Abstract

This study is carried out to investigate the possibility of using Iraqi clay; Duekhla kaolin as filler in the paper industry by reducing the percentage of iron oxide, titanium dioxide, and free silica. Duekhla Kaolin containe about 1.7% iron oxide, 1.2% titanium dioxide, 51.16% silicon dioxide, and 12% free silica. The existence of these oxides in kaolin is undesired in paper-making. The process started by washing Duekhla kaolin with (4N) HCl to remove all the soluble oxides which are not required in paper making. The washed kaolin then separated using filter papers and under a sequence of operations of dilution and filtering until the pH - value become 5. The separated materials then dried at temperature range 40-60 °C for 3 hours, and the dried powders then milled using ball mill of porcelain body, with different sizes of spheres, for 5 hours. Finally the powders of Duekhla Kaolin sieved with a sieve of 65 μm.

The sedimentation method is used for the separation of the above mentioned oxides from clay by using sodium phosphate as dispersant agent. The viscosity parameter of the mixture was studied under the effect of the dispersant agent, and it was found that with the increasing of added dispersant agent the viscosity decreased to a minimum value which is equal to 0.31dyne.cm^2/sec, after that the viscosity increased with the increasing of adding sodium phosphate. The study performed; depending on the minimum viscosity value corresponds to the dispersant amount added.

The zinc hydrosulfite was used as a bleaching agent in a second step for removing the undesired impurities which implies to raise the brightness degree of kaolin Duekhla as a result. As a result of these treatment, the undesired oxides are reduced from sample G_7 by the following percentages; (73% of iron oxide, 91% of titanium dioxide, 15% of silicon dioxide, and 50% of free silica removed), the results of this study reveals that the oxides percentages decreased from (1.71% to 0.3% in iron oxide, 1.2% to 0.09% in titanium dioxide, and 51.16% to 39.7% in silicon dioxide). The crystal structure of kaolin did not change after these treatments to decrease the percents of impurities in this clay to be used as filler in the paper industry.

Table of Contents

Chapter Four

"Discussion of Results, Conclusions, &Future Work"

List of Figures

List of Tables

List of the symbols

W	The percentage of particle diameter
D	The particle size
P	The weight percent
υ	The free falling velocity
t	The time of falling
h	The height of suspension

1-1 Introduction:

The term kaolin is coming from the chine's word kaoliang meaning "high ridge" from which clay originally came from. It is white, soft powder mainly composed fine – grained plate – like particles. Kaolin is formed when anhydrous aluminum silicates which found in feldspar rich rocks, like granite are altered by weathering or hydrothermal process **[1]**. The kaolin clay consist of three types of minerals: kaolinite, Dekite, and Nacrite, the main mineral type in the Duekhla kaolin is kaolinte minerals made from the dissolution of the acidic fire clays by the weathering processes **[2]**. The structure of kaolinite is composed of a single silica tetrahedral sheet and a 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 Fig. (1-1). All the tips of the silica tetrahedrons point in the same direction and toward the center of the unit made of the silica and octahedral sheets **[3]**. Only two-thirds of the possible positions for aluminum in the octahedral sheet are filled, and there are three possible plans of regular population of the octahedral layer with aluminums. The aluminum atoms are considered to be so placed that two aluminums are separated by a hydroxyl above and below, thus making a hexagonal distribution in a single plane in the center of the octahedral sheet. The hydroxyl groups are placed so that each hydroxyl is directly below the perforation of the hexagonal net of oxygen in the tetrahedral sheet **[4]**.

The charges within the structure are balanced, i.e., there are no charges on the lattice due to substitutions within the lattice. The structural formula for kaolinite is ($Al_2O_3.2SiO_2.2H_2O$) and the theoretical composition expressed in oxides is SiO_2, 46.54 %; Al_2O_3, 39.50 %; H_2O, 13.96 %. The analyses of many samples of kaolin have shown that there is very little if any substitution within the lattice. In a few instances the evidence suggests a very small amount of substitution of iron and titanium for aluminum in the relatively poor crystalline variety **[3, 4]**.

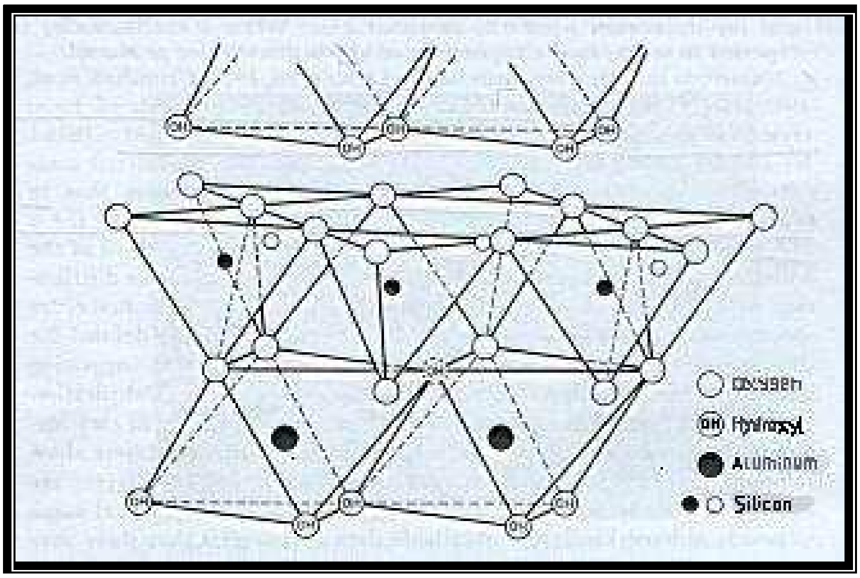

Figure (1-1) The crystal structure of kaolin ***[3].***

The variation between members of the kaolin consists in the way in which the unit layers are stacked above each other and possibly also in the position of the aluminum atoms in the possible positions open to them in the octahedral layers **[3]**.

1-2The previous study:

Fernand and Ceylon (1953) showed that the particles of kaolin are ideal materials for using as filler in the paper industry. They had examined the brightness factor of kaolin and show that when the percentage of particles less than (0.3 μm) exceeds 15% by weight, the brightness is decreased **[5]**.

Murray and Lyons (1955) proved that all ordered kaolin is preferred because they were reported to impart a higher gloss in paper industry than those of poor ordered. It due to the disordered kaolin tends to contain a high percentage of very fine particles, because when these are removed from china clay (which is disordered) excellent reflectance values are obtained **[6]**.

Lyons (1958) used kaolin Georgia clay as filler in the paper industry. He showed that the brightness value is closely related to the percentage of material which is less than 2μm in size, and the percentage of material less than 0.3 μm do not exceed 10% **[7]**.

Uzbaki (1989) has used a physical process dependent on quartz particles separating from the kaolin by passing through the colloidal suspension by leaving the kaolin particles in the top parts of suspension with using Carver method **[8]**.

Sathy et .al (1991) studied the removing of fine graphite impurities from kaolin to produce kaolin clay in the paper industry, and the process is succeeded to remove about 70% of graphite with loosing in kaolin of about 4.5% **[9].**

Weissenborn, (1992) defined the types of clay that can be used in paper - making used to fill the spaces between the fibers in the paper and to coat the paper so that it will have a smooth surface. This makes the paper more suitable for the reproduction of photographs, especially color photos **[10].**

Raghavan, (1996) Studied the process of removing the impurities from kaolin (Titanium and Iron component) by using the colloidal flocculation and magnetic separation methods. By this method it's possible to remove about 50% TiO_2 and 45% of Iron component and the treated kaolin can be used in the paper industry **[11].**

Suito, & Arakawa, (2005) published that Water-washed kaolin can be used as a pigment in coating formulations for printing paper and as a filler in the body of paper because of its optical properties (i.e., brightness, gloss and opacity) **[12].**

1-3 Industrial applications of kaolin:-

Kaolin applications are multiple and diversified. Kaolin’s whiteness and plasticity make it extremely suitable for its extensive use as a filler, extender, ceramic raw material and pigment. It is also an important raw material to refractories, and to catalyst, cement and fiber glass industries **[13]**. Kaolin is a unique industrial mineral, which remains chemically inert over a relatively wide pH range and it offers excellent covering when used as a pigment or extender in coated films and filling applications.

In addition, it is soft and non-abrasive and has a low conductivity of heat and electricity. It's always used in cement, paint **[14].**

The large uses of kaolin are structural clay product industry, which manufactures brick, drain tiles, sewer pipe. It can with stand very high temperature and used in commercial refractory products such fiber brick and block. Major domestic uses for kaolin were paper coating, paper filling, fiber glass, paint, rubber, brick, and cement **[15].** Some of their applications are defined bellow:

1-3-1 Paper Industry:-

Kaolin is used as filler in the bulk of the paper. Kaolin's brightness, large surface area and low abrasively make it an ideal raw material for paper production **[16].** Using kaolin as filler reduce the amount of expensive wood pulp required, enhances the optical properties of the paper and improves its printing characteristics. When used as a coating on the surface of the paper, kaolin's whiteness improves paper brightness, whilst the size and the shape of the individual kaolin particles give the gloss and printed paper quality required for many different kinds of paper. Examples include papers for magazines and brochures, art paper, cartons and boxes etc **[7].**

1-3-2 Ceramics:-

Kaolin converts to mullite and glass when fired to temperatures exceeding 1000° C. It is used in formulations described as white wares, which consists of tableware, and wall and floor tiles. It provides and plasticity in the shaping of these products and reduces the amount of pyroplastic deformation in the process of firing. In tableware, in addition to the strength and plastic qualities, it is essential to the achievement of high fired whiteness. This is because it contains a low content of coloring elements such as iron and titanium. For sanitary ware, the product is formed by casting (either in plaster, or resin moulds under pressure) **[4].** Kaolin contributes the rheological properties that enables the casting slip to flow and drain after the cast formation **[1].**

1-3-3 Refractories:-

Refractories are produced from natural materials, combinations of compounds and minerals, such as kaolin, which are used to build structures subjected to high temperatures, ranging from simple to sophisticated products, e.g. from fireplace brick linings to re-entry heat shields for the space shuttle. In industry, they are used in boilers and furnaces of all types' reactors, ladles, stills, kilns and so forth **[16].**

1-3-4 Paint:-

Kaolin is used very widely in paint formulation. Kaolin used in paint trade range generally in average particle size from 0.5 to 5 µm, the properties in paint vary with the particle size and the same particle size are not equally acceptable in all types of paint. The amount of kaolin in paint formulations varies with the type of paint. In general the kaolin must be water washed chemically bleached and fractionated to produce a controlled particle size distribution **[4].** Kaolin can improve the optical and mechanical properties of paint which is widely used in satin and matt paints where they can deliver increased whiteness and it is particularly useful as a partial replacement for TiO_2 pigment **[17].**

1-3-5 Rubber:-

Kaolin is used in rubber industry. Two varieties of kaolin designated as hard and soft by rubber technicians are used **[18].** Hard kaolin produce high modulus of rupture, high tensile, strength, good resistance to abrasion and stiff uncured compounds and about 90 % of particle size is finer than 2 μm, and about 3 % are coarser than 5 μm.

