at $g \approx 4.3$ and $g \approx 2$ are, therefore, considered as due to structural and non-structural Fe respectively. The structural irons are those resulting from isomorphous substitution in both octahedral-Al and tetrahedral-Si in the kaolinite clay, whereas the non-structural irons are due to the coatings and discrete iron-bearing phases present in the clay. The $g \approx 4.3$ and $g \approx 2$ signals are also termed as due to Fe occupying distorted sites of the crystalline structure and non-distorted sites of the oxy and oxyhydroxy species respectively²⁴. X-ray diffraction study showed that the raw clay from Deopani contains kaolinite and quartz as the major mineral constituents, siderite as the major iron-bearing impurity along with small amounts of mica, goethite and/or hematite^{17,18}. The DTA pattern of the black-coloured impurities, separated from raw clay, also indicates the presence of pyrite¹⁸. XRD and FTIR analysis showed that the -53 μm fraction of the clay is free from quartz, siderite and carbonate-bearing material¹⁸. However, the fraction still contains high amount of iron (Table 1). The spectra also show six-line hyperfine structure in the region of $g \approx 2$, which may be attributed to the presence of very small amount of Mn-bearing impurities in the clay³.

Table 1 shows that for the -53 μm fraction, the value of $g_1/g_2 > 1$. This indicates that the fraction contains relatively high amount of structural Fe compared to non-structural Fe. Substitution of Al and Si in detrital clays by Fe may lead to the formation of chamosite, as indicated below²⁵:

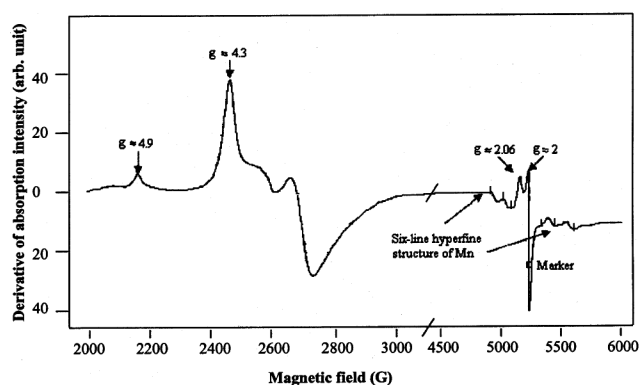
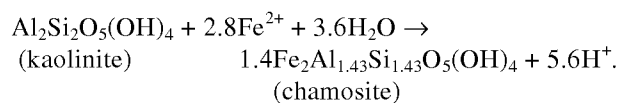


Figure 1. ESR spectrum of -53 μm fraction of the Deopani kaolin, Assam.

Table 1. Oxide content (%) and ESR peak amplitude ratio for iron (g_1/g_2) of the Deopani kaolin, Assam and its fractions

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	CaO	MgO	LOI	g_1/g_2
Raw clay	58.44	19.11	9.48	–	0.218	0.54	0.38	10.98	–
–53 μ m fraction	47.20	35.75	2.86	0.90	0.018	0.17	–	12.23	1.41
–53 μ m (nonmagnetic)	45.04	38.67	1.10	0.70	–	–	–	12.65	1.20
–53 μ m (magnetic)	23.92	33.50	20.94	8.13	0.431	–	–	11.05	–

Table 2. Fe₂O₃ content and ESR peak amplitude ratio for iron (g_1/g_2) of the beneficiated fractions of Deopani kaolin, Assam

Fe ₂ O ₃ : Oxalic acid (M)	Deferration temperature (°C)	Size fraction	% Fe ₂ O ₃	g_1/g_2
1.0 : 0.0	30	Coarse	3.38	1.82
		Medium	2.52	1.38
		Fine	2.21	1.14
1.0 : 0.2	30	Fine	1.17	0.82
	50	Fine	1.04	1.05
	75	Fine	1.00	1.00
1.0 : 0.4	30	Coarse	2.60	1.65
		Medium	1.53	1.39
		Fine	1.01	0.98
1.0 : 2.0	30	Fine	0.95	1.06

Coarse, –53 μ m + 10 μ m; Medium, –10 μ m + 4 μ m, Fine, –4 μ m.

The phase diagram ($\log P_{O_2}$ vs $\log P_{CO_2}$), as reported by Maynard²⁶, shows that chamosite minerals occupy the same O₂ but higher CO₂ range as that of siderite. Similarly, chamosite minerals exist under the same CO₂ but lower O₂ range as that of a combination of pyrite and SO₄²⁻ ions. The presence of siderite, pyrite, CO₃²⁻ and SO₄²⁻ in the raw clay from Deopani, as evidenced by chemical, XRD and FTIR analysis¹⁸ and the acidic soil environment of the Karbi Anglong region²⁷, indicate the possibility of formation of iron-substituted clay minerals.

