REMOVAL OF FERRIC IRON FROM IRON-STAINED KAOLINITE

SOMRIT PUTTHUNBUT

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REMOVAL OF FERRIC IRON FROM IRON-STAINED KAOLINITE.

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ABSTRACT

Kaolinite is a raw material for many industrial processes such as paper manufacturing and the ceramics industry which both require material of high whiteness. The yellowness of kaolinite is mainly due to ferric iron compounds. Chemical leaching of kaolinite is one way of brightening and adding value to the raw material. The objective of this study was to determine the most effective chemical leaching agent.

Kaolinite from Ranong, Thailand was prepared as Na-kaolinite using a sodium chloride solution. Na-kaolinite slurries were separately treated with various single acids at room temperature and at 100 ^{0}C. Equimolar(0.2 M) solutions of hydrochloric, nitric, sulfuric, oxalic, tartaric, acetic, ascorbic, citric, formic and ethylenediaminetetraacetic acids (EDTA), were used. Sodium dithionite and desferroxamine were also used. The kaolinite was also treated with pairs of acids consecutively and the brightness index of the treated kaolinite was determined.

All treated kaolinite samples were digested to liquid and the iron content determined by Flame Atomic Absorption Spectroscopy. The treated clay was examined by FTIR Spectroscopy, X-ray diffraction, Electron Spin Resonance Spectroscopy and Scanning Electron Microscopy.

The oxalic acid treatment was found to be best for iron removal, giving a brightness of about 80 %, presumably due to its higher acidity, reducing ability and complexing ability compared to the other organic acids. Consecutive acid treatments were effective only when oxalic acid was used as the first acid.

In all these treatments, the clay structure was not affected in any way.

KEY WORDS: KAOLINITE / FERRIC IRON / REMOVAL / BRIGHTNESS

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การขจัดเหล็กเฟอร์ริกจากเคโอลิไนต์ที่มีเหล็กปนเปื้อน (REMOVAL OF FERRIC IRON FROM IRON-STAINED KAOLINITE)

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บทคัดย่อ

แร่ดินขาวเป็นวัตถุดิบในอุตสาหกรรมหลายประเภทเช่น อุตสาหกรรมกระดาษ และอุตสาหกรรมเครื่องปั้นดินเผา ซึ่งล้วนแต่ต้องการค่าความขาวสว่างที่สูง สาเหตุหลักของความเหลืองของแร่ดินขาวมาจากสารประกอบของเหล็กเฟอร์ริก การล้างด้วยสารเคมีเป็นวิธีหนึ่งในการทำให้มีความขาวสว่างที่มากขึ้นและสามารถเพิ่มมูลค่าของแร่ดินขาวได้

แร่ดินขาวที่ใช้ในการทดลองคือ แร่ดินขาวจากจังหวัดระนอง ซึ่งได้นำมาล้างด้วยสารละลายโซเดียมคลอไรด์ เพื่อเตรียมเป็นสารประกอบโซเดียมของแร่ดินขาว และได้ทำการล้างด้วยกรดความเข้มข้น 0.2 โมลาร์ของกรดไฮโดรคลอริก ไนตริก ซัลฟิวริก ออกซาลิก ทาทาริก แอซิติก ซิตริก ฟอร์มิก และ เอทธิลีนไดเอมินเตตระแอซิติก(EDTA) รวมถึงโซเดียมไดไทโอไนต์ และ เดสเฟอร์รอกซามีน ซึ่งได้ทำการทดลองทั้งที่อุณหภูมิห้องและที่อุณหภูมิ 100 องศาเซลเซียส รวมถึงได้ทำการล้างติดต่อกันด้วยกรดสองชนิด แล้วนำมาวัดค่าความขาวสว่างของแร่ดินขาวที่เปลี่ยนแปลงไป

แร่ดินขาวที่ทำการล้างแล้วจะมาทำการย่อยให้อยู่ในรูปสารละลาย เพื่อหาปริมาณเหล็กโดยเทคนิคอะตอมิกแอบซอร์พชันสเปกโตรสโกปี และได้นำแร่ดินขาวมาวิเคราะห์ด้วยวิธีอินฟราเรดสเปกโทรสโคปี เทคนิคการเลี้ยวเบนรังสีเอกซ์ อิเล็กตรอนสปินเรโซแนนซ์สเปกโทรสโกปี และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด

ในการศึกษาพบว่าสารละลายกรดออกซาลิก สามารถเพิ่มค่าความขาวสว่างและสามารถล้างปริมาณเหล็กออกได้มาก เนื่องจากมีค่าความเป็นกรดที่สูง เกิดคอมเพลกซ์ได้ดี รวมถึงเป็นตัวรีดิวซ์ที่ดี เมื่อเปรียบเทียบกับกรดอินทรีย์ตัวอื่น ๆ การล้างด้วยกรดสองชนิดต่อเนื่องกันให้ผลดีเฉพาะการทดลองที่มีกรดออกซาลิกอยู่ร่วมด้วยและเป็นกรดชนิดแรกที่ใช้ และในทุกการทดลองล้างแร่ดินขาว โครงสร้างของแร่ดินไม่มีการเปลี่ยนแปลง

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LIST OF ABBREVIATIONS

Å	Angstrom unit
°C	Degree Celsius
CEC	Cation exchange capacity
d_{hkl}	The true lattice spacing for planes hkl
XRD	X-ray diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning electron microscope
g	Gram
M	Molarity
%	Percentage
cm	Centimeter
nm	Nanometer
mL	Milliliter
min	Minute
mT	Milliteslar

THE RELEVANCY OF THE RESEARCH WORK TO THAILAND

Kaolinite is a raw material for many industries and is abundant in Thailand. For most modern industrial applications kaolinite must be extensively refined and processed to enhance certain important commercial characteristics. One of the most important specifications for kaolinite is its brightness. The presence of red to yellow pigments mainly comes from ferric oxide. The study of ferric iron removal from kaolinite is therefore useful in upgrading the raw material.

CHAPTER I

INTRODUCTION

Clay minerals are the most abundant mineral on the surface of the earth. They are present in almost all-sedimentary rocks, the outcrops of which cover about 75 percent of the land surface of the earth and they are an important component in most soil [1].

Clay minerals are hydrous aluminum silicates (crystalline materials) and are classified as phyllosilicates or layered silicates. The particle size is less than 2 microns. There is considerable variation in chemical and physical properties within this family of minerals, but most have in common platy morphology and perfect (001) cleavage, a consequence of their layered atomic structures.

1.1 Classification

The classification of clay minerals has been discussed for many years. At the present time, there is still considerable difference of opinion regarding the proper basis for a satisfactory classification. For example, it frequently is impossible at the present time to determine whether a given clay mineral, which may occur intimately mixed with another mineral, is dioctahedral or trioctahedral. Similarly, the polymorphic form of the mica constituent in a complex clay-mineral assemblage frequently cannot be determined.

Many different classifications have been suggested; one example will be mentioned here. In 1991, The Clay Minerals Society (CMS) suggested the classification scheme for the phyllosilicates shown in Tables 1.1 and 1.2. Layered silicate minerals are classified on the basis of the structural and chemical characteristics. Structural characteristics include, for example, the type of layer or linkage configuration (for modulated layer silicates). Chemical characteristics include both the magnitude of net layer charge (χ) per formula unit and the type of interlayer material.

(a) Planar hydrous phyllosilicate

The planar hydrous phyllosilicate minerals (Table 1.1) are arranged in seven groups according to

(1) the type of silicate layer present (1:1 or 1:2)
(2) the magnitude of the net layer charge (χ) per formula unit
(3) the interlayer material that compensates the layer charge

Each group is divided into subgroups on the basis of the octahedral character (dioctahedral or trioctahedral with 2.5 cations as the boundary). Species are distinguished by different compositions or, for the kaolin minerals, by different layers (nacrite) or octahedral vacancy (kaolinite, dickite) sequences along *z*.

(b) Non-planar hydrous phyllosilicates

Modulated layer silicates are defined as those minerals in which there is a periodic perturbation to the basis silicate structure. The simplest classification scheme for non-planar phyllosilicate (Table 1.2) can be derived by considering the nature of the periodicity and the relationship of the perturbation to the basis 1:1 or 1:2 structure. Species are distinguished primarily by both different compositions and further structural variations with the subdivisions.

Rolled forms, such as coils and spheroids, are probably not periodic within the layers over the entire extent of the crystal because of a continuously varying and non-periodic radius. However, these structures clearly do have a periodicity at the unit cell level. In contrast, modulated layer silicates are ideally periodic within the layers. The distinction, therefore, separates Table 1.2 into two parts.

Table 1.1 Classification of planar hydrous phyllosilicates [2]

Layer type	Interlayer material[1]	Group	Octahedral character	Species
1 : 1	None or H_2O only (x~0)	Serpentine-kaolin	Trioctahedral	Lizardite, berthierine, amesite, cronstedtite, nepouite, kellyite, fraipontite, brindleyite
			Dioctahedral	Kaolinite, dickite, nacrite, halloysite (planar)
			Di-trioctahedral	Odnite
2 : 1	None (x~0)	Talc-pyropyllite	Trioctahedral	Talc, willemseite, kerolite, pimelite
			Dioctahedral	Pyrophyllite, ferripyrophyllite
	Hydrated exchangeable cations (x~0.2-0.6)	Smectite	Trioctahedral	Saponite, hectorite, sauconite, stevensite, swinefordite
			Dioctahedral	Montmorillonite, beidellite, nontronite, volkonskoite
			Trioctahedral	Trioctahedral vermiculite
	Hydrated exchangeable cations (x~0.6-0.9)	Vermiculite	Dioctahedral	Dioctahedral vermiculite
			Trioctahedral	Biotite, phlogopite, lepidolite, etc.
	Non-hydrates monovalent cations (x~0.6-1.0)	True (flexible) mica	Dioctahedral	Muscovite, illite, glauconite, celadonite, paragonite, etc.
			Trioctahedral	Clintonite, kinoshitalite, bityitite, anandite
	Non-hydrated divalent cations (x~1.8-2.0)	Brittle mica	Dioctahedral	Magarite
			Trioctahedral	Clinochlore, chamosite, pennantite, nimite, baileychlore
	Hydroxide Sheet (x=variable)	Chlorite	Dioctahedral	Donbassite
			Di-trioctahedral	Cookeite, sudoite
2 : 1	Regularly interstratified (x=variable)	Variable	Trioctahedral	Corrensite, aliettite, hydrobiotite, kulkeite
			Dioctahedral	Rectorite, tosudite

[1] x is net layer charge per formula unit.

Table 1.2 Classification of non-planar hydrous phyllosilicates [2]

Layer type	Modulated Component	Linkage configuration	Unit layer, c sin βvalue	Traditional affiliation	Spicies
A. Modulated structure					
1 : 1 layer	Tet.sheet	Strips	7 Å	Serpentine	Antigorite, Bemenitite
		Islands	7 Å	Serpentine	Greenalite, caryopilite, pyrosmalite, Manganpyrosmalite, feropyrosmalite, Friedelite, mcgillite, schallerite, nelenite
		Others		None	None
2 : 1 layer	Tet.sheet	Strips	9.5 Å	Talc	Minnesotaite
			12.5 Å	Mica	Ganophyllite, eggletonite
		Island	9.6 – 12.5 Å	Mica/complex	Zussmanite, parsettensite, stilpnomelane, Ferrostilpnomelane, ferristilpnomelane, Lennilenapeite
		Others	12.3 Å	None	Bannisterite
			14 Å	Chlorite	Gonyerite
	Oct.Sheet	Strips	12.7 - 13.4 Å	Pyribole	Sepiolite, loughlinite, falcondoite, palygorskite, yofortierite
B. Rolled and Spheroidal structure					
1 : 1 layer	None	Trioctahedral	-	Serpentine	Chrysotile, pecoraite
		Dioctahedral	-	Kaolin	Holloysite (non planar)

1.2 Structure of the Clay Minerals

The principal building elements of clay minerals involve two structural units. One unit consists of two sheets of closely packed oxygen or hydroxyl in which aluminum, iron, or magnesium atoms are embedded in octahedral coordination (Figure 1.1). When aluminum is present, only two-thirds of the possible positions are filled to balance the structure, which is the gibbsite structure and has the formula $Al_2(OH)_6$. When magnesium is present, all the positions are filled to balance the structure, which is the brucite structure and has the formula $Mg_3(OH)_6$.

The second unit is built of silicate tetrahedrons. The silica tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$ (Figure 1.2). The tetrahedrons are arranged so that the tips of all of them point in the same direction, and the bases of all tetrahedrons are in the same plane.