Soft kaolin produces lower modulus, lower tensile strength, lower resistance to abrasion, and soft uncured compounds and only 60 % are finer than 2 μm, and about 20 % are coarser than 5 μm **[19].** Kaolin has very little covering power in rubber because the indices of refracting of clay mineral and rubber are nearly alike. Kaolin adds strength, abrasion resistance and rigidity to rubber **[3].**

1-3-6 Polyester Industry:-

Kaolin is used in plastic filling by leaching the kaolin and firing at 650 ^{0}C for 5 hours, and cooling immediately by water and re firing again to 450 ^{0}C in vacuum chamber, to achieve micro porous. This kaolin has surface area larger than kaolin used before treating, so the electrical resistance will increase 43% - 73% **[20].**

1-4 Kaolin as fillers:-

Kaolin is used as fillers. The selection is frequently a matter of coast and the preference of individual paper – mill operators. A compilation of the properties of widely used kaolin is given in table (1-1). The brightness varies from about (80-84) % although sometimes slightly lower values are acceptable. The residue on a 325 mesh screen is generally lower than about 15%.

The particle size distribution varies considerably from one kaolin to another, usually there are relatively small amount of particle coarser than about 10 μm and finer than 1-2 μm. A moderate range of particle size is desired as it favors increased characteristics of filler kaolin is not important, but the kaolin must be easily dispersed **[3, 4].**

Kaolin has been slurred in water and centrifuged to remove impurities and produce specific particle size fractions. The refined slurry is either dewatered (to reduce soluble impurities) and dried, or concentrated to 70% solids and sold in slurry form to the Paper Industries. Kaolin often treated to improve brightness. This includes chemical bleaching and/or high-intensity magnetic separation to remove iron and titanium impurities **[21].**

(Figure 1-2) clearly demonstrate the importance of filler and coating pigments in the manufacturing of paper **[22].** Coating base papers are loaded with secondary pigments coated broke and, if paper quality demands, with some primary filler as a top up. Another source of pigment is represented by the reused waste paper. Newsprint produced in Europe, contains up to 12 % filler and 88 % fiber **[23].**

Table (1.1) properties of kaolin as filler ***[21].***

	Filler wt% clay	**Coating wt% Clay**
Particle size range (μm)		
0 - 0.5	27	44
0.5 – 1	28	28
1 – 2	24	18
2 – 5	21	10
Maximum screen residue, wet 325 mesh	0.15	0.005
Brightness	82.5 – 84	86.5 – 88
pH-value	4.2 – 5.0	6.3 – 7.0

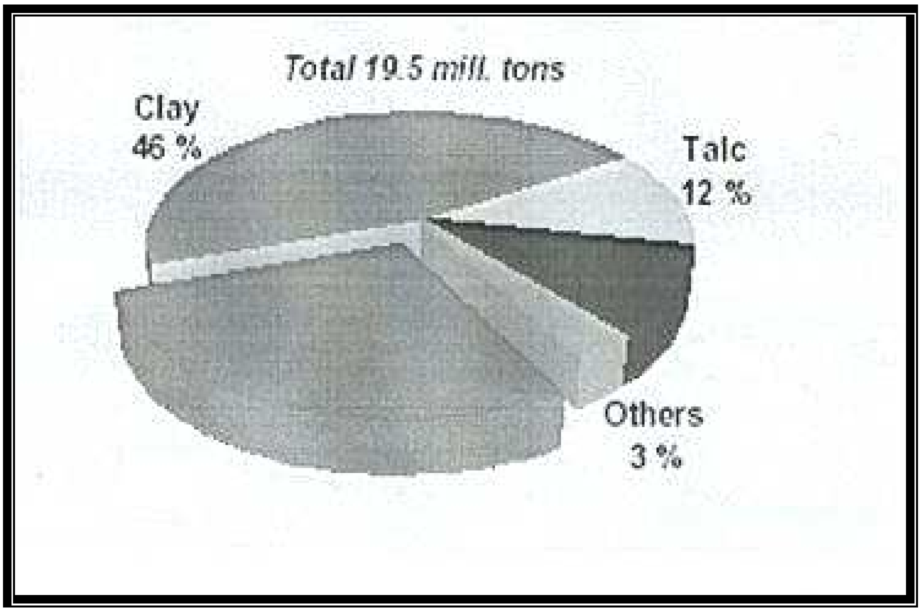

Figure (1-2) percentages of the clay used in the industries in world ***[23]***

1-5 Kaolin as coating:-

Coating kaolin is usually produced the wet process and are chemically bleached to attain the desired brightness, which is frequently in the range from 85-88 %. Table (1-1) shows that coating kaolin yields only a trace of residue on a 325 mesh screen (less than 1%) and a very small quantity of particles coarser than 2µm. In the best grades of coating kaolin the bulk of particles are finer than about 1µm**.** Kaolin particles are inherently white flakes with smooth surfaces. In the coating operations these flakes are plastered on the fiber surface with their plane surfaces parallel **[3]**. Kaolin particles smaller than about 2µm, appears as single flakes, whereas larger particles tend to be aggregates of these flakes. This, according to the literatures, explains the superior coating qualities of clays with all particles smaller than 2 µm, the suitability of kaolin for paper coating increases as the perfection of the crystallinity of the kaolin particles increases. That crystallinity is not a function of the size of the particle; i.e., particles less than 0.25 µm may be well crystallized **[24]**. To produce the kaolin for coating uses, usually water washed used to partially remove surface hydroxyl groups. It is increases brightness; it useful in the Paint Industry, as well as oil absorption and hardness. The partial or complete removal of surface hydroxyls provides a corresponding decrease in surface activity **[25]**.

1-6 The effect parameters for kaolin in the paper industry:-

1-6-1 Viscosity:-

Viscosity means the resistance to flow, it arises from internal forces between the ions or molecules in the liquid. The unit of the viscosity measurement is the poise, which is equal 1 dyne $.cm^2/sec$ **[26].** The difference in viscosity of kaolin reside somewhat in the surface characteristics of kaolin particles, and in variation in their shape which extremely difficult to detect. The surface characteristics would be a consequence of slight variations in kaolin. Viscosity is generally measured in rotational viscometer; there are various types of such instrument **[27].**

1-6-2 pH - Value:-

Is the measure of acidity or alkality of the suspension, in other words, it means the measure of the balance of the positive hydrogen ions and negative hydroxyl ions. When pH is balanced, it has a measure of 7.0 and the suspension considered neither acidic nor alkali. When pH is tested to be below 7.0 (6.9 or less), the suspension considered to be acidic. When the suspension is tested to be above 7.0 (7.1 or more), the suspension is considered to be alkaline. When the measuring is neutral (7.0) has equal number of hydrogen ions and hydroxyl ions, when suspension is low in pH have more hydrogen ions than hydroxyl ions **[28, 29].**

1-6-3 Particle size distributions:-

The particle size distributions vary from one kaolin to another, there are relatively small amount of particles coarser than 10 µm, they can reduce performance rather than extend or reinforce. And finer than (1-2 µm) are used primarily as diluents and usually have significant affect, positive or negative. The ranges (1-30 µm) reinforce kaolin as filler, significantly improve kaolin properties. The particles shape plays significant role in its ability to intercept stress applied to the kaolin **[30, 3].** In general isometric particles those having an important difference in length, width are more effective as reinforcement than isometric particles, those similar in length and width. The basic particles shapes characteristics of kaolin are shown in (figure 1-3).

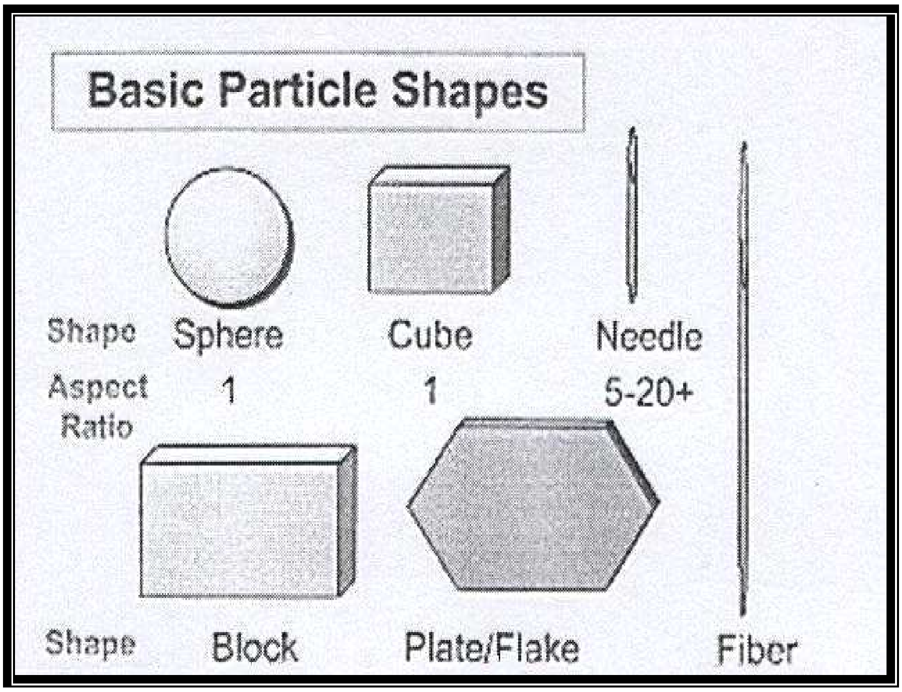

Figure (1-3) some shapes of the particle size ***[31]****.*

1-6-4 Brightness:-

Brightness is the important property of kaolin in the paper industry. For this purpose the material has to be white, the extremely fine particle size must be less than (2μm), and to be of smooth texture to give requisite degree of brightness. The measurement of brightness factor has become standard procedure for acceptance in paper industry. Kaolin to be tested is dried at 105 ^{0}C, and brushed through a 200 mesh screen. A cylindrical of clay weighing about 15 gm is pressed under a load of about 40 N/cm^2 against a glass plate. The compacted kaolin cylinder is carefully removed from the glass plate, which has given it a smooth surface **[32].**

It should be capable for accepting reflected light over a reasonably wide angle to allow for the scatter which normally occurs. The total reflected light is concentrated in a prism system, and focused on a photocell where its intensity is measured. The particle shape has an appreciable effect on the brightness, so TiO_2 is valued for this purpose and it is most effective when present in small particle size (0.5 μm) and when the particles are in the form of perfect spheres **[30, 32].**

1-7 Process Parameters:

1-7-1 Mixing

The mechanism of mixing is influenced by many factors such as the shape and size of the mixing vessel, the physical properties of the solid particle and the operating condition **[33].** Mixing, an important operation in chemical process industries can be divided into five areas: -liquid-solid dispersion, gas-liquid dispersion, liquid-liquid dispersion, the blending of miscible liquids, and the production of fluid motion.