Although the g_1/g_2 value for the nonmagnetic fraction is less than that of the –53 μ m fraction, it is still higher than 1 (Table 1). The fraction, therefore, contains relatively high amount of structural Fe. SEM–EDX and chemical analyses reveal that the fraction is comparatively free from iron-bearing minerals^{19,20}. Therefore, highly coated clay platelets and other minerals, which are removed as magnetic fraction, contain high amounts of both structural and non-structural Fe, resulting in the reduction of g_1/g_2 value of the nonmagnetic portion.

The g_1/g_2 values of the various deferrated kaolinite samples, obtained by size-separation and oxalic acid leaching, are shown in Table 2 along with their iron contents. In general, for all the samples $g_1/g_2 > 1$, barring a few with values ≈ 1 . The samples, therefore, contain relatively higher amount of structural than the non-structural Fe. The g_1/g_2 values of the coarse, medium and fine fractions, obtained without and with oxalic acid leaching, progressively decrease with size, indicating a decreasing trend in

the relative amount of the structural Fe. SEM–EDX analysis of clay shows that the coating and its iron content decrease in the order: coarse > medium > fine fraction. The coating and the iron content of these fractions decrease considerably on oxalic acid treatment w.r.t. the corresponding untreated fractions. The decreasing order of coating and iron content was also observed within the oxalic acid-treated coarse, medium and fine fractions^{19,20}. The larger size fractions, associated with higher amount of iron, therefore contain higher amount of structural iron, possibly due to enhanced substitution.

The g_1/g_2 values of the coarse, medium and fine fractions decrease on oxalic acid treatment. This indicates that oxalic acid that acts both as complexing agent and leachant, removes structural Fe preferentially in all fractions. The FTIR spectra of the –53 μ m fraction and the coarse, medium and fine fractions separated from it after oxalic acid leaching exhibit only one band at 3653 cm⁻¹, indicating that kaolinite is weakly crystalline in nature (as against crystalline kaolinite that exhibits two bands at 3669 and 3652 cm⁻¹)¹⁸. The relative intensity of the bands at 794 and 754 cm⁻¹ of the –53 μ m fraction clay and the coarse, medium and fine fractions obtained after oxalic acid leaching indicates that it is comparable to dickite-type clay²⁸. Searle and Grimshaw¹ reported that dickite is kaolinite-type clay, where successive layers are displaced in the *b*-direction with shifts alternating between +1/6 and –1/6. Bahrnowski *et al.*³ have reported that in kaolinite with low degree of crystalline order, acid treatment results in removal of structural iron. Wells *et al.*²⁹ have reported in detail, the Fe dissolution rates from Al-substituted hematite particles. The TEM micrographs showed that Al-substituted hematite particles have pseudo-hexagonal platy morphology. Incorporation of Al in hematite particles results in structural defects and incorporation of structural H₂O. Structural water losses occurred in the temperature range of 105 to 700°C. The behaviour of these Al-substituted hematite particles can therefore be assumed to be like that of clay particles. The activation energy for iron dissolution by HCl from these Al-substituted hematite particles is in the range of 66.1–75.5 kJ/mol. For pure hematite particles, the activation energy is in the range of 94.6–97.9 kJ/mol. This is attributed to the difference in metal–oxygen bond energies for Fe³⁺ (390.4 kJ/mol) and Al³⁺ (512.1 kJ/mol), ionic radii of Fe³⁺ (0.0645 nm) and Al³⁺ (0.0535 nm) along with difference in electronegativity and ionic potential of Fe and Al. Such differences result

in increased structural disorderliness into the Al-substituted hematite and consequently lower activation energy for iron dissolution, compared to hematite. The lower activation energy resulted in higher rates of iron dissolution in Al-substituted hematite than that in hematite particles²⁹. Connotation of the words 'structural' and 'non-structural iron', used in clay chemistry, requires to be understood in proper perspective. Structural irons are those that substitute Al and Si in clay structure and have $-O-Al-O-Fe-O-$ or $-O-Si-O-Fe-O-$ type of 'inhomogeneous environment'. On the other hand, non-structural irons are not simply structureless entity. The word 'non-structural' means that these are not in the clay structure, but have structures of their own like that in hematite, goethite, etc. which have a more 'homogeneous environment'. It is therefore easier to remove structural Fe than non-structural Fe by oxalic acid leaching of the iron-rich Deopani clay.