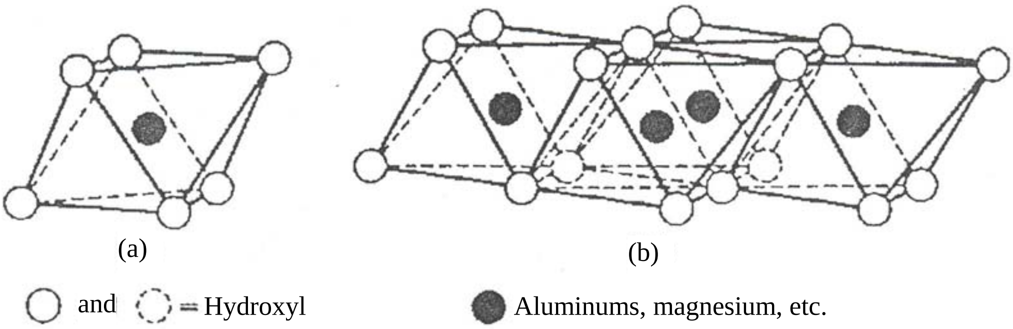


Figure 1.1 Diagrammatic sketch showing (a) a single octahedral unit and (b) the sheet structure of the octahedral units.

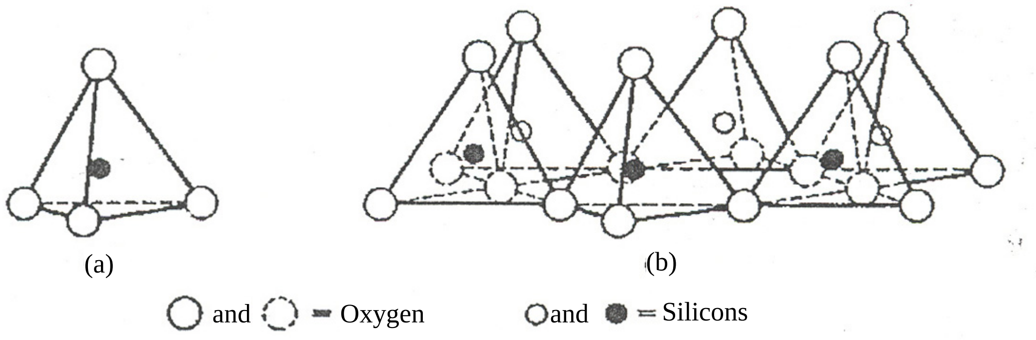


Figure 1.2 Diagrammatic sketch showing (a) a single silica tetrahedron and (b) the sheet structure of silica tetrahedrons arranged in hexagonal network.

1.2.1 Kaolinite [$Si_4Al_4O_{10}(OH)_8$]

The structure of kaolinite was first suggested in general outlines by Pauling[3]. It was worked out in some detail by Gruner [4] and later revised by Brindley and his colleagues [5,6]. The structure of kaolinite was studied in detail by Weaver [7], Newnham [8], Brindley and Nagahira [9], Zvyagin [10], Drits and Kashaev [11], Brindley [12], Radostovich [13], and Bailey [14], and the following statements are taken from their work which has shown that the structure diagrammatically illustrated in Figure 1.3 is modified substantially by distortion in the lattice.

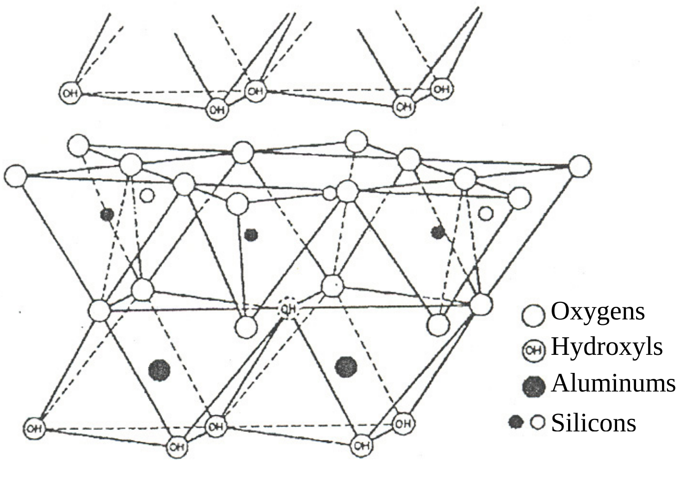


Figure 1.3 Diagrammatic sketch of the structure of the kaolinite layer.

Kaolinite is a 1:1 layered clay composed of single silica tetrahedral sheet and single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer (Figure 1.3). All the tips of the silica tetrahedrons point in the same direction and toward the center of the unit made by the tetrahedral and octahedral sheets.

In the layer common to the octahedral and tetrahedral sheets, two-thirds of the atoms are shared by the silicon and aluminum, and then they become O instead of OH. Only two-thirds of the possible positions for aluminum in the octahedral sheet are filled, and there are three possible planes of regular population of the octahedral layer with aluminums. The aluminum atoms are considered to be so placed that two aluminums are separated by an OH above and below, thus making a hexagonal distribution in a single plane in the center of the octahedral sheet. The OH groups are placed so that each OH is directly below the perforation of the hexagonal net of oxygen in the tetrahedral sheet.

The forces that keep the kaolinite layers together are believed to be the summation of Van der Waals attractive forces, hydrogen bonding between adjacent layers and electrostatic interactions due to net fractional charges of opposite sign on each basal surface, with the main contribution coming from the electrostatic term [15]. With this in mind, the driving force for intercalation involves the “solvation” of the dipolar kaolinite layers with the intercalating agent.

The mineral is triclinic, with the lattice parameters given in Table 1.3. Newnham [8] recomputed the parameters by a systematic least-squares method, employing only those reflections having single indices. His results are in substantial agreement with those published by Brindley and Robinson [5] for a triclinic unit cell, which has $d_{001}=c(1-\cos^2\alpha-\cos^2\beta)^{1/2}=7.15$

Table 1.3 Lattice parameters of kaolinite

	Newnham [8]	*Brindley and Robinson [5]*
a	5.139 ± 0.014 Å	5.15 Å
b	8.392 ± 0.016 Å	8.95 Å
c	7.371 ± 0.019 Å	7.39 Å
α	91.6° ± 0.2°	91.8°
β	104.8° ± 0.2°	104.5 - 105°
γ	89.9° ± 0.1°	90°

Newnham and Brindley's [16] analysis of dickite showed that the departure from ideal geometrical arrangements takes the form of distortions, mainly of rotations of Si-O tetrahedrons, which are alternately left-handed and right-handed rotations, and a shortening of the shared edges of Al-O(OH) octahedrons (Figure 1.4).

Zvyagin [10] studied the structure of kaolinite by electron diffraction and found the following parameters: a=5.13 Å, b=8.89 Å, c=7.25 Å, α=91.40°, β =104.40°, γ=90°. He also reached the following conclusions: Relative to the positions that correspond to closest packing of anions, the lower and upper bases of the octahedrons are rotated through angles corresponding to 3 and 5°, and the bases of the tetrahedrons, on an average, through 20°. The common edges of the octahedrons are shortened, and the octahedrons as a whole are somewhat flattened. The aluminum atoms are displaced toward the lower OH bases and the silicon atoms toward the bases of the tetrahedrons; hence the atoms of the bases of the polyhedrons do not lie in one plane and are of several different z coordinates. The closest atoms in successive layers are grouped in pair (O-OH) which, however, differ somewhat in their length.

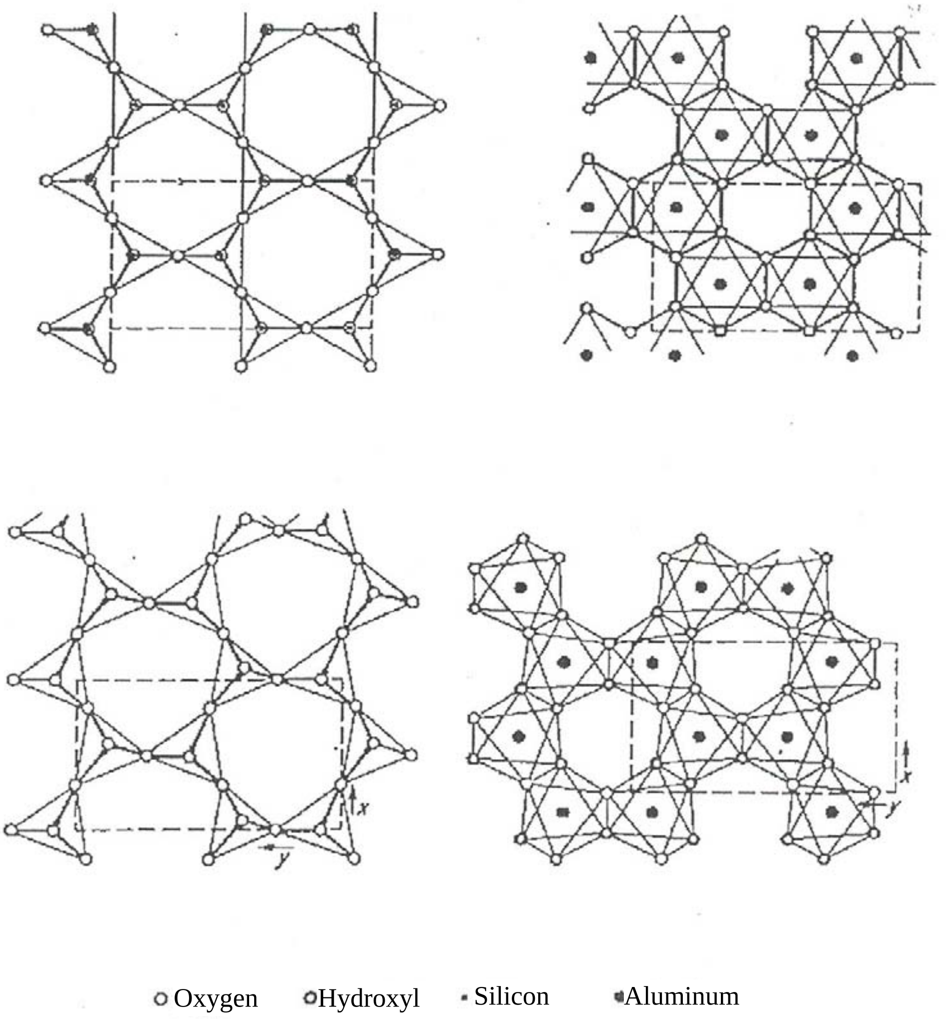


Figure 1.4 Tetrahedral and octahedral configurations in kaolinite minerals. Broken lines show the unit -cell boundary. (After Brindley [12])

1.3 Properties of Clay Minerals

The clay minerals have many important properties that influence their behavior, such as ion exchange, interaction with water, thermal decomposition, interaction with organic molecules, solubility in acids and alkalis and optical characteristics. Some properties will be discussed.

1.3.1 Ion Exchange

Clay minerals have the property of sorbing certain anions and cations and retaining these in an exchangeable state; i.e., they are exchangeable for other anions or cations by treatment with such ions in an aqueous solution. The exchangeable ions are held around the outside of the silica-alumina clay mineral structure units, and the exchange reaction generally does not affect the structure of the silica-alumina packet.

The ion exchange capacity is measured in milliequivalents or millimoles per gram or, more frequently, per 100 grams. More information is available regarding cation exchange than anion exchange.

a) Cation Exchange

The range of the cation exchange capacity (CEC) of the clay minerals is given in Table 1.4

Table 1.4 Cation exchange capacities, in milliequivalents per 100 grams [17]

Kaolinite	3-15
Halloysite.2H_2O	5-10
Halloysite.4H_2O	10-40
Montmorillonite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Sepiolite-Attapulgite	20-30

It follows from the consideration of the factors influencing cation exchange capacity that there is no single capacity value that is characteristic of a given group of clay minerals.

The clay minerals are not the only component of clay materials that have cation exchange capacity. All inorganic materials of extreme fineness have a small cation exchange capacity as a result of broken bonds around their edges. This capacity increases as the particle size decreases, but even with the small size in which nonclay minerals occur in clays the exchange capacity is generally insignificant.

Way's studies [18] of cation exchange capacity phenomena led to a conclusion that the exchanging power of the common ions increased in the following order: $Na^+ < K^+ < Ca^{2+} < Mg^{2+} < NH_4^+$. This means, for example, that in general Ca^{2+} will more easily replace Na^+ than Na^+ will replace Ca^{2+}. As the cation exchange reaction was studied, it became obvious that there was no single universal replaceability series. The series varied depending on the experimental condition, on the cations involved, and on the kind of clay materials.

b) Anion Exchange

Investigation of anion exchange reaction is very difficult, because of the possibility that the clay minerals will decompose in the course of the reaction. Thus, in studies of the adsorption of phosphate by kaolinite there has been considerable argument as to whether many of the results observed are due to adsorption, to replacement of hydroxyl ions in the kaolinite by phosphate ions, or to reaction between the phosphate and alumina produced by some destruction of the kaolinite lattice taking place during the reaction. Table 1.5 gives the anion-exchange capacity for some of the clay minerals.