Mixing performance is evaluated by two criteria, the first is physical uniformity, i.e., physical properties required in terms of samples of uniformity in various parts of mixing vessel, and the other criterion is based on mass transfer or chemical reaction.

The elements of mixer design are the process design fluid mechanics of impellers, impeller power characteristics-relate impeller power, mechanical design shafts and drive assembly **[32, 33].**

1-7-2 Drying

Drying can be defined as the removal of water from a granular material by evaporation **[34].** This process involves both the transfer of heat from the surrounding environment to the solid-water system and the simultaneous transfer of water vapor in the reverse direction **[4].** Drying is accomplices by shrinkage, which tends to bring the particles so close together that attractive

forces become so strong that water can no longer penetrate between them, the wetting and moderate drying, frequently tend to increase the plastic properties of clay mineral **[3].**

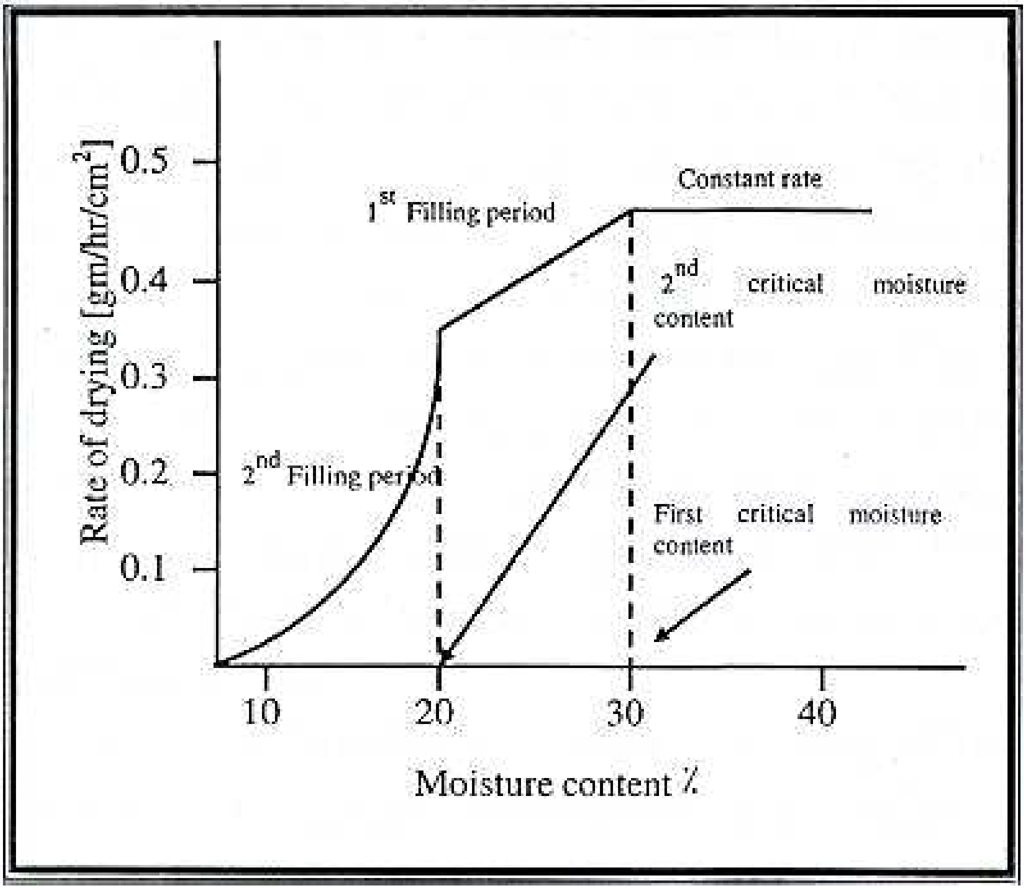

Figure (1-4). Rate of drying curve ***[35]***

The rate of drying process is illustrated in figure (1-4), in this figure there are three periods can be distinguished, the first: - is the constant rate period, during which the rate of evaporation is independent on moisture content. The second is the first filling-rate period, during which the rate of drying is very often a linear function of the moisture content, and the third is the second filling-rate period with a curvilinear relation between rate of drying and moisture content. The constant-rate period and the first falling-rate period ends are termed the first and second moisture content respectively **[35].**

1-7-3 Settling

The rate of settling of the particles in a stable colloidal dispersion depends on the size and shape of the particles and on the difference between the density of the particles and that of the liquid. The distinction between a sol and a suspension is based on the different settling rates of the particles. The large particles of suspensions are of the coarsest sols settle to a bottom sediment, leaving a particle-fn supernatant liquid. In finely dispersed sols, settling may be effective counteracted by diffusion forces. Barring convection currents, an equilibrium state is attained in which the particles are distributed in the same way as the gas molecules in the earth's atmosphere. Settling is sometimes also counteracted by particle-interaction forces **[36, 37].**

1-7-4 Filtration:-

In the filtration of suspensions, the properties of the filter cake depend on the degree of peptization or flocculation of the suspension in the same way the sediment properties do. When a stable suspension is filtered on a filter which retains the small individual particles, a thin and compact filter cake is obtained. Such a filter cake is rather impermeable, and soon after he first layers of the cake are deposited, the filtration process becomes very slow **[38].** The filtration of a flocculated suspension yields a rather thick and porous filter cake. Usually, although not necessarily always, the permeability of such a porous filter cake is high, and a reasonable filtration rate is maintained. of course, it is possible for the pore openings of the filter to be dogged by the particles, and this clogging effect may occur in stable as well as in flocculated suspensions. In that case, the filtration process determined by the filter clogging, and the permeability may be independent of the degree of stability of the suspension **[36, 38].**

1-8 Aim of the study:-

This study is carried out to investigate the possibility of using Iraqi clay as filler in the paper industry according to the existence of the large amount of Duekhla kaolin in Iraq. The clay propriety criterion is limited by the amount of titanium dioxide (TiO_2), iron oxide (Fe_2O_3), and Free silica (SiO_2) as impurities, so this research is concentrated on removing these impurities for improving the Iraqi clay properties which is important in the paper industry. Also making different measurements to optimize new properties that have been observed after removing these impurities to support the possibility of using Duekhla kaolin as filler in the paper industry and other industry branches as mentioned before.

2-1 Introduction:-

Clay minerals are the main components of suspended solid material in natural waters, responsible for the transport of inorganic and organic contaminants. A colloidal solution may be defined in general terms as a suspension of particles in liquid, where the grain size of the solid is so small that they will not settle; yet at the same time they cannot be regarded as being in true solution **[39].** When clay minerals are dispersed in water there is an adsorption of ions on the surface of the constituent particles, one type of ion (either positive or negative) attaching itself to the solid and the other, counter ion, free in water yet held in close proximity by attraction. As a consequence the solid particles become charged. Various forces act on colloidal particles suspended in a medium, and these determine the behavior of slips and slurries which are essentially fine-particles suspensions, gravitational forces, and colloidal particles. Colloidal particles when suspended in water are charged and are surrounded by a water shell. The molecules of water within this shell are rigidly held by particle and have a different character and properties from those in the remainder of the dispersion medium **[40].**

2-2 Flocculation and Deflocculation process:-

Flocculation means the process of the formation of aggregates which the rate of the aggregation is not negligible, this term is often used interchangeably, but some authors prefer to introduce a distinction between flocculation, implying the formation of compact aggregates, loading to the macroscopic separation of flocculation, implying the formation of a loose or open network which may or may not separate microscopically **[41]**.

The reversal of flocculation, i .e, the dispersion of aggregates to form a colloidal stable suspension, is called deflocculation, which means that the particles do not aggregate at a significant rate. The rate of aggregation in general is determined by the frequency of collisions because of the Brownian motion of the dispersed clay particles, after collision they separate again. But it different when a few amount of salt is added to the clay dispersion. The particles begin to stick together upon collision, and agglomerates grow in the suspension, the agglomerates appear as flocs which settle rather quickly. The suspension is finally separated in bottom sediment and a clear **[41, 42].**

The deflocculation process increases the repulsion on receptive particles so that they move a part, but flocculating salts have the opposite effect. Fine particles no longer repel each other but aggregate into flocs. The sedimentation is the settling of suspended particles under the action of the gravity. In the flocculation or unstable colloid the attractive forces between particles is attributed to the general van de Waals attraction forces between all the atoms of one particle and all the atoms of another particles. The total attractive force between the particles is the sum of the forces between the atom pairs. The magnitude of this total force depends on the size and the shape of particles and one the character of the dispersion medium **[43].**

In the deflocculation or stable colloid, the particles attraction is practically the same as in the flocculated sol, and counteract by a repulsive force between the particles, which is often an electrical nature. The magnitude of the electrical repulsion due to particle charge depends on the presence or absence of ionized salt in the sol. Hence the attraction is independent of the salt concentration, but repulsion decreases with the increasing salt concentration **[42, 44].**

2-3 Dispersion method:-

The dispersion can be defined as the propagation of the fine for any materials like clay in a certain medium like water, where these particles are arranged in a liquid medium regularly. The later can be called as "dispersion phase", and the system take place in this dispersion medium is called "colloidal state". The propagation process is either mechanical or any another process. The stirring of the mixture during the dispersion process make the particles to colloid with each other and work on coagulate these particles, the vander waals forces act between these particles to bring them together by vander waals bonds. Therefore it is necessary to use dispersion agent called peptizer which have the following effect **[45]**:-

1- Wetting the powder which includes three periods.

A- Adhesion period the adhesion that happene between dispersant medium liquid and the clay particles.

B- Penetration period the penetration means penetrating the dispersant medium liquid into the clay prose.

C- Spread period this means spreading the dispersant medium liquid as a thin film on pores interior surface.