The structural Fe content in the fine fraction initially at Fe_2O_3 : oxalic acid = 1 : 0.2 mol ratio treatment at 30°C, as indicated by the g_1/g_2 values, decreases (Table 2). However, on increasing the oxalic acid concentration further, the g_1/g_2 values of the fine fraction increase. This indicates that increase in acid concentration in the later stage has more pronounced effect on non-structural Fe, thereby resulting in its increased removal. The effect of increasing the deferration temperature was investigated in the fine fraction of the clay at Fe_2O_3 : oxalic acid = 1 : 0.2 mol ratio. The total Fe content of the fine fraction initially decreases on increasing the temperature from 30 to 50°C and becomes almost constant on further increasing the temperature to 75°C. The g_1/g_2 value, however, increases initially and then becomes almost constant. Therefore, the increase in deferration temperature initially removes relatively higher amount of non-structural Fe and then the preference for both the structural and non-structural Fe-removal becomes more or less the same.

The ESR spectra reveal that the $-53 \mu m$ fraction of the Deopani kaolin, Assam contains both structural and non-structural Fe, with the former predominating. It also contains minor amounts of Mn. WHIMS treatment removes considerable amount of highly coated clay platelets and other minerals as magnetic fractions containing both structural and non-structural Fe, resulting in the reduction of g_1/g_2 values of the nonmagnetic fraction. The fraction, however, contains significant amount of structural Fe. The g_1/g_2 values show that the fractions obtained by size-separation and oxalic acid leaching contain relatively high amount of structural Fe. The relative amount of structural Fe, in fractions obtained without oxalic acid leaching, decreases in the order coarse > medium > fine. The larger size fractions, associated with higher amount of iron, contain relatively higher amount of structural Fe, possibly due to enhanced substitution. Oxalic acid, initially up to a certain acid concentration, preferentially removes structural Fe from all fractions. Further increase in the acid

concentration enhances removal of non-structural Fe from the fine fraction. The g_1/g_2 value increases initially and then becomes constant with increase in deferration temperature. Accordingly, on increasing the deferration temperature from 30 to 50°C initially, removal of non-structural Fe in the fine fraction is enhanced. Further increase in temperature to 75°C, however, removes both structural and non-structural Fe in the same ratio. It is easier to remove structural Fe having an inhomogeneous environment than non-structural Fe with a homogeneous environment, from the weakly crystalline, iron-rich Deopani clay.

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Antioxidant activity of *Garcinia indica* (kokam) and its syrup

Akanksha Mishra¹, Mrinal M. Bapat¹,
Jai C. Tilak² and Thomas P. A. Devasagayam^{2,*}

¹Department of Biochemistry, The Institute of Science, Madam Cama Road, Mumbai 400 032, India

²Radiation Biology and Health Sciences Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

***Garcinia indica* (kokam) is an Indian spice, the fruit rind of which is used in cooking, cosmetics and has several medicinal properties. Its syrup is consumed as a soft drink during summer. We have examined the antioxidant activity of aqueous and boiled extracts corresponding to their use in cooking and home remedies, besides the commercial kokam syrup. The assays employed are ORAC, FRAP, ABTS and the ability to inhibit lipid peroxidation in rat liver mitochondria. Kokam syrup and the two aqueous extracts had significant antioxidant effects in the above assays. They have high ORAC values (29.3, 24.5 and 20.3), higher than those reported for other spices, fruits and vegetables. The high antioxidant activity of kokam adds one more positive attribute to its known medicinal properties and hence its use in cooking, home-remedies and as a soft drink may be promoted.**

Keywords: Antioxidant activity, kokam, medicinal properties, syrup.

ANTIOXIDANTS are micronutrients that have gained importance in recent years due to their ability to neutralize free radicals or their actions¹. Free radicals have been implicated in the etiology of several major human ailments, including cancer, cardiovascular diseases, neural disorders, diabetes and arthritis^{2–4}. Due to the recent trends in nutrition towards development of healthy foods in the form of ‘functional foods’, one of the desirable properties in a dietary component is considered to be its antioxidant effect^{5,6}.

Garcinia indica (dried rind known as ‘kokam’) is an Indian spice used in many parts of the country for making several vegetarian and non-vegetarian ‘curry’ preparations, including the popular ‘solkadhi’. The fruits are steeped in sugar syrup to make ‘amrutkokam’, a healthy soft drink to relieve sunstroke, which is popular during summer^{5,7,8}. It is a traditional home remedy in case of flatulence, heat strokes and infections⁷. Many therapeutic effects of the fruit have been described in traditional medicine based on Ayurveda. These include its usefulness as an infusion, in skin ailments such as rashes caused by allergies; treatment of burns, scalds and chaffed skin; to relieve sunstroke; remedy for dysentery and mucous diarrhoea; an appetizer and a good liver tonic; to improve appetite and to allay thirst;

*For correspondence. (e-mail: tpad@apsara.barc.ernet.in)