Table 1.5 Anion exchange capacities, in milliequivalents per 100 grams [19]

Montmorillonite, Geisenheim	31
Montmorillonite, Wyoming	23
Beidellite, Unterrupsroth	21
Nontronite, Untergriesbach	20
Nontronite, Pfreimdtal	12
Saponite, Groschlattengrum	21
Vermiculite, South Africa	4
Kaolinite (colloidal)	20.2
Kaolinite, Melos	13.3
Kaolinite, Schnaittenbach	6.6

Wey [20] pointed out that adsorption of anions is not comparable to the adsorption of cation because of the greater dependence on the nature of the anion than cation and on pH. In cation-exchange experiments with kaolinite, Weiss [21] found that polyvalent cations may act like monovalent ions and may bind an equivalent amount of anions on the surface of the particle; that is, one of the valences is tied to the kaolinite lattice and the others are free for union with anions.

1.3.2 Interaction with Water

This topic is concerned with water which can be held by clay materials only at relatively low temperature and which is driven off by heating to about 100° to 150°C. The water lost at such temperatures may be classed in three categories:

(1) the water in pores, on the surfaces, and around the edges of discrete particles of the minerals composing clay materials
(2) in the case of vermiculite, montmorillonte, and the hydrated form of halloysite, the interlayer water between the unit silicate layers of these minerals which causes their swelling and expansion characteristics
(3) in the case of sepiolite-attapulgite minerals, the water within the tubular openings between the elongated structural units

Water of type (1) requires generally very little energy for its removal, and drying at temperatures only a little above ordinary room temperature is adequate for its substantially complete elimination. Water of type (2) and (3) requires definite energy for its complete removal. In the case of the hydrated form of halloysite, drying at room temperature is adequate to remove most of the interlayer water, but higher temperatures are required for total removal. The rate of removal of the interlayer water increases as the applied temperature increases. In the case of halloysite, the reaction is not reversible, and the hydrated mineral ordinarily cannot be formed again.

Hendricks and Jefferson [22] have suggested the configuration of the interlayer water between the unit silicate layers, illustrated in Figures 1.7 and 1.8; it is based on the orientation of water molecules with a structure tied to the configuration of the oxygens or hydroxyls in the basal surface layers of the unit cells of the clay minerals. A water layer composed of water molecules joined into hexagonal groups of an extended hexagonal net.

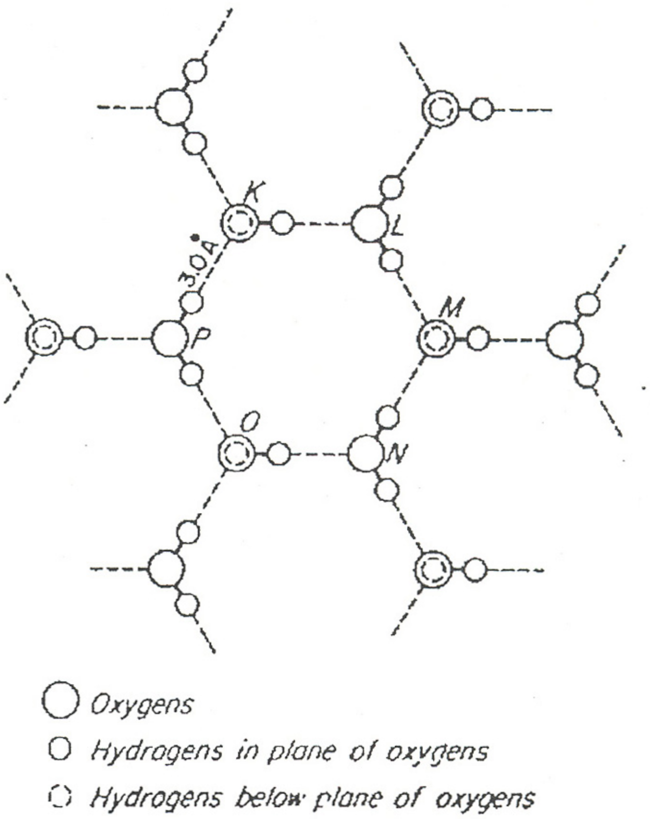


Figure 1.5 Arrangement of oxygens and hydrogens in the water net, after Hendricks and Jefferson [22].

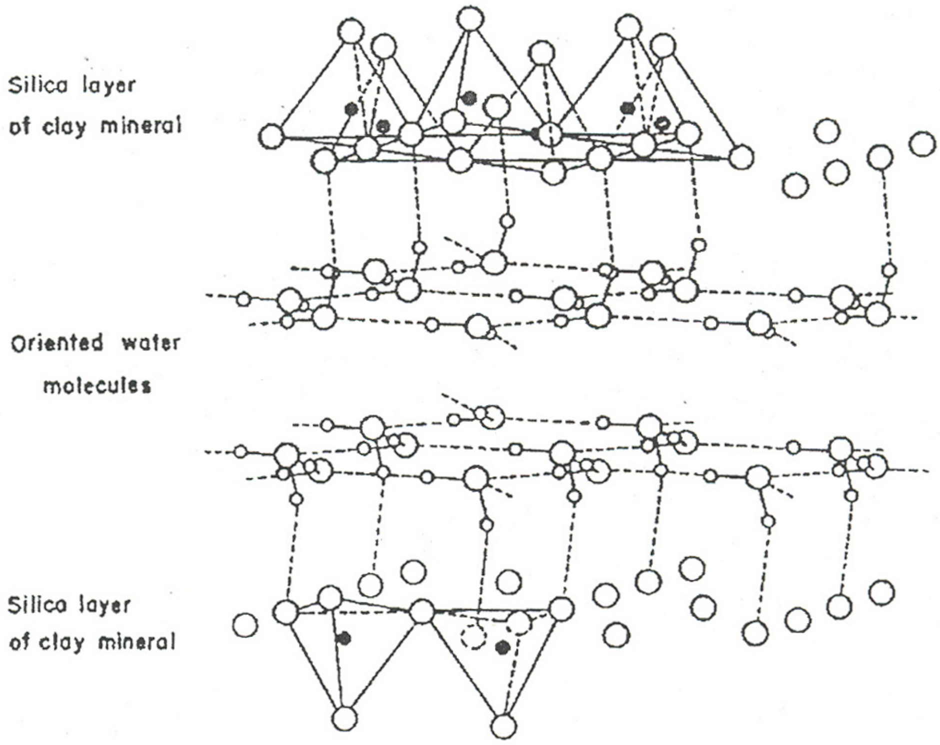


Figure 1.6 Configuration of the water net proposed by Hendrick and Jefferson [22] showing the binding through hydrogens to the adjacent clay mineral surface.

1.3.3 Thermal Decomposition [23]

The thermal decomposition of the kaolin group has attracted a good deal of attention. It has been known that after the removal of adsorbed water at about 105°C, kaolin decomposes at about 450°C, to form *metakaolin*:

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \xrightarrow{450°C} \underset{\text{metakaolin}}{Al_2Si_2O_7} + 2H_2O \qquad \ldots\ldots\ldots \quad (1.1)$$

At 1000 °C, a silicon-alumina spinel ($2Al_2O_3.3SiO_2$) was formed. This compound then loses silicon by a progressive diffusion of Si ions from the lattice, forming a mullite-like compound ($Al_2O_3.SiO_2$), at an intermediate stage, and by further loss of silica, true mullite ($3Al_2O_3.2SiO_2$), is formed. The entire process may therefore be represented by the following chemical equations:

$$\underset{\text{metakaolin}}{2[Al_2Si_2O_7]} \xrightarrow{925°C} \underset{\text{silicon-aluminum spinel}}{2Al_2O_3.3SiO_2} + SiO_2 \qquad ……….(1.2)$$

$$\underset{\text{silicon-aluminum spinel}}{2Al_2O_3.3SiO_2} \xrightarrow{1100°C} \underset{\text{pseudo-mullite}}{2[Al_2O_3.SiO_2]} + SiO_2 \qquad ……….(1.3)$$

$$\underset{\text{pseudo-mullite}}{3[Al_2O_3.SiO_2]} \xrightarrow{1400°C} \underset{\text{mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{cristobalite}}{SiO_2} \qquad ……….(1.4)$$

In the case of halloysite, heating to temperatures of the order of 60° to 100°C causes an irreversible dehydration to develop, and result in a substantial reduction in plasticity in the $2H_2O$ form.

1.4 Method of Removal of Iron from Kaolinite

Iron in kaolinite causes the red to yellow pigmentation noticed due to the associated oxides, hydroxides and hydrated oxides form such as hematite (red), maghemite(reddish brown), goethite(brownish yellow), lepidocrocite(orange), ferrihydrite(brownish red), etc., which declines in brightness with increasing iron content. Quantities as low as o.4% of ferric iron may be sufficient to impart color to the deposit. A brightness of 79 – 83.5 % is required for filler clay and 83.5-85.5 % for coating clay [24]. Removal of these ferric-associated oxides becomes imperative to make the material more value-added.

The methods of iron removal can be classified as physical or chemical methods or both and involve four techniques.

1.4.1 High Intensity Magnetic Separation

Clay slurry is allowed to flow through a magnetic field. Gradient intensity superconducting magnetic separation is used. The separated iron is usually in a discrete fine form.

1.4.2 Selective Flocculation

A clay slurry is stirred in selective media; starch is most successfully use. The iron oxide is absorbed on a polysaccharide in the solution phase. The solid/liquid phase is then separated.

1.4.3 Froth Flotation

Froth flotation is usually used in mineral mining. It is a process for concentrating the metal-bearing mineral in an ore. Froth flotation of kaolinite is also done. Kaolinite is grounded to a fine powder and mixed with water, frothing reagents, and collecting reagents. When air is blown through the mixture, kaolinite particles cling to the bubbles, which rise to form froth on the surface. The unwanted material (also iron oxide) settles to the bottom. The froth is skimmed off, and the water and chemicals are distilled or otherwise removed, leaving a clean concentrate.

The method that used to combine with froth flotation is a gravity separation which is a physical process where .The separation of particles is based on the density difference of the material whereas the froth flotation is a surface-based on the difference in the surface hydrophobicity of materials.

The combination of these two methods is useful in special application in which neither process alone can affect an adequate separation which cal a cyclonic flotation column (CFC). The CFC mostly use in coal and mineral process [25].

1.4.4 Chemical Leaching Method

The clay slurry was stirred in solutions of various concentrations, pHs and temperatures. The single or mixture solutions were used. The leaching solutions most used nowadays are those of strong reducing agents, having high acidity and complexing ability.

CHAPTER II
LITERATURE REVIEW

The presence of iron oxides in kaolinite has detrimental effects on the color of the clay thus greatly lowering its market value. The study by Stoch [25] showed that iron oxides are adsorbed on the surface of kaolinite that is proportional to the surface area of kaolinite.

The physical method was the first to separate it. Schultz [26], Hughes [27], Russel [28] and Shoumkov [29] use magnetic separation to remove iron in different medium. The flocculation method was used by Kitchner [30].

However those two methods can leach out on some iron oxides, usually fine articles. The chemical leaching was the other method to use. Some reagent such as sodium dithionite, sodium hypochlorite and sulfur dioxide were use by Conley and Lloyd [31] but there is not effective because sodium and sulfite cannot reduce and eliminate all the iron present in different form, not environmentally acceptable.

The uses of both physical and chemical methods were use. The chemical method consist of leaching with mineral acid and treatment with reducers, such as sodium dithionite plus aluminium sulphate, sulphur dioxide plus aluminium powder and sulphur dioxide plus zinc powder were also used [32,33]. These methods are usually suitable for achieving a high content of iron removal but, at the same time, they are more expensive, the conditions are very complicated and not environmentally acceptable.

Heterotrophic microbial leaching has been studied for many industrial minerals. Groudev [34] demonstrates that iron could be removed from sand by using microbial leaching. This group also demonstrated microbial removal of iron from clays and improvement of kaolin and ceramic properties via the action of metabolic products [35]. Aspergillus niger which create citric acid and oxalic acid in its metabolism was use in fermentate media to leaching out of iron by Mesquita [36].

Chlorination was use in fluidized fix bed to remove ferric by Brin [37] and about 82% of iron was removed.

EDTA was the most selected chemical substance used to remove too but it is not much effective in kaolinite [38].

1-Hydroxyethane-1,1-diphosphonic acid(HEDPA), L-ascorbic acid,oxalic acid, sodium dithionite, sodium formaldehydesulphoxylate(SFS) are potential reagents for ferric iron dissolution [31,39].

Oxalic-sulfuric mixture acid has been used for the production of industrially significant kaolin [40-44].

Ambikadevi and Gopalakrishna [45] have use a Full Factorial Design with sucrose-sulfuric acid and dithionite-sulfuric acid mix solution in iron dissolution.

Acetic, formic, citric, tartaric, L-ascorbic and succinic acid were used to remove iron by Ambikadevi [46] to be an environmental friendly method.

All chemical leaching methods in iron dissolution do not affect the kaolinite structure.

CHAPTER III
OBJECTIVES

The purpose of this study is firstly to attempt remove ferric iron that presumably reduce the brightness of kaolinite. Secondly, the study arises to compare several organic acids and compounds in removing iron at room temperature and at 100 ^{o}C. Quantitation of iron in untreated and treated kaolinite stage was done by flame atomic absorption spectroscopy. The brightness of each sample was also determined by the brightness meter.