2- Dispersant agent helps into breaking the flocs and the large particles

2-4 Stability of kaolin particles in an aqueous:-

When an electric field is applied to a hydrophobic sol, the particles move toward one of the electrodes. When the polarity of the field is reversed, the particles immediately change direction and move to the other electrode. In some types of sols, the particles move toward the positive electrode; in other sols, they move toward the negative electrode. Apparently, both negative and positive sols exist. For example, the particles in clay sols are negatively charged, since they move toward the positive electrode. Other negative sols are silica and quartz sols, sulfur sols, and sols of several sulfides. Examples of positive sols are ferric hydroxide sols and other metal hydroxide sols. Like an ionic solution, the hydrophobic sol does not have a net electric charge; therefore, the particle charge must be internally compensated in the sol. The internal balance of charges in a sol is incorporated in the concept of the electrical double layer. The double layer consists of the particle charge and an equivalent amount of ionic charge which is accumulated in the liquid near the particle surface. The accumulated ions of opposite sign are called the counter-ions **[41, 42].**

The particle charge may be created in two different ways:-

1. Imperfections of the crystal structure of the particle may be the cause of a net positive or a net negative charge. Such a net charge will be compensated by the accumulation of an equivalent amount of ions of opposite sign in the liquid immediately surrounding the particle, keeping the whole assembly electro neutral. This situation is schematically sketched in figure (2-1) this origin of an electric double layer is comparatively rare in hydrophobic colloids, but, actually, the clay particle is an example in which an electric double layer originates from crystal imperfections.

This fact is responsible for certain unusual properties of clay sols and suspensions which are not generally encountered in hydrophobic colloids **[42].**

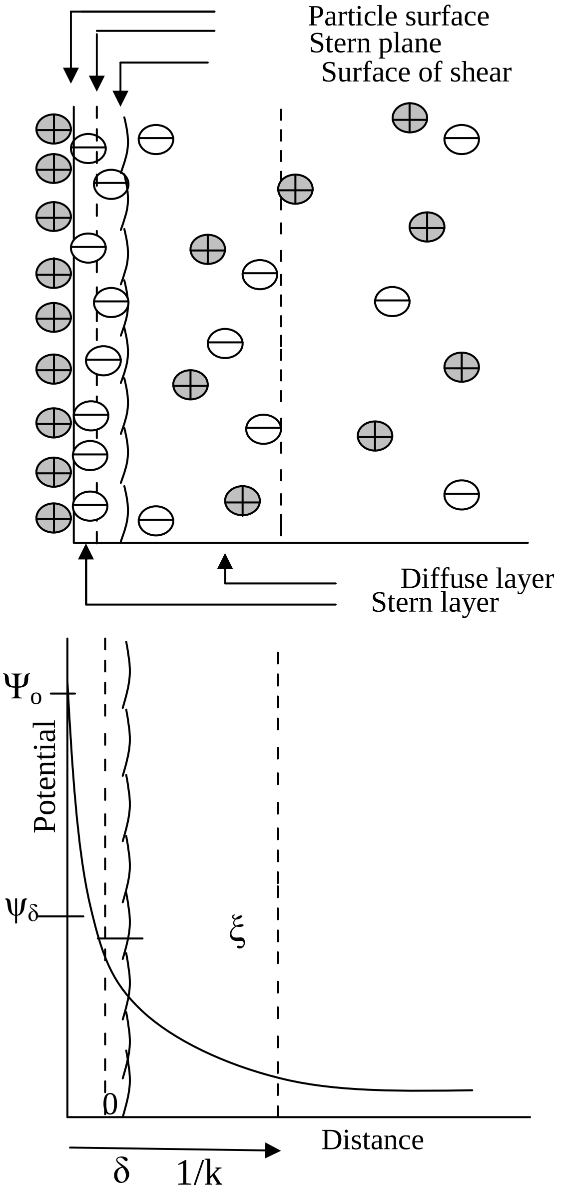

Figure (2–1).Schematic presentation of the distribution of dissociated charges expanding into the liquid phase ***[42].***

2. In most hydrophobic sols, the particle charge is created by the preferential adsorption of certain specific ions on the particle surface. Such ions are called peptizing ions for the sol, since they create the stabilizing or peptizing charge. The adsorbed peptizing ions constitute the inner coating of the electric double layer. An equivalent amount of counter-ions is accumulated near the charged surface, constituting the outer coating of the double layer. The charging process requires the presence of a sufficient amount of an electrolyte containing the kind of ions which are specifically adsorbed on the particle surface. Such an electrolyte is called a peptizing electrolyte.

The other ions of the electrolyte supply the counter-ion charge in the outer coating of the double layer. For those sols which acquire their particle charge by peptizing ion adsorption, the previous statement that a sol in pure water is stable must be amended; a certain amount of peptizing electrolyte must be present. However, it is not always necessary to add a peptizing electrolyte, since the dissolution products of the colloidal material or the dissociation products of water sometimes act as peptizing electrolytes **[36, 46].**

2-5 Dispersant agents and their importance in dispersion:-

The importance of using the dispersant agents to improve the efficiency of dispersed medium wetting period of the clay particles, and improve the best particles stability in the dispersant medium. Kaolin particles stability properties have been greatly affected propagation into the dispersant medium in the case of using the dispersant agent. Because the later one will lead to the formation of the micelles colloid in the water system with the external surfaces of kaolin particles **[46, 47].**

So this process could improve the particles stability in the dispersant medium and making the ionic exchange between the disintegrated ions and dispersant agent's positive ions, in order to improve the stability of these particles in the dispersant medium. Also these dispersant agents can make the fluidity of kaolin particles in the water system more easily during shaking process, and this process will decrease the dispersant medium viscosity **[47].** The most important dispersant agents are:

Sodium phosphate, Sodium carbonate, Sodium hydroxide, Sodium oxalate, Ammonia, and Sodium silicate. And the best dispersant agent is sodium phosphate that improved high efficiency on the dispersed clay particles.

2-6 Sedimentation method:-

The rate of sedimentation of suspended particles increases markedly upon flocculation because of the large size of the aggregates. The effect is more pronounced in sols than in suspensions since the larger particles of a stable suspension settles rather rapidly **[47].**

Often of greater importance in technology is the difference between the structure of sediments of flocculated and of stable suspensions. Sediments of flocculated suspensions are usually much more voluminous than those of stable suspensions of the same concentration. At first sight, it seems somewhat paradoxical that the repelling particles of a stable suspension should obtain a higher degree of compaction in the sediment than the attracting particles of a flocculated suspension. However, when the individual particles of a stable suspension reach the lower part of the vessel, they are able to slide and roll past each other because of their mutual repulsion, and therefore they reach the lowest position in the vessel.

In this way, rather closely packed and dense sediment is obtained, although the mutual repulsion between the particles may keep them from coming into actual contact (illustrated in Figure2-2a*)* **[36, 48].**

In the flocculated suspension, on the other hand, the haphazardly formed voluminous floes settle as such and pile up at the bottom of the vessel to form voluminous sediment with large void spaces in and between the agglomerates (fig2-2b).

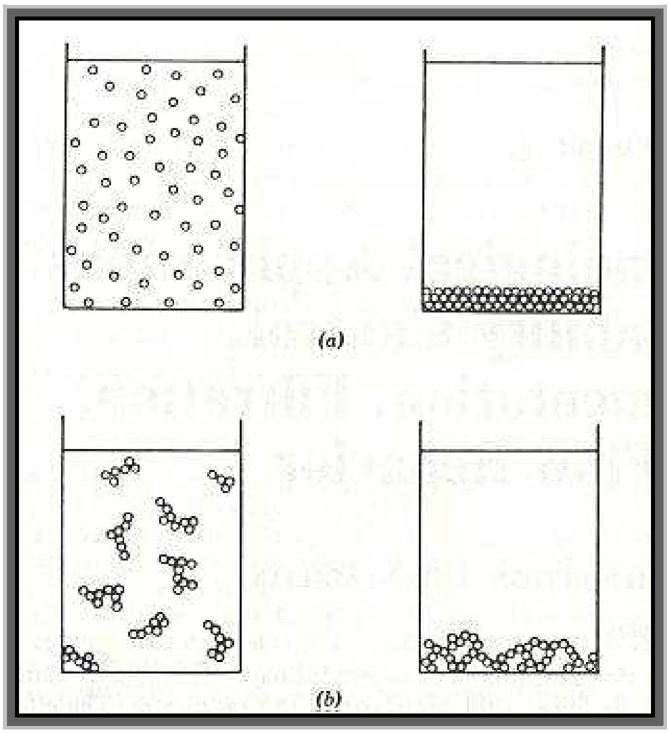

Figure (2-2) sedimentation in a peptized and in flocculated suspension. (a) Peptized suspension. (b) Flocculated suspension ***[36, 48]***

When the particles are nearly spherical, the floes and the sediment may have a string-of-beads character, whereas rods or plates will assume a scaffolding or house-of-cards type sediment structure **[36].**

It should be stressed that such differences in sediment volume will not occur when the particles are so large that gravity forces easily break the links between the particles in the settled floe. Hence coarse sands or suspensions of glass beads would settle to the same volume in both fresh and salt water **[36].**

2-7 Cumulative methods of sedimentation:-

The cumulative method is an incremental method involves the determination of the rate of change of density or concentration with time or height or both, always its used to determine the size distribution of a sediment suspension. In this method the rate at which the powder is settling out of suspension is measured **[31].** It consists of two techniques assumed as: Line – start and homogeneous suspension techniques. In both these two techniques, the analyses can be carried out more rapidly by these methods. The big advantage of cumulative techniques is that the amount of powder required is small (about 0.5 g), which reduces interaction between particles to a minimum. This is particularly useful when only a small quantity of powder is available **[49].**

2-7-1 Line-start technique:-

The powder is initially concentrated in a thin layer floating on the top of the suspending fluid; the size distribution may be directly determined by plotting the fractional weight settled against the free-falling diameter of the particles. The line-start technique is also operating on the layer principle but utilize a liquid suspension on top of clear liquid. This methods has found little favors since the basic instability of the system, a dense fluid on a less dense fluid, is responsible for what is commonly known as 'streaming';

some of the suspension settles on masse in the form of pockets of particles which fall rapidly through the clear liquid leaving a 'tail' of particles behind. To eliminate this fault by using a clear liquid with a density greater than that of the suspension, and extended the range of the technique by using centrifugal settling for the finer fraction **[50, 51].**

The line-start technique has also been used to size and fractionate $U0_3$ particles. The weight that had sediment out was determined by a device to measure the radioactivity at the bottom of the tube and the settled powder was washed out at fixed time intervals without disturbing the settling suspension **[52].**

2-7-2 Homogeneous suspension technique:-

The principle of this method is the determination of the rate at which particles settle out of a homogeneous suspension. This may be determined by extracting the sediment and weighing it, allowing the sediment to fall on to a balance pan or determining the weight of powder still in suspension by using a manometer **[53].** Consider a distribution of the form $W= f(D)$ where W is the percentage of particles having a diameter greater than D, the weight per cent P which has settled out at time t is made up of two parts; one consists of all the particles with a free-falling speed greater than that of D as given by Stokes' law, where D is the size of particle which has a velocity of fall h/t and h is the height of suspension; the other consists of particles smaller than D which have settled because they started off at some intermediate position in the fluid column. If the free-falling velocity of one of these smaller particles is v, the fraction of particles of this size that have fallen out at time t is vt/h giving:

$$P = W + t\,(dP/dt) \qquad \ldots (2.1)$$

Where W is the percentage oversize D_t. Since *P* and *t* are known, it is possible to determine W using this equation, to use the form of equation (2.1).

$$W = P - [dP / (d \ln t)] \qquad \ldots (2.2)$$

Several methods have been suggested for the determination of W using these equations. The most obvious is to tabulate t and P, hence derive dP, dt and finally W.

2-8 Swelling:-

The swelling of clays can be discussed in terms of particle interaction. Two stages of swelling should be distinguished. The first stage, up to four monolayer of water penetrate between layers of expanding clay, or between flat surfaces of adjoining particles. In the parting of the surfaces, three forces are operative-the van der Waals attraction, the electrostatic interaction of charged surfaces and cations, and the adsorption energy of the water.

From the net interaction energies, the forces operating in the stage of swelling are derived to be of the order of a few thousand atmospheres for the entrance of the first monolayer of water. The forces decline rapidly with the entrance as successive water layers. In the second stage of the swelling process in which the plates are separated to distances larger than equivalent with the thickness of four layers of waters, the swelling is now governed by double layer repulsion, which is identical with the "osmotic pressure" of the system **[52].** Seen that these micro pores vary in shape and size with changes in chemical potential and electrolyte type.

The electrolyte type affects both, the number of platelets in each stack and the average size of micro pores, the treatment of electrolyte type effects on the basic size of micro pores, with the decrease in the bulk liquid potential (more negative), both platelet spacing and micro pore size decrease **[53].**

2-9 Ion Exchange:-

Clay minerals have the property of sorting certain anions and cations, retaining these in an exchangeable state; i.e. they are exchangeable for other anions or cations by treatment with such ions in a water solution (the exchange reaction also take place sometimes in anon aqueous environment). The exchangeable ions are held around the outside of silica-alumina clay mineral structural units, and the exchange reaction generally does not affect the structure of silica-alumina clay packet. In clay minerals the common exchangeable cations are calcium, magnesium, hydrogen, potassium, and sodium, frequently in about that order of general relative abundance **[3].**

2-10 Titanium and Iron components in kaolin:-

Kaolin generally contaminated with titanium dioxide minerals to the extent of about 1.3 – 2.5 % expressed as TiO_2 which has been identified as anatas, though minor amounts of rutile are present in some deposits. The rutile mostly is inherited and the anatase formed authigenically from the chemical weathering of the other Ti containing minerals. These impurities are presumably responsible for the gray color of the anatase. This gray color decrease the whiteness of the kaolin and considerable effort is expended to remove it. It is usually heavily stained by iron and as a result varies from yellow to dark brown in color **[54].**

The iron apparently accounts for the weak magnetic properties of the anatase that allow some of it to be removed by a strong magnetic, iron is a common impurity which is rarely completely absent in kaolin, iron compounds contribute in kaolin corrosion as it used in certain applications.

They existed in kaolin as oxides or as hydroxyls they give rise to yellow, red, and grays of different intensities and degrees. So the fineness of size of iron compounds is also of importance in the color which is produced **[55].** As mentioned kaolin may colored by the presence of iron and titanium compounds. In the paper industry, the white kaolin is essential so that the color, if it exists must be removed prior to use. Four processes are claimed to be successful **[30].**

(a) Washing, in which kaolin is dispersed in water and the slurry passed through a fine sieve (60-mesh). Large iron particles are retained along with coal and stones and may be discarded. The purified clay is freed from objectionable iron-spotting which would normally have developed on firing.
(b) Magnetic separation can often be effective in kaolin which has been prior-fired to between 500-750° C. Under these conditions, some iron compounds are converted into magnetite Fe_3O_4 and can be removed by magnetic methods.
(c) Chemical solution usually by acids, although most minerals are not readily attacked and the process is expensive.
(d) Flotation methods in which iron and titanium which have a darkening effect are removed from kaolin by froth flotation.

2-11 Infrared Analysis:-

Infrared spectroscopy can be described as the use of instrumentation in measuring a physical property of matter, and then relating the data to chemical composition. The instruments used are called infrared spectrophotometers and physical property measured is the ability of matter to absorb, transmit, or reflect infrared radiation **[56].**

The basic principle of infrared instruments is to measure the vibration spectrum of a sample by passing infrared radiation through it, that wavelengths have been absorbed and what extent. Since the amount of energy absorbed is a function of the number of molecules present. The source of infrared may be a glowing filament or hot silicon carbide rod, both of which emit radiation over a wide range of frequency. The infrared beam passes through a collimator to the specimen which should be in the form of a thin film. The transmitted rays then pass through a system of mirrors on the rock salt prism, which can be rotated, so vary the frequency of radiation received on the detector **[30].** The analysis for these spectrums was carried out using two frequency regions. The details are as following:

1 - Wave, number between 3500 and 3700 cm^{-1}

The absorption in this range is due to hydroxyl group (O-H). In the structure of dioctahedral minerals, each pair of aluminum ions shares two hydroxyl groups, which are related by a center of symmetry between the aluminum ions. Sarasota **[57]** through that the absorption frequency of (O-H) bonds depends on the degree of association of these groups.

Miller **[58]** concluded that the bonds at (3718 and 3677) cm $^{-1}$ for kaolin are due to stretching vibrations of relatively unassociated (O-H) groups, i.e due to hydroxyl groups nearly free of hydrogen bounding to the other atoms.

In general, the layer-silicate structural OH groups that are comparatively slightly show absorption of high frequencies of 3600 to 3700 cm^{-1}, where as the absorbed water- shows absorption at low frequencies 3400 cm^{-1}, and another band 1640 cm-^{1} corresponding to the deformation vibration of water **[59].**

2 - Wave number between (1500 and 600) cm^{-1}.

The position and sharpness of the perpendicular vibration varied with physical state; thus in the spectra of kaolin of large crystal size, the node appears as a broad shoulder near (1080) cm^{-1} **[60].** The band intensities and shift to higher frequencies in the spectra of smaller crystals until in very finely ground material the band is at 1109 cm^{-1} smaller but distinct shifts in frequency, together with sharpening and intensification of bands as particle size decreases **[61].**

2-12 Raw materials:-

2-12-1 Kaolin Duekhla:-

Kaolin Duekhla has been collected from the west of Iraq. It is white raw material. The chemical formula is $Al_2O_3.2SiO_2.2H_2O$ (39.5% $A1_2O_3$, 46.5% $SiO_{2/}$14.0% H_2O). In systemic mineralogy, kaolin Duekhla ranks among phyllosilicates, which are stratified clay minerals formed by a net of tetrahedral and octahedral layers **[1].** Phyllosilicates are classified into the main groups according to the type of the layers, interlayer content, charge of the layers and chemical formulas. Group of kaolin includes dioctahedral minerals (1:1) with two layers, one silica [SiO_4] tetrahedral layer and one aluminum [$A1_2(OH)_4$] octahedral layer. The layers are bonded together by sharing oxygen anion between Al and Si. Together, these two layers are called platelets **[62].**

2-12-2 Sodium Carbonate"Na_2CO_3":-

Sodium Carbonate is a white, crystalline and hygroscopic powder with a purity of > 98%. Sodium Carbonate has melting point of 851 °C, it decomposes when heated at temperature greater than 400 °C, and sodium carbonate is a strong alkaline compound with pH of 11.6 for 0.1 M aqueous solution. Tensile strength and elasticity are decreased as the content of soda increase of sodium although to a lesser degree than with the other alkalis. Small increases of sodium oxide in a glaze will increase the coefficient of thermal expansion and reduce the softing point with rapid and noticeable consequences to the glaze body fit **[44].**

2-12-3 Sodium Phosphate"Na_2PO_3":-

Sodium phosphate is a white powder with density 2.484, easily soluble in water, but not in organic solution, absorbent to dampness, and turn sticky when absorbed dampness in air. It is possible to form solvent compound with metallic ions such as Ca, Ba, Mg, Cu, and Fe; it is a fine agent for water treatment **[63].** It can be used in many applications for industrial use, such as oil field, paper- making, textile, and dyeing, petrochemical industry. It is mainly used as a water softening agent in solution for printing, dyeing and boiler; diffusant in paper – making; slow corroding, floating agent, dispersing medium, high temperature agglomerant, detergent and soil analytical chemistry reagent **[44].**

2-12-4 Zinc Hydrosulfite "$ZnH_2SO_4.7H_2O$":-

It is a white, crystalline powder with density 2.87 gm/cm^3, can soluble in water easily. It has melting point 754 ^{0}C. It considered as bleaching agent has been used with considerable success to improve the brightness of kaolin, ball clay, talc, etc. zinc hydrosulfite in amounts up to 0.5 % of the raw clay are often effective. It is claimed that the greatest benefit results from a double treatment with a stage of filtration and dispersion following the first treatment. Hydrosulfite is also called dithionite in the U.K.; they are salts of the organic radicals (S_2O_4) **[64].**

2-13 the reduction of impurities in the kaolin clay:

The percentage of impurities in the kaolin clay as TiO_2, Fe_2O_3, and SiO_2 can be reduced by using $ZnSO_4.7H_2O$ according to the following equations:

$ZnSO_4.7H_2O + TiO_2 \longrightarrow TiSO_4 + ZnO_2 + 7H_2O$

$ZnSO_4.7H_2O + SiO_2 \longrightarrow SiSO_4 + ZnO_2 + 7H_2O$

$ZnSO_4.7H_2O + Fe_2O_3 \longrightarrow Fe_2 [SO_4]_3 + ZnO_2 + 7H_2O$

The salts produced from these reactions can be removed by dissolving them in distilled water and filtering with filter paper **[64].**

3-1 Raw Materials:-

The raw materials used in preparing the samples required for our investigation are:

1- Duekhla Kaolin "$Al_2O_3.2SiO_2.2H_2O$"

2- Sodium Carbonate "Na_2CO_3"

3- Sodium Phosphate "Na_2PO_3"

4- Zinc Hydrosulfite "$ZnSO_4.7H_2O$"

3-2 Sample preparation:-

Duekhla Kaolin has been collected from the west of Iraq. It is white raw material. Duekhla Kaolin treated by washing it with HC1 (4N), for time duration 24 hours, with stirring, at room temperature. The acid treatment for Duekhla Kaolin carried out to remove the free iron oxide and other impurities, which can be dissolved in HCl. The washed kaolin then separated using filter papers and under sequence of operation for dilution and filtering until the pH - value become 5. Then the separated materials dried by using furnace (GCA\PRECTSIONSCIENTIFC, model 16) at temperature range 40-60 °C for 3 hours. The dried powders of Duekhla Kaolin then milled using ball mill of porcelain body, with different sizes of spheres, for 5 hours. And finally the powders of Duekhla Kaolin then sieved with a sieve of 65 μm.