X-ray diffraction, FTIR spectroscopy, electron spin resonance (ESR) and scanning electron microscopy (SEM) were used to study structure of kaolinite before and after the treatment.

CHAPTER IV
MATERIALS AND METHODS

4.1 Raw Materials

Kaolinite

The kaolinite used was from Ranong, Thailand and supplied by Banpu Public Co., Ltd. The particle size range was < 45 μm (365 mesh). The chemical composition and specification, as analysed by Banpu Research and Development Facilities are list in Table A1 (Appendix A). The scanning electron micrograph of Banpu kaolinite is shown in Figure 4.1.

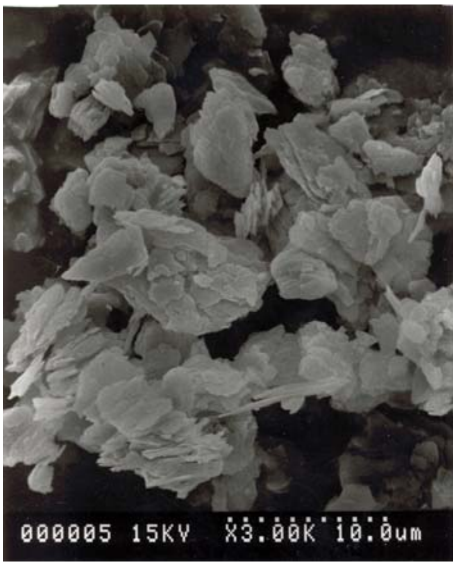


Figure 4.1 Scanning electron micrograph of Banpu kaolinite

4.2 Chemicals

The chemicals and reagents used in this work were analytical grade and purchased from various sources as shown in Table 4.1.

Table 4.1 Chemicals and reagents

Chemicals	Supplier
Hydrochloric acid (36.5-38%)	J.T. Baker(Phillipsburg, USA)
Nitric acid (65%)	Merck (Darmstadt, Germany)
Sulfuric acid (98%)	Merck (Darmstadt, Germany)
Oxalic acid (>99%)	Merck (Darmstadt, Germany)
Tartaric acid	Merck (Darmstadt, Germany)
Acetic acid(100%w/w)	J.T. Baker(Phillipsburg, USA)
Ascorbic acid (>99%)	Merck (Darmstadt, Germany)
Citric acid (>99%)	Fluka (Switzerland)
Formic acid	Fluka (Switzerland)
Sodium dithionite	Merck (Darmstadt, Germany)
Desferroxamine	Zuellig(Switzerland)
Ethylenediaminetetraacetic acid	Merck (Darmstadt, Germany)
Hydrofluoric acid (48%)	Merck (Darmstadt, Germany)

4.3 Instruments

The instruments used in this investigation are listed in Table 4.2

Table 4.2 Instruments used in this investigation.

Instruments	Manufacturer & Model
Flame Atomic Absorption Spectrophotometer[1]	Perkin-Elmer model 3100
Microwave digestion system[1]	Milestone model MLS-1200 MEGA
Brightness Meter[2]	Elrepho data color model 2000
Powder x-ray Diffractrometer (PXRD)[3]	Bruker model D8 advance
Scanning Electron Microscope (SEM)[1]	Hitachi model 2500
Fourier Transform Infrared (FT-IR) Spectrometer[3]	Perkin-Elmer system 2000
Electron Spin Resonance spectrometer(ESR)[4]	JEOL JES-RE 2X[2]

[1] Central of Instrument Facilities, Mahidol University

[2] Department of Science Service, Ministry of Science and Technology

[3] Department of Chemistry, Faculty of Science, Mahidol University

[4] Scientific and Technological Research Equipment Center, Chulalongkorn University

4.4 Preparation of Na-kaolinite

The kaolinite sample was converted to Na-kaolinite by soaking in a sodium chloride solution (0.1M), stirring for 1 hour, filtering and washing twice with distilled water. After washing, Na-kaolinite was heated at 100 ^{o}C in an oven overnight. The dried Na-kaolinite was stored in a plastic bottle.

4.5 Methods of Removal of Ferric Iron

4.5.1 Single Acid Treatment

20% Slurries of Na-kaolinite slurry were separately treated with various acids at room temperature for 2 hours. Equimolar (0.2 M) solutions of hydrochloric, nitric, sulfuric, oxalic, tartaric, acetic, ascorbic, citric, formic and ethylenediaminetetraacetic acids (EDTA), were used. Sodium dithionite and desferroxamine were also used. All treatments were repeated again in 100 ^{o}C.

4.5.2 Consecutive Acid Treatment

20% Slurries Na-kaolinite were consecutively treated with two acids at room temperature for 2 hour each reagent. Equimolar (0.2 M) solutions of acids in table 4.3 were used. All treatment conditions were repeated at 100 ^{o}C.

Table 4.3 Acids used in consecutive acid treatment.

First acid	Second acid
Oxalic	Ascorbic
Ascorbic	Oxalic
Oxalic	Formic
Formic	Oxalic
Oxalic	Tartaric
Tartaric	Oxalic
Acetic	Ascorbic
Ascorbic	Acetic
Oxalic	Acetic
Acetic	Oxalic

4.6 Quantitation of Ferric Iron

4.6.1 Microwave Digestion

A Milestone microwave digestion system was equipped with MLS-1200 MEGA plus EM-45 Exhaust Module for operations with Microwave digestion rotor (MDR). The MDR consists of 6 vessels.

Approximately 0.20xx g of kaolinite was weighed accurately fill into PTFE vessels. 2.5 mL of hydrochloric acid, 2.5 mL of concentrated nitric acid and 4 mL of hydrofluoric acid were added to each vessel. The sample vessels and a reagent blank vessel were sealed and digestion was begun using the heating program in table 4.4.

Table 4.4 Operating parameters of microwave digestion system.

Step	Power (watts)	Time (min)
1	250	5
2	400	5
3	500	10
vent	0	5

4.6.2 Flame Atomic Absorption Spectroscopy

Ferric iron in solutions from microwave digestion was determined in the flame atomic absorption spectrometer using standard conditions for iron analysis (248.3 nm with air-acetylene flame gas).

4.7 Methods of Characterization

4.7.1 Brightness Measurement

The percentage brightness was measured by reflectance of light at 475-nm compare with MgO (100% brightness index).

A small amount of dried powder sample was packed into the sample holder. The sample surface was smoothed and flattened using a clean glass slide.

4.7.2 Powder X-ray Diffraction

X-Ray diffraction data in this study were obtained from Bruker (D8 Advance) at 40 kV and 40 mA. A step size of 0.010° was used with a step time of 0.2 s/step. Diffraction patterns were plots of 2θ vs. counts per second.

A small amount of dry powdered sample was packed into the sample holder. The sample surface was smoothed and flattened using a clean glass slide or a spatula.

4.7.3 Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained from a Perkin-Elmer system 2000 spectrophotometer. A range of frequency from 4000 to 370 cm^{-1} with 160 averaged scans at 1 cm^{-1} resolution was set for each measurement. Spectra were plots of frequency (cm^{-1}) versus percentage transmittance.

All samples were prepared by the KBr technique. A small amount of each sample was mixed with KBr powder and lightly ground in an agate mortar, then the ground sample was pressed to a pellet.

CHAPTER V
RESULTS

5.1 Quantitation of Iron in Kaolinite

5.1.1 Single Acid Treatment

Kaolinite was digested to solution by microwave digestion, using mixed acids. The content of iron in the digested kaolinite was determined by the flame atomic absorption spectroscopic method. Quantitation of iron in untreated and treated kaolinite from single acid treatment at room temperature and at 100 ^{o}C is shown in Figure 5.1.

5.1.2 Consecutive Acid Treatment

Kaolinite was digested to solution by microwave digestion, using mixed acids. The content of iron in the digested kaolinite was determined by the flame atomic absorption spectroscopic method. Quantitation of iron in untreated and treated kaolinite by the consecutive acid treatment at room temperature and at 100 ^{o}C is shown in Figure 5.2.

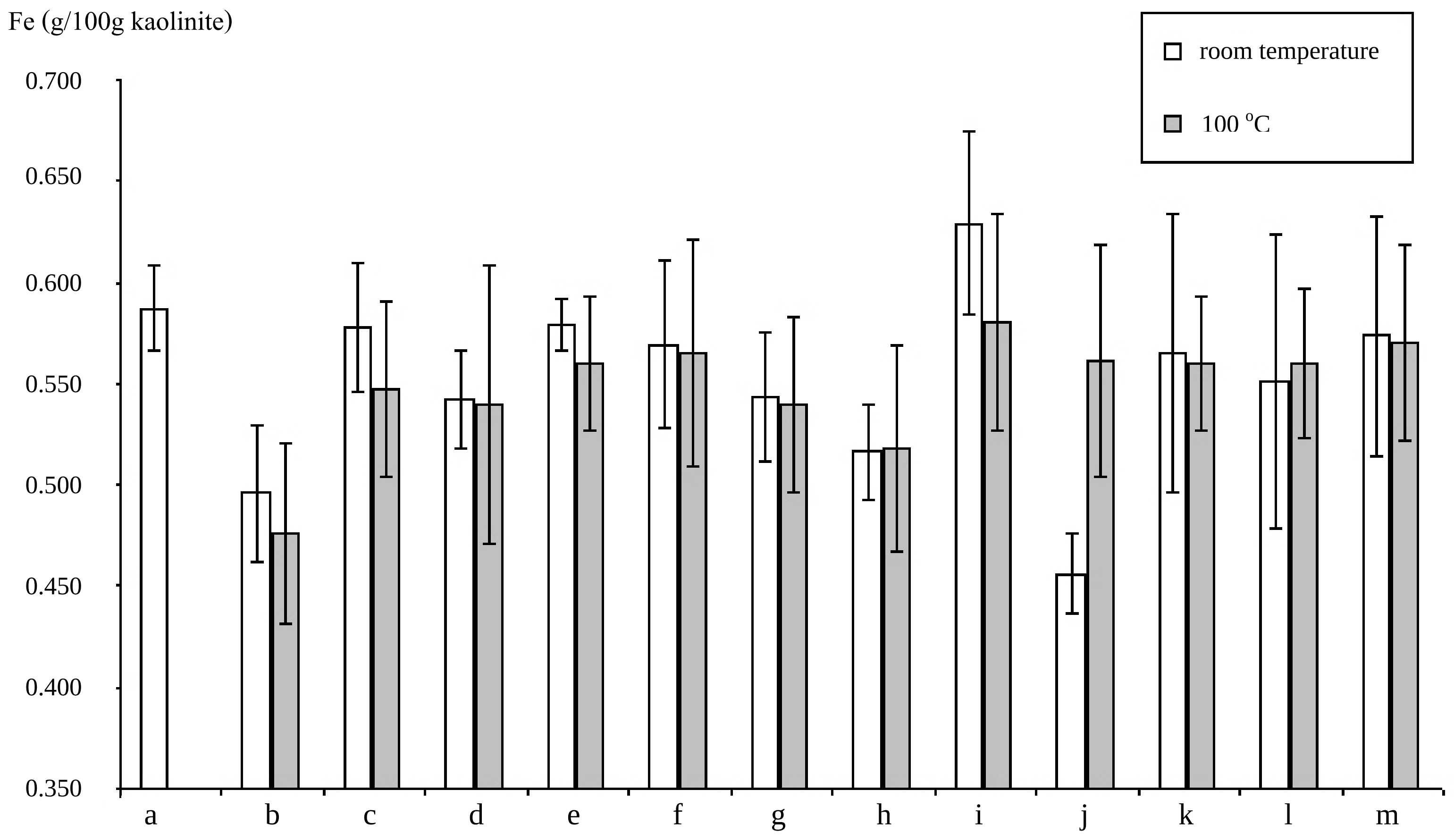


Figure 5.1 the iron content in untreated kaolinite and kaolinite treated with single acids

(a) untreated kaolinite (b) oxalic acid (c) tartaric acid (d) acetic acid (e) ascorbic acid (f) citric acid (g) formic acid (h) hydrochloric acid (i) nitric acid (j) sulfuric acid (k) dithionite (l) desferroxamine (m) EDTA