Table (3.1) Sample preparation

Process Parameter		Group No.					
Washed Duekhla Kaolin with 4N HCl, milled, particle size< 65µm.		M_1	M_2	M_3	M_4	M_5	M_6
Dispersant Material (gm)	Na_2PO_3	2.0	2.5	3.0	4.3	5.0	6.8
	Na_2CO_3	----	----	----	13	----	----
Bleaching Material (gm)	$ZnSO_4$	----	----	----	10	----	----

The study was performed by using the cumulative method as mentioned in chapter two. This method requires the using of sedimentation system which consists of six glass cylinders with height 138 cm and 4.5 cm in diameter stand vertically in order to have the sedimentation state as shown in Figure (3-1). These units are built in the laboratories to control the process. The final washed Duekhla kaolin with particle size < 65µm is divided into six parts to prepare six prepare six different groups of samples according to the added amounts of dispersant and bleaching materials, as shown in Table (3-1). The samples were prepared by using constant weight percentage of washed kaolin which is equal to 10 gm for each group. This quantity was mixed with different amounts of dispersant agent Na_2PO_3 = 2.0, 2.5, 3.0, 4.3, 5.5, 6.8 gm and diluted with distilled water till the volume becomes equal to 250 ml, with continuous stirring process for 15 minutes using magnetic stirrer (model Great Britain, serial 11750).

All six glass cylinders were filled by 750 ml distilled water then, the prepared six samples that having defined amounts of Na_2PO_3 were added to the cylinders. Volume of each cylinder becomes equal to 1000 ml then the fluid in the cylinders left to settle for 24 hour. After this period, we have got sediment in the bottom of the cylinders that related inversely to the amount of dispersant agent. The suspension over the sediment was found to be in the range from 68 cm in cylinder no. one to the height 92 cm in cylinder no. six as shown in Figure (3-1). Table (3-2) shows the parameters used in the sample preparation. Six samples were prepared, each sample take the number of the cylinder from which it prepared. Sample one is taken from cylinder one and so on. The first 20 cm of the top from all six cylinders was drawn by siphon after the period of the sedimentation to be used in measuring the viscosity of each suspension by using the device (Brook Field Viscosity, model Philips, serial 124759).

Table (3-2) The parameters used in the sample preparation at room temperature

Groups	Sodium phosphate (gm)	Duekhla Kaolin (gm)	Suspension viscosity (dyne.cm^2/s)	Height of suspension (cm)	Drawn suspension length (cm)
M_1	2.0	10	0.89	68	20
M_2	2.5	10	0.61	74	20
M_3	3.0	10	0.42	79	20
M_4	4.3	10	0.31	83	20
M_5	5.0	10	0.41	88	20
M_6	6.8	10	0.65	92	20

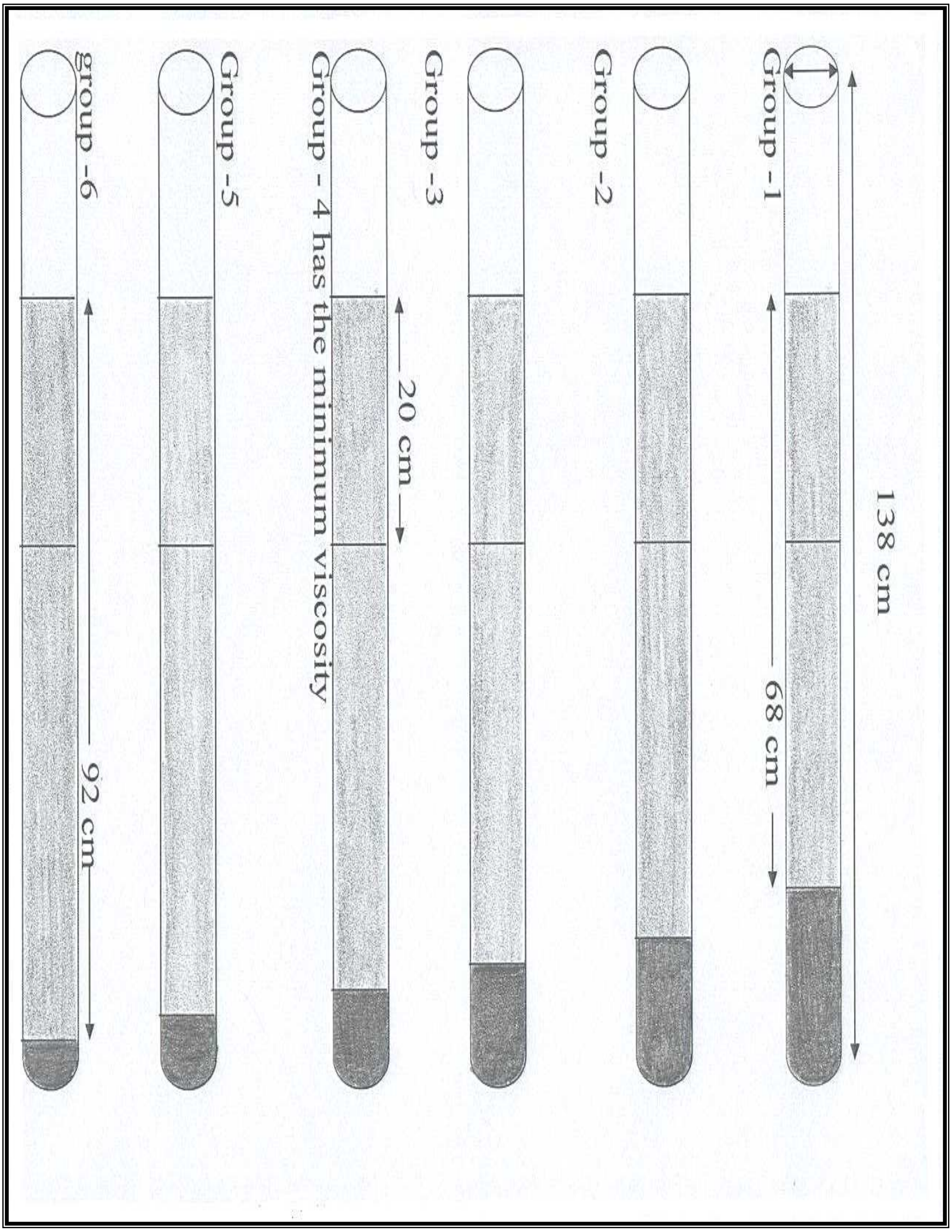

Figure (3-1) sedimentation system.

The suspension drawn from M_4, which has the lowest value of viscosity, equal to 0.31 dyne.cm^2/sec was chosen to be used in the preparation of the samples required for our study. This suspension then mixed with 10 gm of Na_2PO_3 and 13 gm of Na_2CO_3. The mixture added to distilled water to get a final volume of 250 ml with continuous mixing using magnetic stirrer for 10 minutes then powered in a clean cylinder and left to be settled for 14 hours.

The total suspension then drowns from cylinder and filtered using filter paper to remove the excess soluble salts. The filter cake then washed by distilled water three times after that it removed from the filter paper and mixed with 10 gm of zinc hydrosulfite. The mixture then added to the distilled water and the volume completed to 250 ml with continuous mixing by using the magnetic stirrer at temperature 60 ^{0}C for 30 minutes.

The mixture then dried in temperature at 30 ^{0}C, because the high temperature will convert the clay to the brick-like. So this sample is named as G_1. The above procedure then repeated six times to prepare another six samples from G_2 to G_7 using different amounts of zinc hydrosulfite as shown in table (3-3).

Table (3-3) the values of zinc hydrosulfite in each group

Group M_4							
Sample No.	G_1	G_2	G_3	G_4	G_5	G_6	G_7
$ZnSO_4.7H_2O$ (gm)	10	12	14	16	18	20	22

3-3 Measurements:-

Duekhla Kaolin was examined before and after treatment using the following techniques.

3-3-1 The chemical composition:-

The chemical composition of Duekhla kaolin was examined by (The General Company of Mining and Geological Survey). The results are given in Table (3-4) it is clear from the table that Duekhla kaolin contains many impurities before treatment which are not preferred in the paper industry.

The final samples of Duekhla kaolin after many process of bleaching with zinc hydrosulfite of all samples (G_1 to G_7) were analyzed again in (The General Company of Mining and Geological Survey) and the results are giving in Table (3-5).

Table (3-4) Chemical composition for Duekhla kaolin

Oxide	percentage
SiO_2	51.16
Fe_2O_3	1.71
Al_2O_3	33.2
TiO_2	1.2
CaO	0.23
MgO	0.41
SO_3	0.45
Na_2O	0.41
K_2O	0.40
L.o.I	10.83

Table (3-5) The chemical analysis for impurities percentages remained in Duekhla Kaolin.

Group No.	**$ZnSO_4.7H_2O$ (gm)**	**Free silica%**	**SiO_2 remained%**	**TiO_2 remained%**	**Fe_2O_3 remained%**
G_1	**10**	**12**	**46.5**	**0.98**	**1.1**
G_2	**12**	**13**	**44.1**	**0.71**	**0.93**
G_3	**14**	**14**	**43.5**	**0.52**	**0.86**
G_4	**16**	**15**	**42.2**	**0.45**	**0.67**
G_5	**18**	**16**	**41.4**	**0.28**	**0.48**
G_6	**20**	**17**	**40.8**	**0.1**	**0.32**
G_7	**22**	**18**	**39.7**	**0.09**	**0.30**

3-3-2 X- Ray measurements:-

The phase structure for kaolin Duekhla is measured by XRD Tech. by using (SIEMENS X–RAY DIFFRACTION, UNIT MODEL D – 500, KV = 40, CU Kα line, $\lambda = 1.542^{o}A$). These results are shown in fig. (4–10) for Duekhla kaolin as raw material, (4–11) is for Duekhla kaolin treated with zinc hydrosulfite respectively.

3-3-3 The infrared measurements:-

The effect of treated kaolin with zinc hydrosulfite studied qualitatively by IR measurement. The measurement has been made by using (Shimadzu Fourier Transforms Infrared model FTIR 8300 (Kyoto, Japan)). The IR spectrum for kaolin raw material shown in figure (4-12), (4-13) is for kaolin Duekhla treated with Zinc Hydrosulfite.