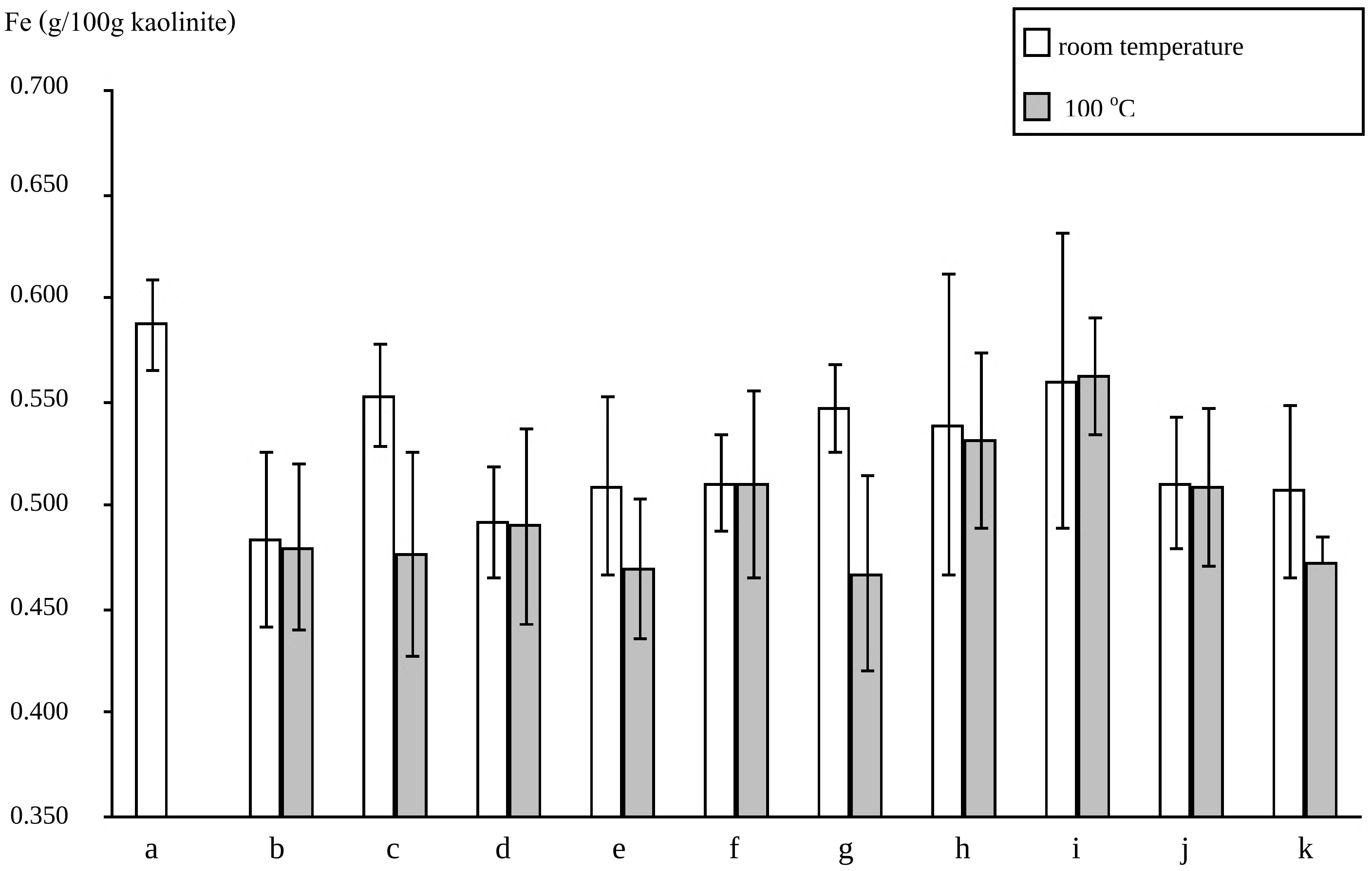


Figure 5.2 the iron content in untreated kaolinite and kaolinite treated with consecutive acids

(a) untreated kaolinite (b) oxalic-ascorbic (c)ascorbic-oxalic (d) oxalic-formic (e) formic-oxalic (f) oxalic-tartaric (g) tartaric-oxalic (h) acetic-ascorbic (i)ascorbic-acetic (j) oxalic-acetic (k) acetic-oxalic

5.2 Kaolinite Characterization

5.2.1 Brightness

Brightness is one of the most important specifications for kaolinite. A brightness of 79 – 83.5 % is required for paper industry and 83.5 – 85.5 % for coating [24]. The presence of red to yellow pigments is mainly due to ferric oxide. Brightness measurement was done in the path of untreated kaolinite and treated kaolinite.

5.2.1.2 Single Acid Treatment

Brightness measurement results for kaolinite treated with a single acid at room temperature and at 100 ^{o}C are shown in Figure 5.3.

5.2.2.2 Consecutive Acid Treatment

Brightness values for kaolinite treated with two acids consecutively at room temperature and at 100 ^{o}C are shown in Figure 5.4.

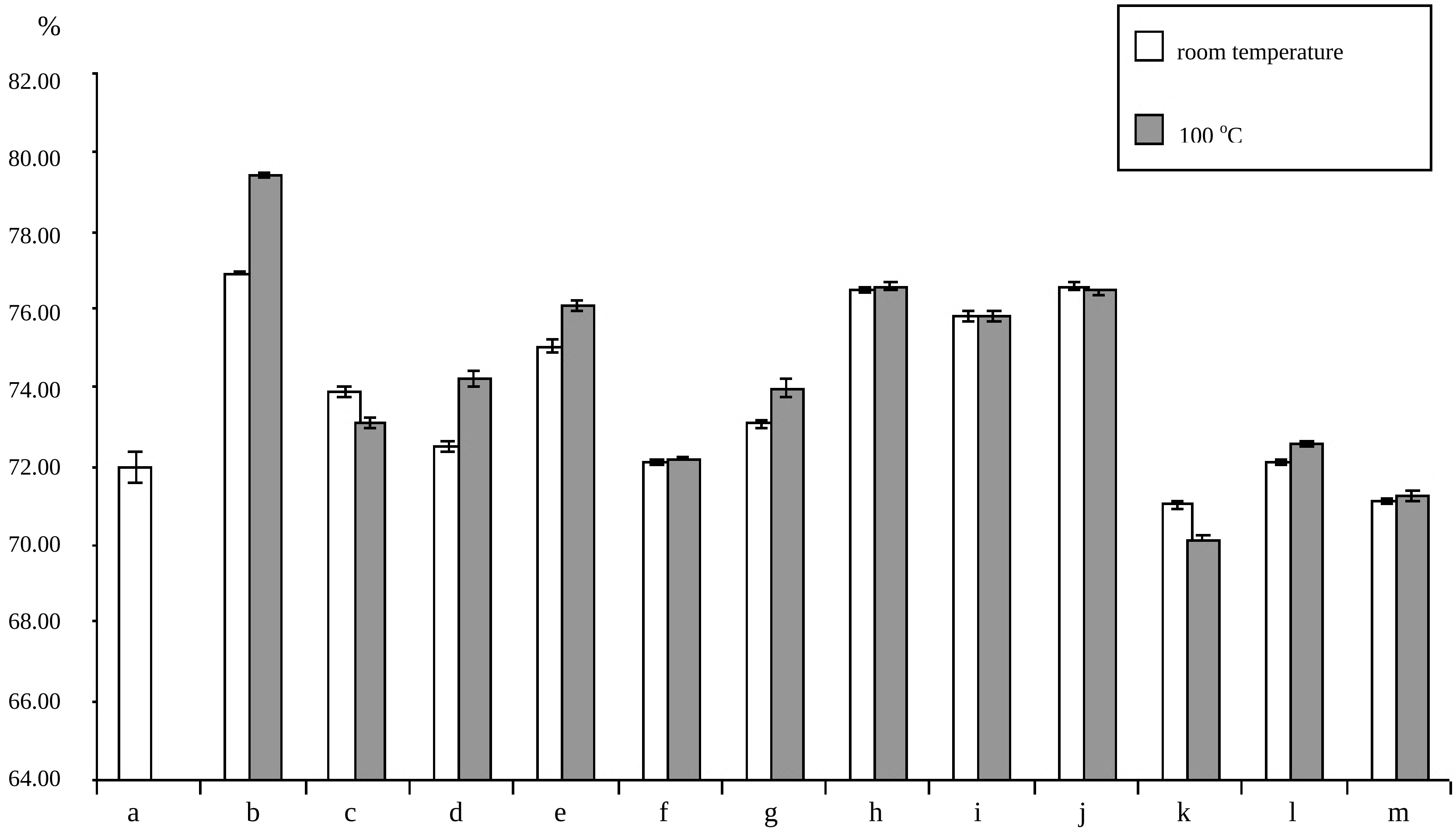


Figure 5.3 Percentage brightness in untreated kaolinite and kaolinite treated with single acid

(a) Untreated kaolinite (b) oxalic acid (c) tartaric acid (d) acetic acid (e) ascorbic acid (f) citric acid (g) formic acid

(h) hydrochloric acid (i) nitric acid (j) sulfuric acid (k) sodium dithionite (l) desferroxamine (m) EDTA

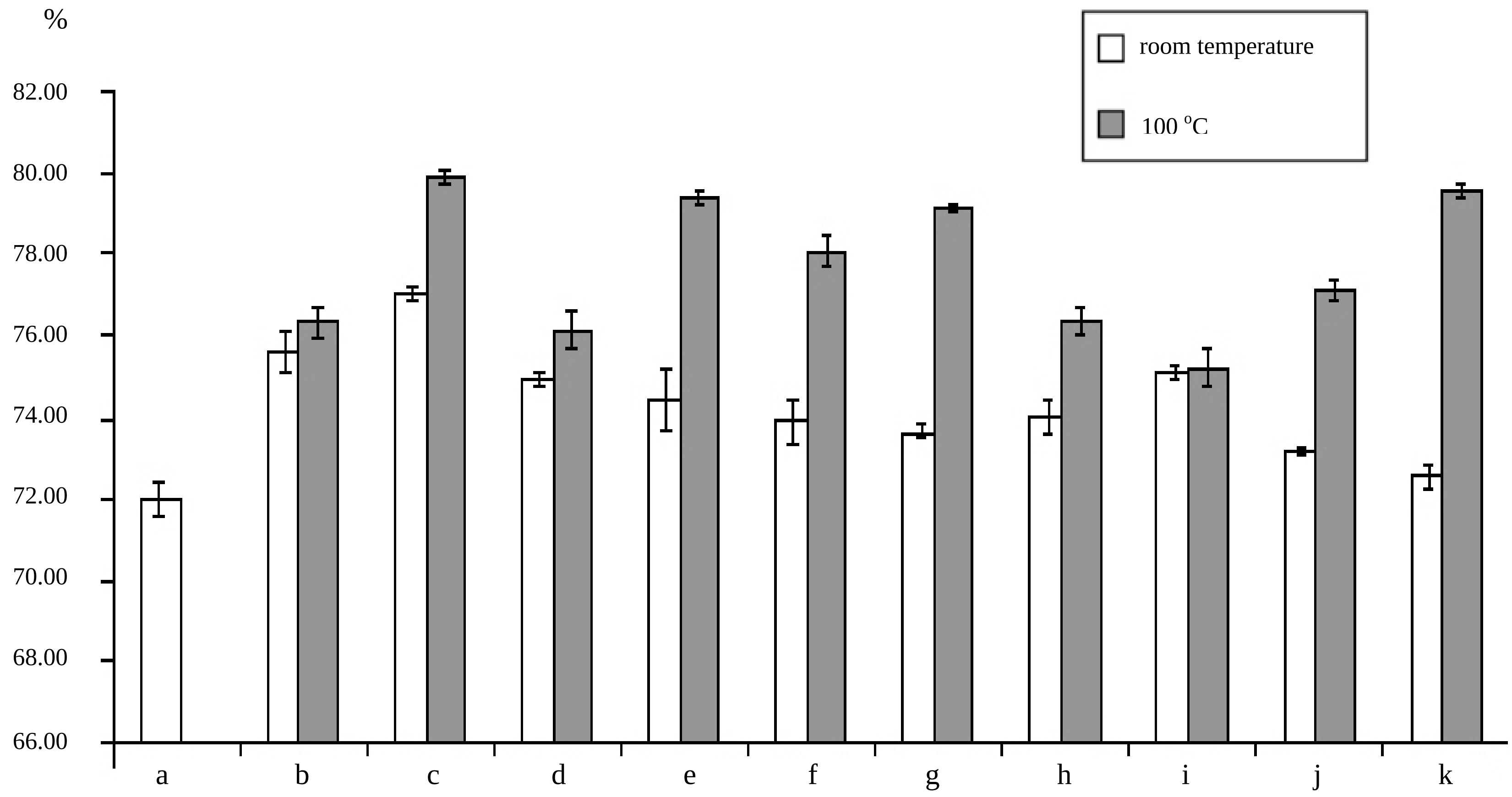


Figure 5.4 Percentage brightness in untreated kaolinite and kaolinite treated with consecutive acid (a) untreated kaolinite (b) oxalic-ascorbic (c)ascorbic-oxalic (d) oxalic-formic (e) formic-oxalic (f) oxalic-tartaric (g) tartaric-oxalic

5.2.2 Powder X-Ray Diffraction

Figure 5.5 showed the XRD pattern of treated kaolinite using single acids by oxalic acid, tartaric acid, acetic acid, ascorbic acid, citric acid, formic acid, hydrochloric acid, nitric acid, sulfuric acid, sodium dithionite, desferroxamine and EDTA compared with untreated kaolinite.

Figure 5.6 showed the XRD pattern of treated kaolinite using consecutive acid by oxalic-ascorbic, ascorbic-oxalic, oxalic-formic, formic-oxalic, oxalic-tartaric, tartaric-oxalic, acetic-ascorbic, ascorbic-acetic, oxalic-acetic, and acetic-oxalic compared with untreated kaolinite.

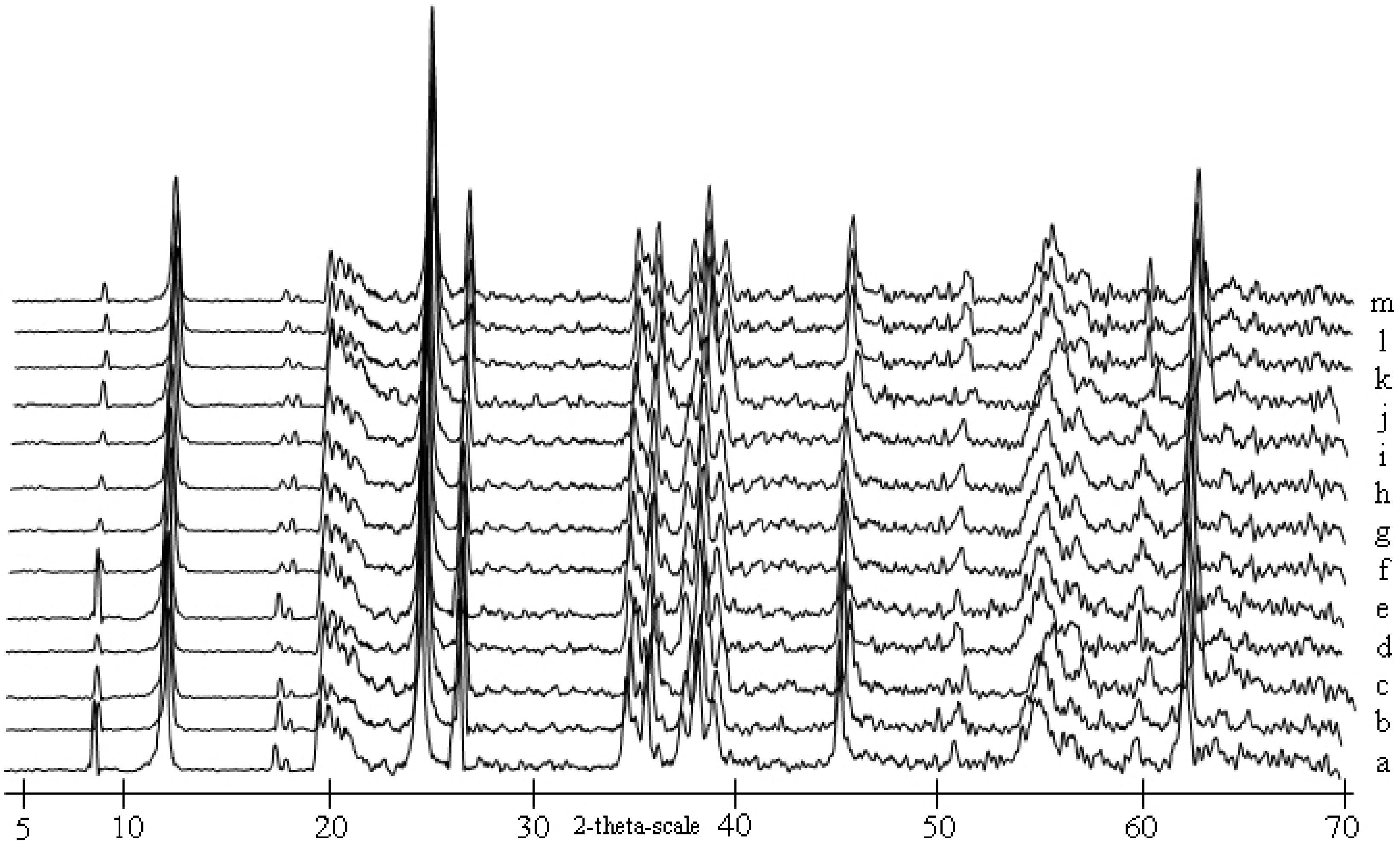


Figure 5.5 XRD patterns of untreated kaolinite and kaolinite treated with single acids.

(a) untreated kaolinite (b) oxalic acid (c) tartaric acid (d) acetic acid (e) ascorbic acid (f) citric acid (g) formic acid (h) hydrochloric acid (i) nitric acid (j) sulfuric acid (k) sodium dithionite (l) desferroxamine (m) EDTA

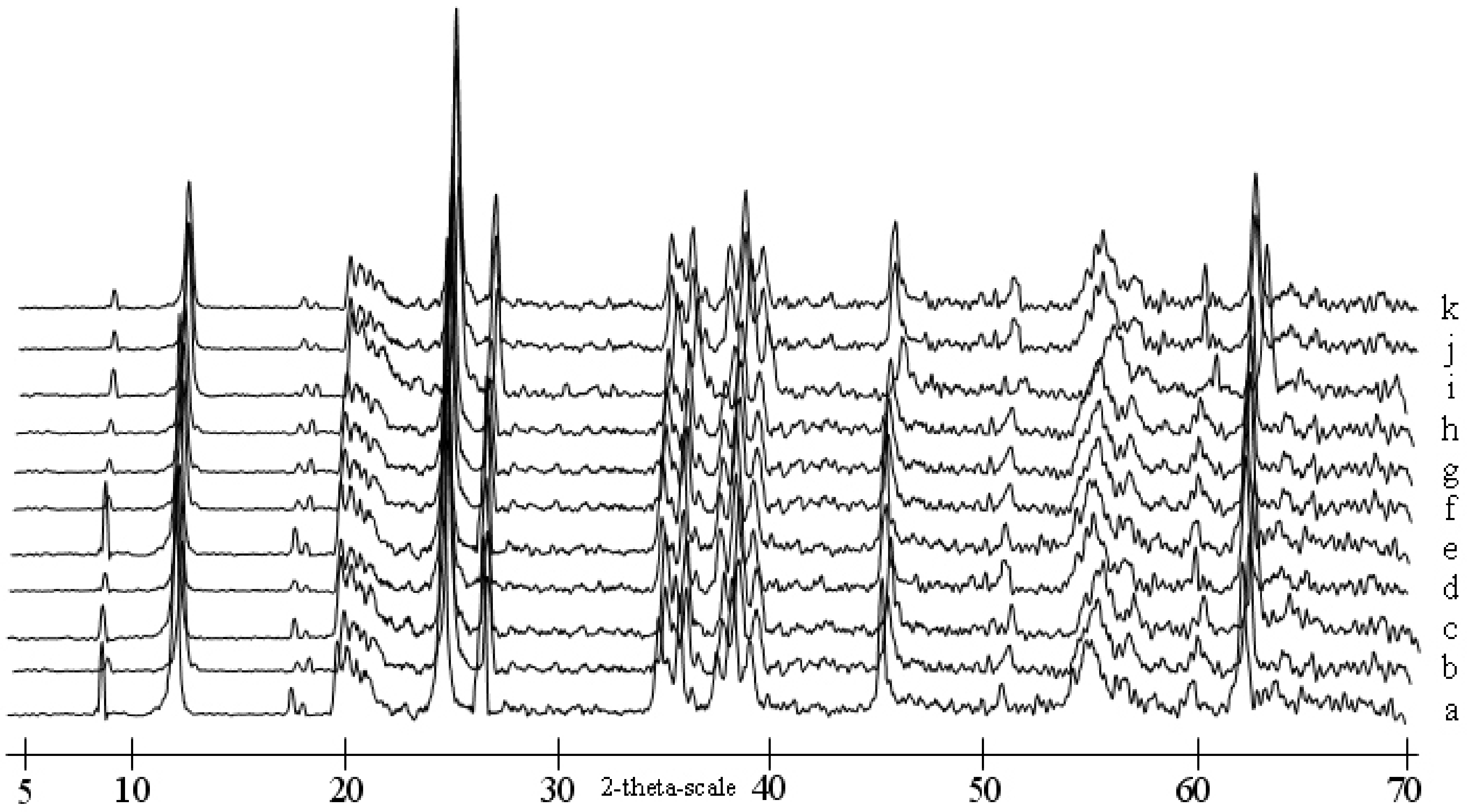


Figure 5.6 XRD pattern of untreated kaolinite and kaolinite treated with consecutive acids.

(a) untreated kaolinite (b) oxalic-ascorbic (c)ascorbic-oxalic (d) oxalic-formic (e) formic-oxalic (f) oxalic-tartaric (g) tartaric-oxalic (h) acetic-ascorbic (i) ascorbic-acetic (j) oxalic-acetic (k) acetic-oxalic

5.2.3 Fourier Transform Infrared Spectroscopy

The FTIR spectra of kaolinite are shown in Figure 5.7 for single acid treatment using oxalic acid, tartaric acid, acetic acid, ascorbic acid, citric acid, formic acid, hydrochloric acid, nitric acid, sulfuric acid, sodium dithionite, desferroxamine and EDTA compared with untreated kaolinite.

The FTIR spectra of kaolinite are shown in Figure 5.8 for consecutive acid treatment using oxalic-ascorbic, ascorbic-oxalic, oxalic-formic, formic-oxalic, oxalic-tartaric, tartaric-oxalic, acetic-ascorbic, ascorbic-acetic, oxalic-acetic, and acetic-oxalic acids, compared with untreated kaolinite.

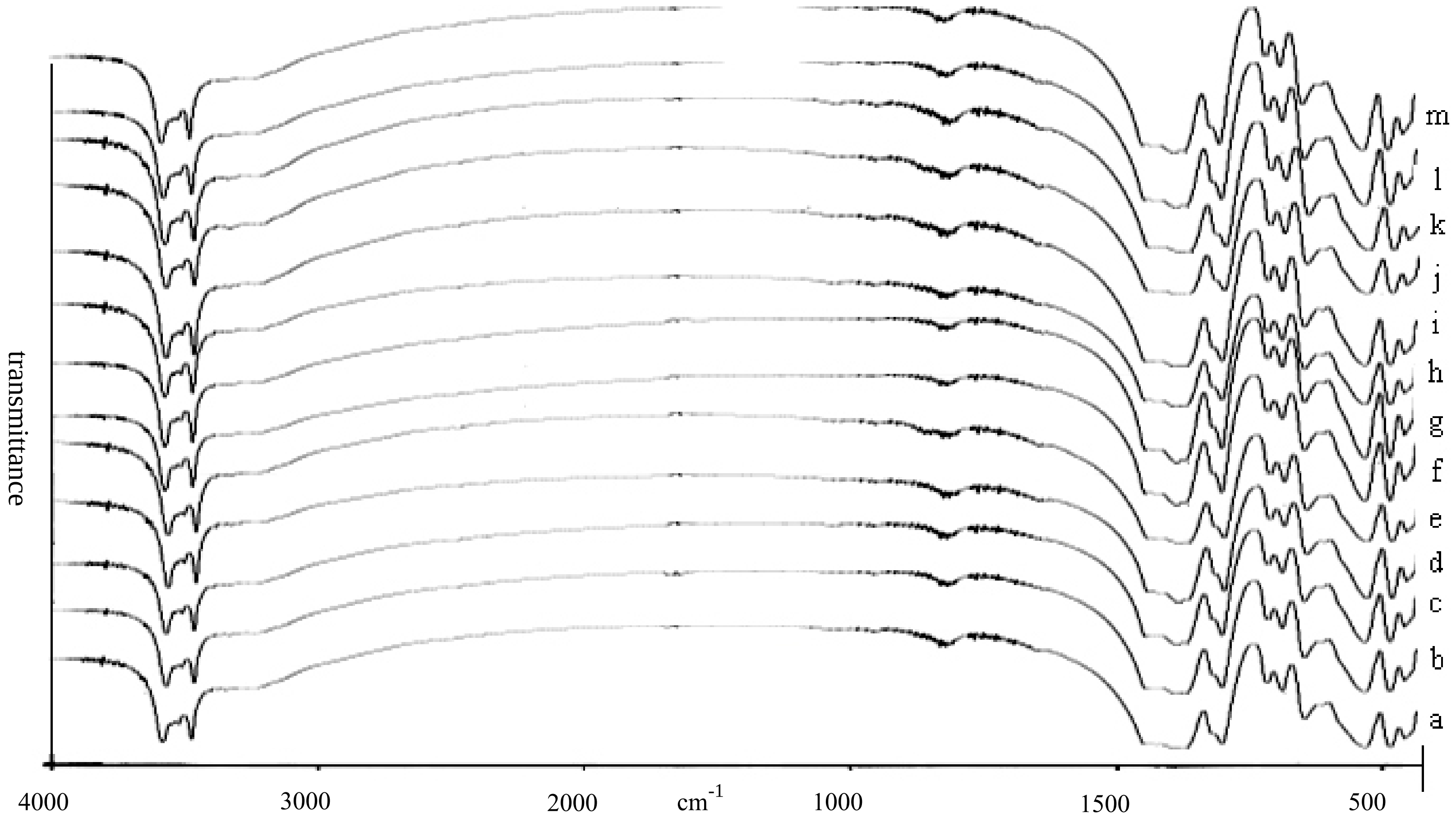


Figure 5.7 FTIR spectra of untreated and treated kaolinite using single acids

(a) untreated kaolinite (b) oxalic acid (c) tartaric acid (d) acetic acid (e) ascorbic acid (f) citric acid (g) formic acid (h) hydrochloric acid (i) nitric acid (j) sulfuric acid (k) sodium dithionite (l) desferroxamine (m) EDTA