4.1 Discussion of results:-

4-1-1Chemical analysis:-

The chemical analyses of the treated Duekhla kaolin samples by zinc hydrosulfite are given in Table (3-5) which show the remain impurities free silica loss, SiO_2, TiO_2, and Fe_2O_3 in kaolin samples. So the values of these impurities of sample G_1 are considered to be remaining in the kaolin by percentage equal to 100%. Therefore in Table (4-1) the percentages of the removed impurities of sample G1 are equal to zero

Fig (4-1) shows the direct relation between the zinc hydrosulfite and free silica loss. Figs (4-2) to (4-4) are reveal the percentage of the impurities remain in treated samples after treated with zinc hydrosulfite. It can be noted that the values of free silica increases with increasing the amount of zinc hydrosulfite, but the other impurities decreases with increasing the amount of zinc hydrosulfite.

Table (4-1) and Figures (4-5 to 4-8) show the percentage of the removed impurities from kaolin after treatment. Fig (4-5) shows the relation between zinc hydrosulfite vs. free silica loss percentage, it increases with increasing the bleaching agent. The percentage of free silica loss is raised from 3% in sample G_2 to 50% in sample G_7. Fig (4-6) shows the relation between zinc hydrosulfite vs. the percentage of silica removed is raised from 5% in sample G_2 to 15% in sample G_7 which means that the compound silica removed increased with increasing zinc hydrosulfite. Fig (4-7) shows the relation between zinc hydrosulfite vs. titanium dioxide percentage removed from the kaolin. The percentage of titanium dioxide removed increased with increasing the added amount of zinc hydrosulfite, where the percentage is raised from 28% in sample G_2 to 91% in sample G_7. Fig (4-8) shows the relation between zinc hydrosulfite vs. iron dioxide percentage. This varies from 15% in sample G_2 to 73% in sample G_7, which is good evidence that using this bleaching agent to remove high percentage of impurities from kaolin and it can be used with considerable success to improve the brightness of kaolin for preparing it in the paper industry.

By comparing these results with other studies like Maynard studies **[65]** who worked to remove TiO_2 from kaolin which was contained about 1.64% before treating and decreased to 0.8% after treatment which means that the percentage of removed anatase from treated kaolin is 49%.Also Raghavan **[11]** reached to remove about 50% of anatase and 45% of Fe_2O_3 from kaolin by using the colloidal flocculation and magnetic separation methods.

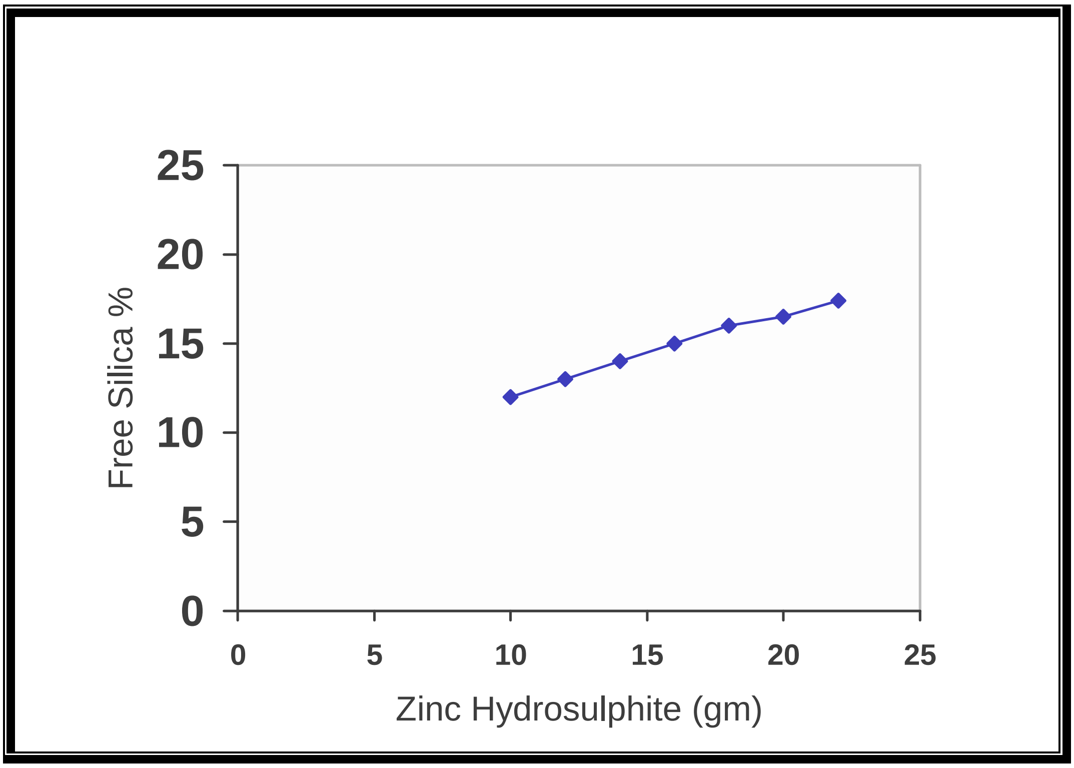

Figure (4-1) the relation between zinc hydrosulfite and free silica

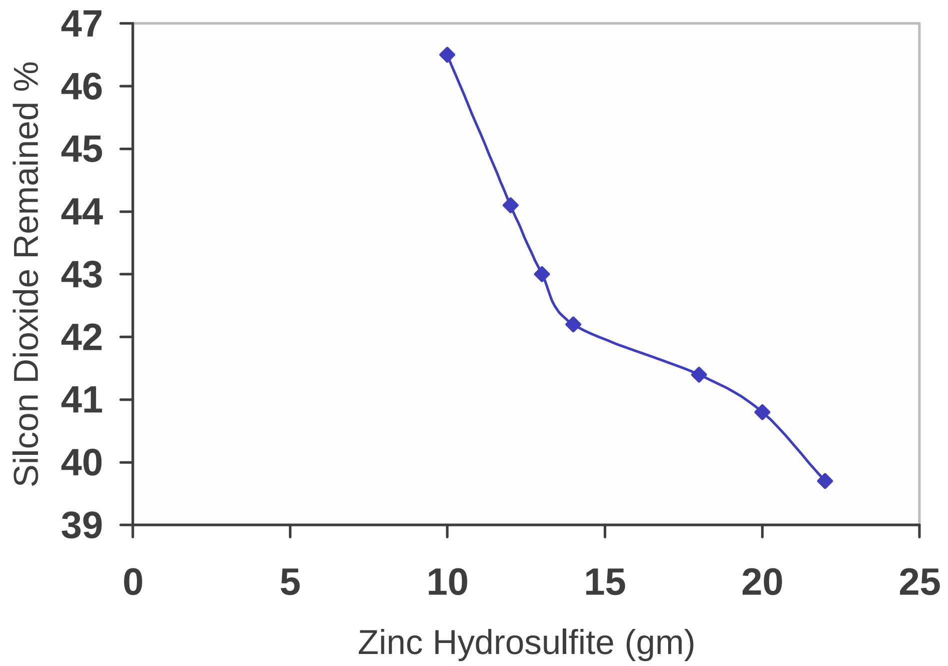

Figure (4-2) the relation between zinc hydrosulfite and silicon dioxide

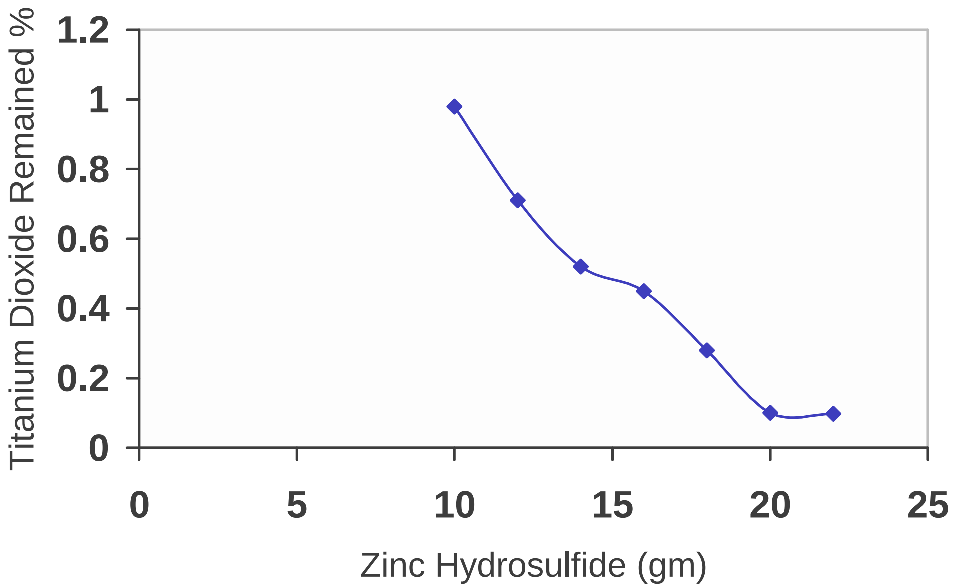

Figure (4-3) the relation between zinc hydrosulfite and titanium dioxide

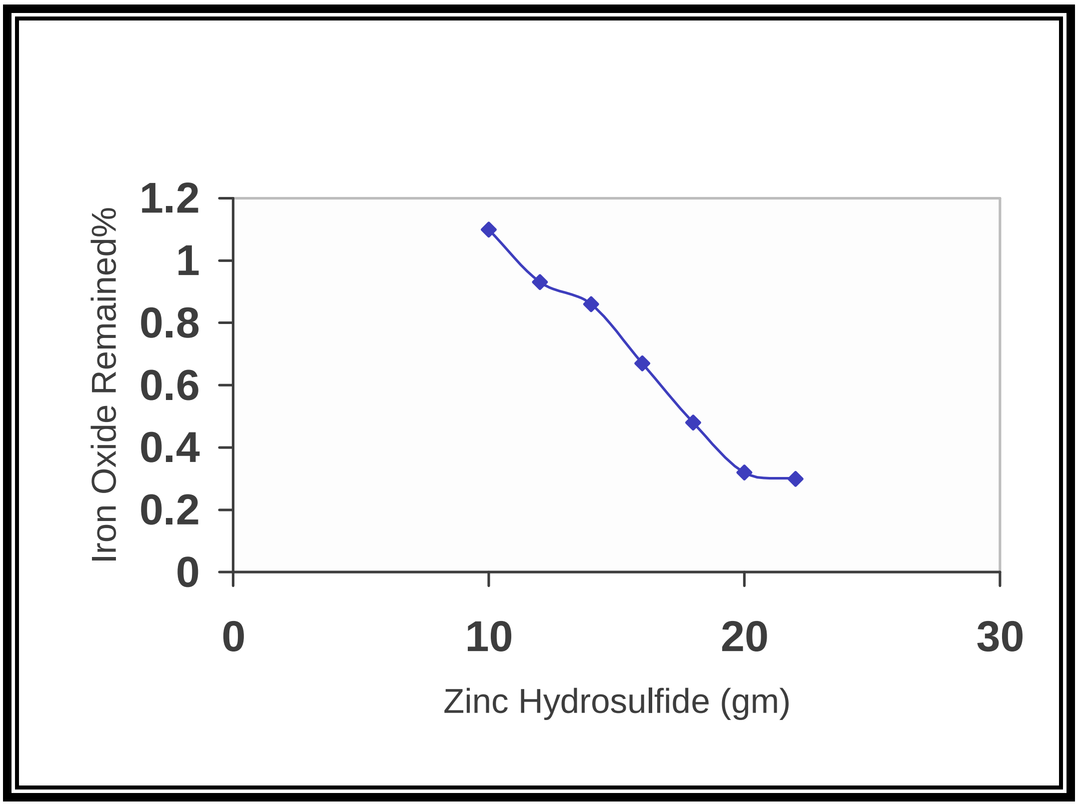

Figure (4-4) the relation between zinc hydrosulfite and iron oxide

Table (4-1) the percents of the removed impurities from Duekhla kaolin.