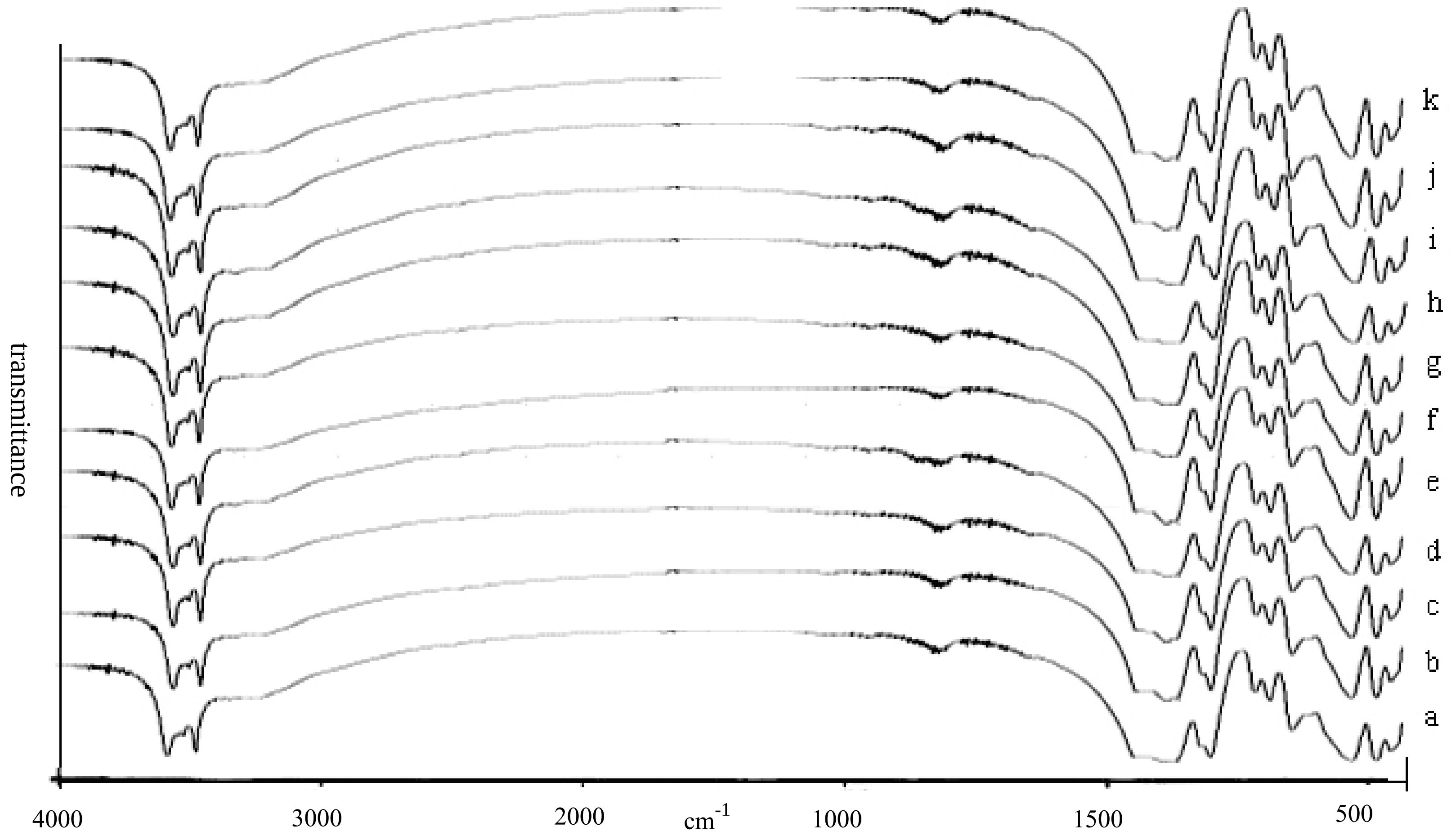


Figure 5.8 FTIR spectra of untreated and treated kaolinite using consecutive acids

(a) untreated kaolinite (b) oxalic-ascorbic (c)ascorbic-oxalic (d) oxalic-formic (e) formic-oxalic (f) oxalic-tartaric (g) tartaric-oxalic (h) acetic-ascorbic (i)ascorbic-acetic (j) oxalic-acetic (k) acetic-oxalic

5.2.4 Electron Spin Resonance

Figure 5.9 shows ESR spectra of kaolinite after single acid treatment using oxalic acid and desferroxamine, compared with untreated kaolinite.

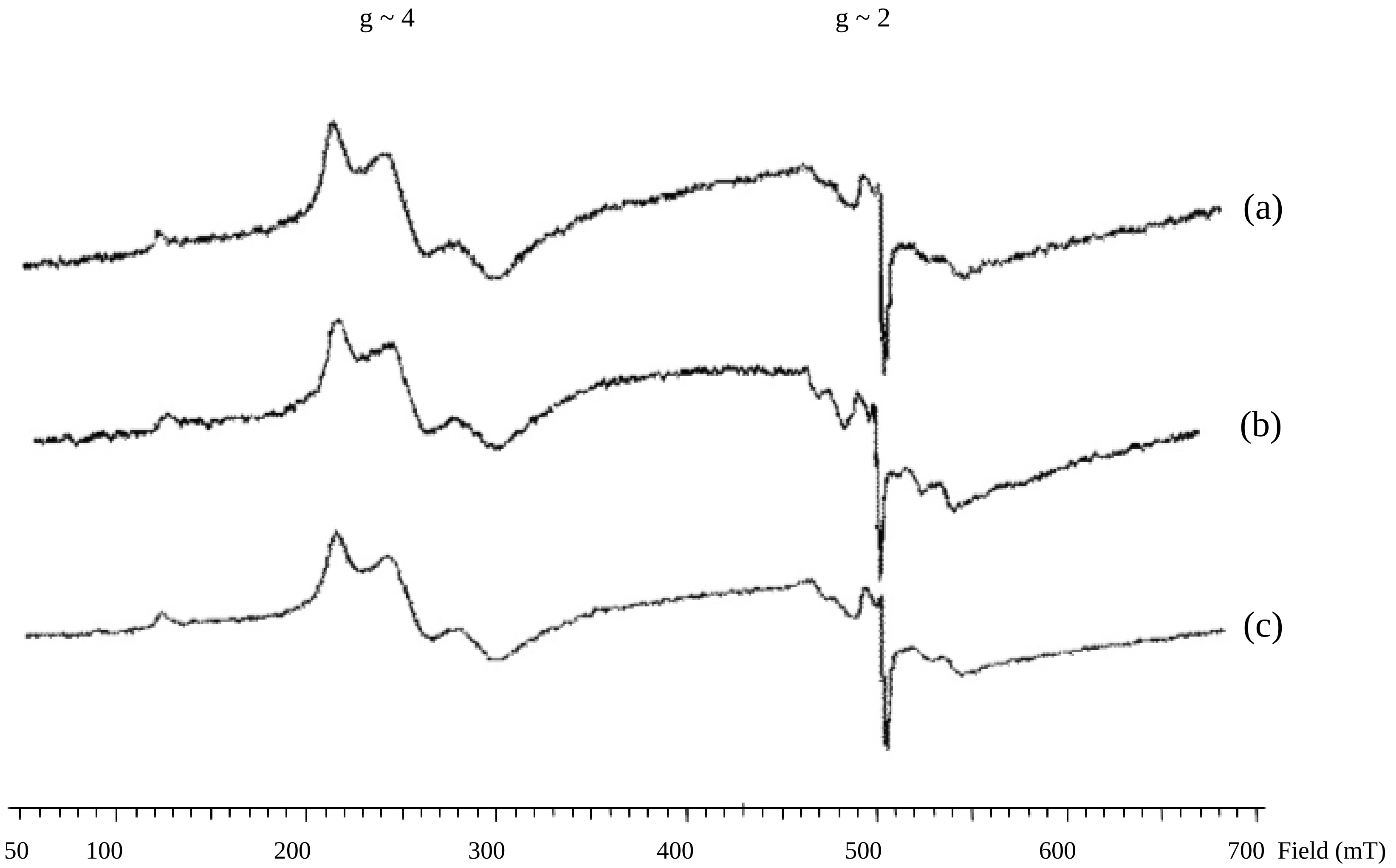
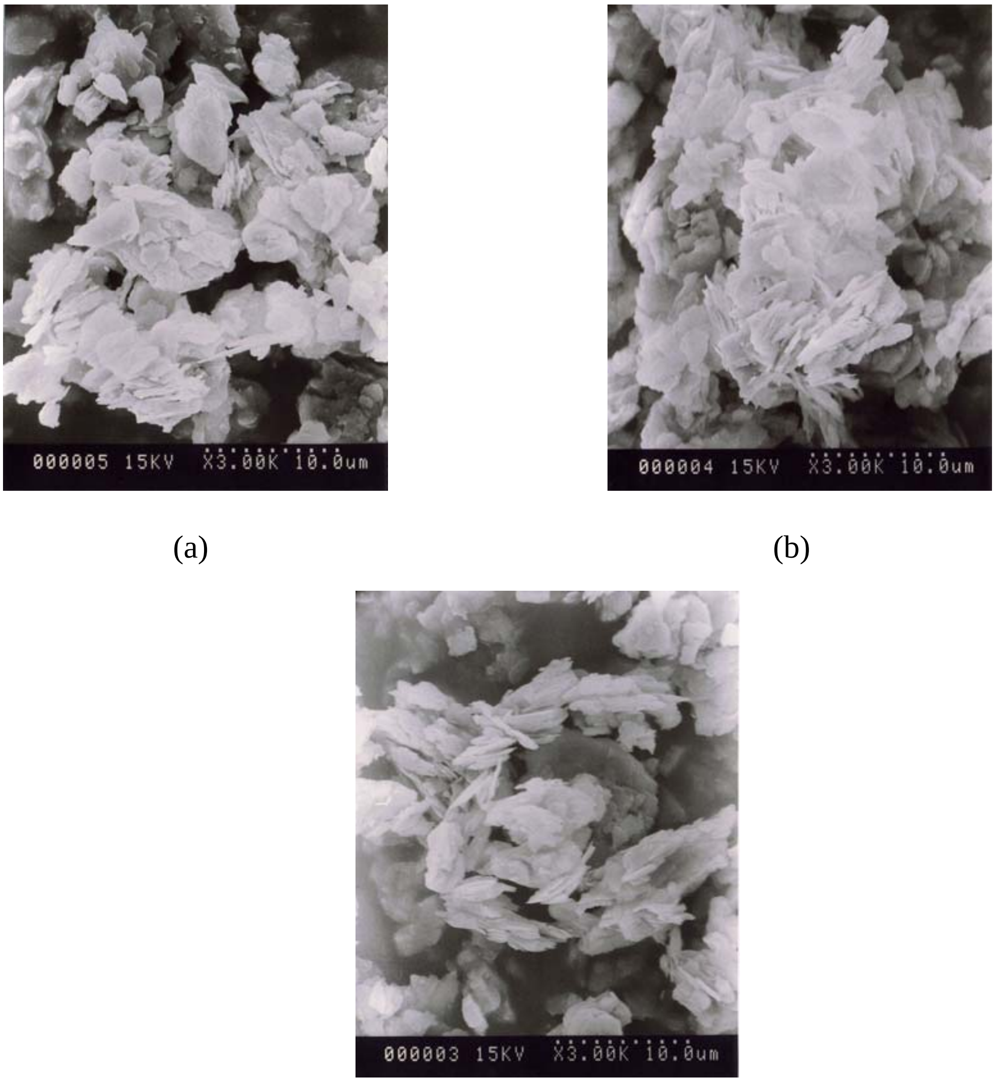


Figure 5.9 ESR spectra of (a) untreated and (b) kaolinite treated with oxalic acid and (c) kaolinite treated with desferroxamine

5.2.5 Scanning Electron Microscope

The scanning electron micrographs of untreated kaolinite, kaolinite treated with oxalic acid in room temperature and with oxalic acid at 100 ^{o}C are shown in Figure 5.10.



(a) (b)

(c)

Figure 5.10 Scanning electron micrographs of (a) untreated kaolinite
(b) kaolinite treated with oxalic acid at room temperature
(c) kaolinite treated with oxalic acid at 100^{o}C

CHAPTER VI

DISCUSSION

6.1 Quantitation of Iron in Kaolinite

6.1.1 Single and Consecutive Acid Treatment

The content of iron in each single acid experiment varied in the range 0.5-0.65 %. In most cases, the iron contents of acid-treated kaolinite are lower than those for untreated kaolinite but not significantly. Room temperature and at 100 ^{o}C are mostly comparable.

It can be seen that sulfuric, hydrochloric and oxalic acids can each remove considerable amounts of iron from kaolinite, especially sulfuric acid at room temperature. Kaolinite washed with nitric acid, however shows a higher iron content than the original value. This is believed to be due to iron impurities in the nitric acid (0.1%) depositing onto the clay. Nitric acid might also have partly destroyed the clay structure, releasing Fe^{2+} and/or Fe^{3+} ions.

The study of dissolution of iron oxides in solutions of complexing agents has previously been done. It has been recognized [47] that in the case of iron oxides the rate constant for the dissolution increases linearly with the logarithm of the stability constant of the complex of Fe (III) with the anion of the electrolyte; in the order $HNO_3 < H_2SO_4 \leq HCl$. Thus HCl apparently has a higher capability to remove more iron than do the other two acids.

Ascorbic acid is not stable in air and at high temperatures. This fact may affect the concentration of the acid during each experiment especially under high temperature conditions.

Citric acid has been used for extraction of iron impurities in kaolinite but it is especially most effective for nickel extraction, achieving recoveries up to 60% [48].

Oxalic acid has been used to remove iron from kaolin [31, 36, 39, 46] and has also been found to display higher selectivity in iron extraction compared with other organic acids, releasing more than 60 % of iron oxides[49]. Presumably, the iron oxide removing mechanism is a combined effect of acidity, complexing ability and reducing capacity. Oxalic acid, therefore, displays a better performance than the other organic acids.

The iron content in each consecutive acid treatment is not significantly different from the result of single acid treatment. Oxalic acid seemed to have leached out more iron than the partner acid except when it was used as the second acid. These consecutive acid treatments have no better efficiency than a single oxalic treatment. Temperature variation seems to have little effect on the double acid treatment.

6.2 Kaolinite Characterization

6.2.1 Brightness

6.2.1.1 Single and Consecutive Acid Treatment

Treatment with oxalic acid resulted in the highest brightness, especially at 100 ^{O}C. Sodium dithionite and EDTA, on the other hand, gave brightness values which were even lower than that for untreated kaolinite. Although both reagents are believed to have removed some iron from the clay, some undesirable reactions might have taken place during the treatment. For example, these reagents may have formed some precipitates which reduce the brightness of the clay. The acid leaching by HCl has been reported [50] for removal of Fe from kaolinite with little increase in brightness.

Most acids are able to increase the brightness of the clay to some extent, except for sodium dithionite and EDTA. Assuming that brightness depends only on the absence of Fe^{3+} ions, variation in the brightness of kaolinite after the acid treatment is most probably related to the ability of the anion of the acids to complex with Fe^{3+}**.**

From Appendix C the formation constant of iron (III) complex is in the order of EDTA > oxalate > citrate > tatarate > acetate > chloride ≥sulfate > nitrate. But according to the brightness improvement results hard acids (HCl, H_2SO_4 and HNO_3) can improve brightness better than do organic acids except for oxalic acid. In this case acidity probably plays a major role, removing some colored components which are usually hard to remove.

The brightness of kaolinite after the consecutive acid treatment is highest whenever oxalic acid is used, especially at 100 ^{o}C. It is interesting that the consecutive acetic-oxalic acid treatment give the highest brightness compared to others at 100 ^{o}C. However, oxalic acid alone produces a higher brightness. Ascorbic-oxalic treatments at room temperature and 100 ^{o}C are not significantly different, probably due to the rather unstable nature of ascorbic acid at 100 ^{o}C. Brightness improvement is therefore due mainly to oxalic acid.

6.2.2 Powder X-Ray Diffraction Study

6.2.2.1 Kaolinite and Treated Kaolinite with Acids

Figure 5.5 shows the X-ray diffraction patterns of untreated kaolinite and kaolinite treated with acids. The untreated kaolinite has prominent basal reflections at 7.16 Å and 3.57 Å, which correspond to the 001 and 002 spacings according to Brindley and Robinson [5]. Table 5.1 compares the diffraction data of kaolinite in the present study with those obtained by Brindley and Robinson [5]. Four additional reflections in Banpu kaolinite, which are not kaolinite reflections, were observed at 9.96 Å, 4.82 Å, 3.33 Å and 1.99 Å. These are most probably the reflections of illite. Kuetag et al. [51] reported that generally in Thailand kaolinites are found together with illite. This kaolinite sample therefore contains a little amount of illite that could not be removed. The diffraction data of illite are given in Table B1 (Appendix B).

The XRD patterns of acid-treated kaolinite are the same as that for untreated kaolinite indicating that the acid treatments did not affect the clay structure and the only externally adsorbed iron oxides and colored components were removed.

Wilson [51] summarized the investigative methods in clay mineralogy and stated that the XRD method gave only an average picture of the material, one where the major components were highlighted, but the minor phases disappeared into the background, and were undetected. Even though the reaction between the acids and the clay occurred at the hydroxyl groups and most probably led to some changes on the clay surfaces, it could not be detected by the XRD technique.

Also the fact that the XRD pattern of kaolinite remained unchange after the acid treatment strongly suggests that Fe^{3+} ions in the clay structure were not removed by the acid. The clay structure, therefore, did not collapse.

Table 6.1 X-ray diffraction data for kaolinite.

d001 (Å)		Indices
Present study (Banpu kaolinite)	Brindley and Robinson [5]	
9.96		
7.16	7.16	001
4.82		
4.44	4.46	020
4.34	4.33	110
4.24	4.18	$11\bar{1}$
4.14	4.13	$1\overline{11}$
3.57	3.57	002
3.33		
2.55	2.55	$1\bar{3}0$, $20\bar{1}$, 130
2.49	2.49	$1\overline{31}$, 200, 112
2.38	2.37	003
2.33	2.33	$11\bar{3}$
2.29	2.28	$1\overline{31}$, 131
1.99		
1.66	1.68	$24\bar{1}$
1.48	1.48	060, $3\overline{31}$, $33\bar{1}$

6.2.3 Fourier Transform Infrared Spectroscopy Study

6.2.3.1 Kaolinite

The FTIR spectra of kaolinite are shown in Figure 5.7 and 5.8. Four OH-stretching absorption bands are found at 3696, 3670, 3651 and 3620 cm^{-1}. These four absorptions correspond respectively to the bands at 3695, 3670, 3650 and 3620 cm^{-1} reported by Serratosa et al [53]. The absorption bands at 3696 and 3620 cm^{-1} are very strong, whereas those at 3670 and 3651 cm^{-1} are much less intense. The band at 3620 cm^{-1} has been assigned to the stretching frequency of the internal hydroxyl groups of kaolinite. These hydroxyl groups are believed to be oriented almost parallel the (*001*) layers, pointing towards unoccupied octahedral holes [54, 55]. The inner-surface hydroxyl groups associated with the remaining bands (3696, 3670 and 3651 cm^{-1}) are believed to make an angle of 60-73° with the (001) plane [54]. The band at 3696 cm^{-1} is due to almost free OH bonds but the absorptions at 3670 and 3651 cm^{-1} correspond to OH group which are participating in weak hydrogen bonding between the layers [55].

6.2.3.2 Kaolinite Treated with Single Acids and Consecutive Acids

Figures 5.7 shows the infrared spectra of kaolinite singly treated with oxalic acid, tartaric acid, acetic acid, ascorbic acid, citric acid, formic acid, hydrochloric acid, nitric acid, sulfuric acid, sodium dithionite, desferroxamine and EDTA. Figure 5.8 shows the spectra for consecutive acid treatment by oxalic-ascorbic, ascorbic-oxalic, oxalic-formic, formic-oxalic, oxalic-tartaric, tartaric-oxalic, acetic-ascorbic, ascorbic-acetic, oxalic-acetic, and acetic-oxalic acids. No significant differences can be observed among these spectra, suggesting that treating kaolinite with all these acids did not lead to any change in the clay structure. Only the minor phases externally adsorbed were affected, agreeing with the XRD results.

Mendelovici [56] suggested that Fe in the octahedral sheet of lateritic kaolinite is characterized by two absorption bands, at 865-875 and 3607 cm^{-1}, assigned as δ Al-OH-Fe and νOH, respectively. However, the detection of the 865 cm^{-1} band requires a special preparation with CsCl. The absorption band at 3607 cm^{-1} can be detected only with KI pellet technique.

6.2.4 Electron Spin Resonance Study

Kaolinite exhibits two principal resonances centered at $g \sim 4$ and $g \sim 2$. The resonances on both sides of the central line at $g = 4.2$ are believed to be associated with octahedral Fe^{2+} in regions of high crystallinity and regular stacking, while the central line has been attributed to octahedral Fe^{3+} associated with layer stacking disorder [57]. The $g = 2.0$ signal has been assigned to a defect centre adjacent to an octahedral Mg^{2+} ion or an O_2^- ion trapped between adjacent Al^{3+} and Mg^{2+} ions in the octahedral layer.

Figure 5.8 shows the ESR spectra of (a) untreated kaolinite and (b) kaolinite treated with oxalic acid and (c) kaolinite treated with desferroxamine. No significant difference can be detected between the untreated and treated samples, either in the $g \sim 4$ region or the $g \sim 2$ region. This agrees with the XRD results that structural iron has not been removed.

Herbillon [58] suggested that integration of $g \sim 4$ resonance band of the ESR spectra allows a semiquantitative estimate of the structural iron in the samples. A multiple relationship seems to exist between the crystallinity index, the ‘structural iron’ content and the shape and intensity of both $g \sim 4$ and $g \sim 2$ signals. The kaolinite with high content of iron (>2% structural Fe_2O_3) has a specific spectrum exhibiting strong $g \sim 4$ resonance band and no or weak $g \sim 2$ sharp doublet. The absence of a sharp doublet at $g \sim 2$ probably means that the structural iron content is below 2 % and/or that the observed signals arise from another paramagnetic source.

Apparently, external iron oxide phase did not give rise to an ESR signal.

6.2.5 Scanning Electron Microscopic study

In Figure 5.10 the scanning electron micrographs of untreated kaolinite and kaolinite treated with oxalic acid at room temperature and 100 ^{o}C show that they were not significantly different. The chemical leaching did not affect the particle form of kaolinite.

CHAPTER VII
CONCLUSIONS

The brightness improvement of kaolinite via removal of ferric-iron starts with a well-crystallized raw material which contains a small amount of illite as shown by the XRD pattern. Acid treatments did not lead to any observable change in the structure of the clay.

The single acid which gave the best result for iron removal is oxalic acid at 100 ^{o}C, most probably because of its acidity, complexing ability and reducing ability. Some hard mineral acids (HCl, H_2SO_4 and HNO_3) could also remove reasonable amounts of iron. Other organic acids and substances (ascorbic, acetic, tartaric, citric acids, desferroxamine, sodium dithionite and EDTA) all showed low efficiencies in iron removal.

For consecutive acid treatments good results were obtained only when the first acid used was oxalic acid

In most cases, efficiency removal of iron resulted in a high brightness although other phases also influencing brightness included non-iron oxides such as $TiO_{2.}$

The other characterization (FTIR, ESR and SEM) results confirmed that the clay structure was not significantly changed by leaching with acids. The external iron oxide and other colored components may be removed. The remaining iron in the clay was mostly structural iron which could not be removed.

Further study should include variable of pH of leaching solution.

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APPENDIX

Appendix A

Table A1 The chemical composition and specification of Banpu kaolinite

Banpu kaolinite	Mass %
Chemical composition	
SiO_2	46.00
Al_2O_3	38.00
TiO_2	0.03
Na_2O	< 0.001
K_2O	1.00
MgO	< 0.001
CaO	< 0.001
Mineral composition	
Kaolinite	83
Quartz	3.5
Micaceous	8.5
Gibbsite	3
Feldspar	< 1
Others	2
Particle size distribution	
< 10 micron	60.0
< 1 micron	12.0

Appendix B

Table B1 X-ray diffraction data for illite [59]

Indices	*d* (Å)
001	9.9
002	4.9
020, 110	4.45
111	3.87
022, 003	3.35
200, $13\bar{1}$	2.56
201, $13\bar{2}$	2.39
202, $13\bar{3}$	2.14
005	1.98
060, $33\bar{1}$	1.49

Appendix C

Table C1 Formation constants for iron (III) complexes with some ligands [60]

ligand	log K_1	log K_2	log K_3	log K_4
chloride	1.48	2.13	1.99	0.01
sulfate	2.03	2.98		
nitrate	1.0			
oxalate	9.4	16.2	20.3	
tartarate	7.49			
acetate	3.2			
citrate	12.5*(25.0**)			
EDTA	24.23			

*HL^{2-} anion
**L^{3-} anion

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