Group No.	$ZnSO_4.7H_2O$ gm added	Free SiO_2 loss%	SiO_2 % removed	TiO_2 % removed	Fe_2O_3 % removed
G_1	10	0	0	0	0
G_2	12	3	5	28	15
G_3	14	17	6	47	22
G_4	16	25	9	54	40
G_5	18	30	10	71	56
G_6	20	42	12	90	71
G_7	22	50	15	91	73

The reason behind reducing the percentage of impurities is the chemical reaction happened when adding the bleaching agent as zinc hydrosulfite to the samples from G_1 to G_7 by making a soluble salts represented as $TiSO_4$, $SiSO_4$, $Fe_2[SO_4]_3$ as shown in the chemical equations in section (2-14).

In this condition, adsorbed impurities are released from the kaolin surface and gradually form visually observable flocs which are capable of penetrating and settling from the clay system, and can be removed from kaolin by filtration process and dilution with distilled water.

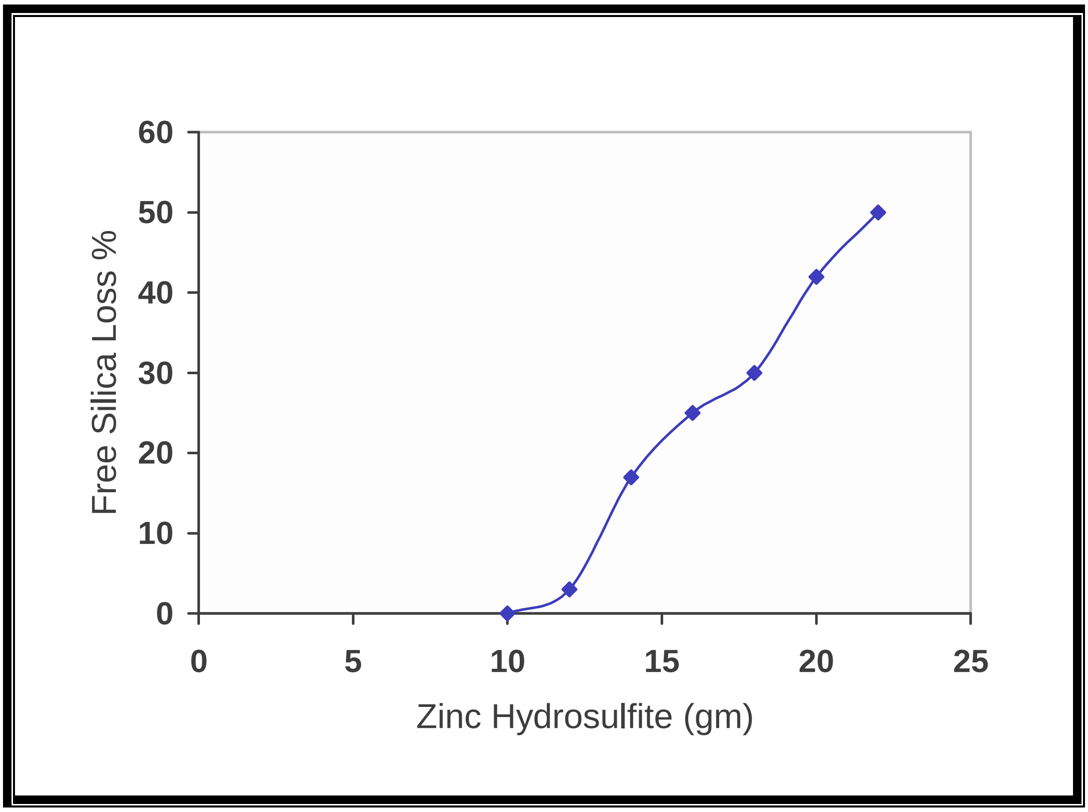

Figure (4-5) The relation between zinc hydrosulfite and free silica loss

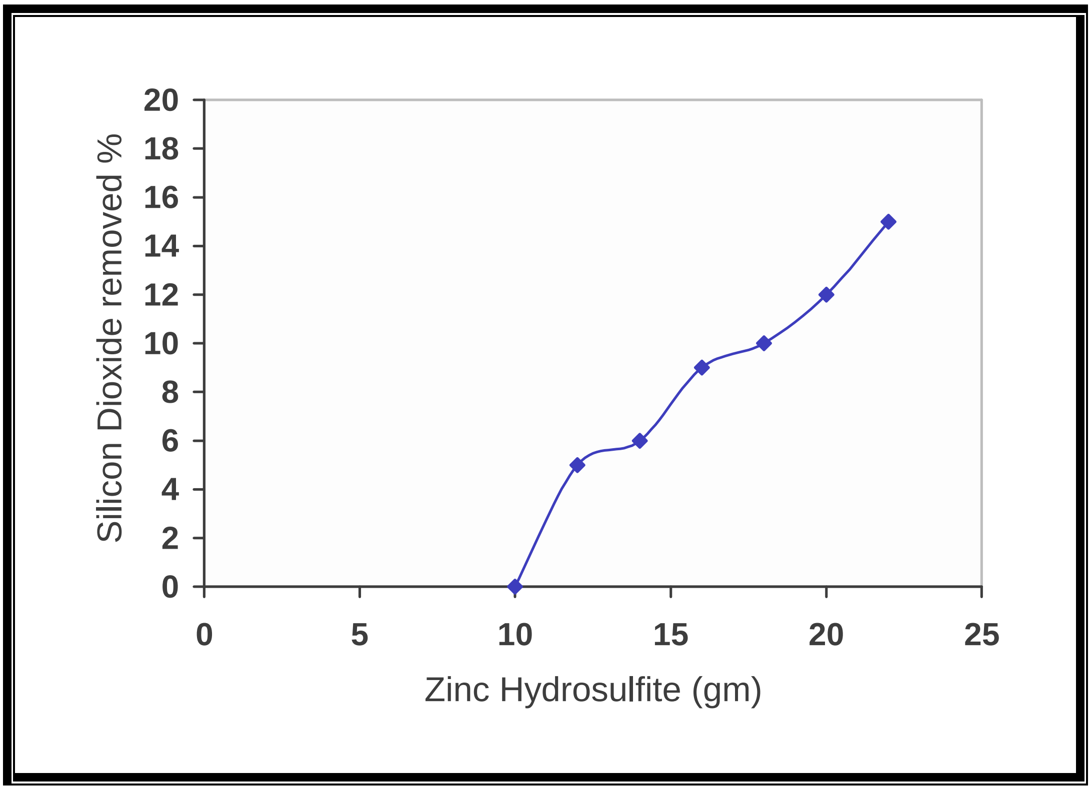

Figure (4-6) The relation between zinc hydrosulfite and compound silica

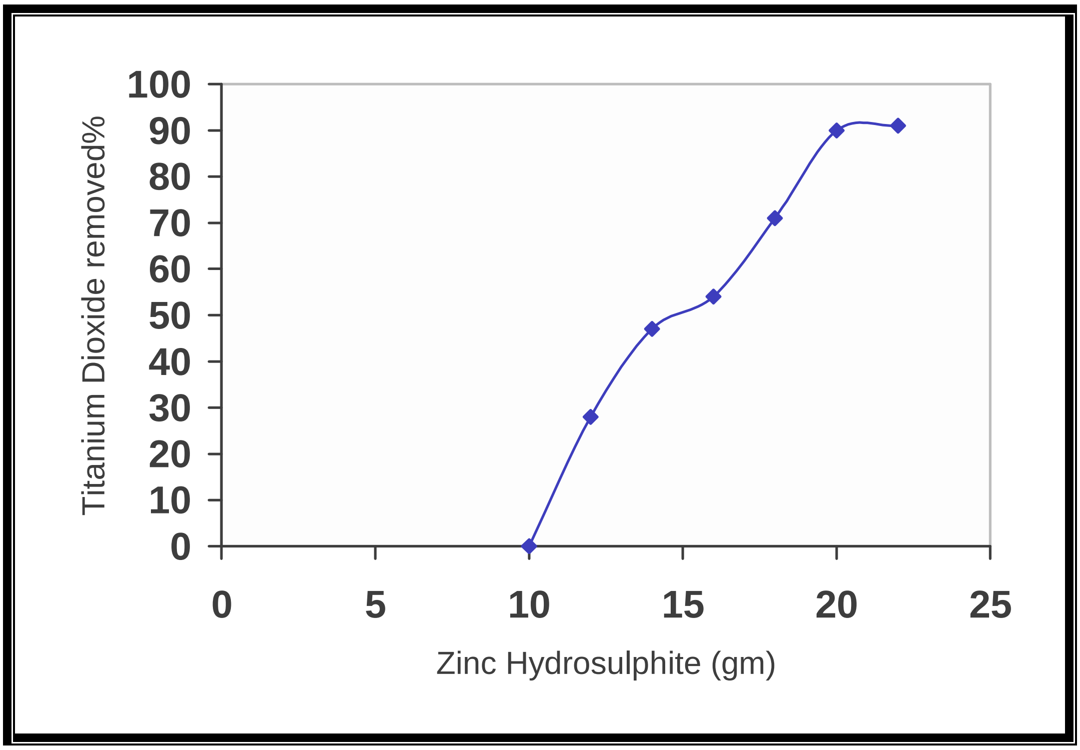

Figure (4-7) The relation between zinc hydrosulfite and titanium dioxide

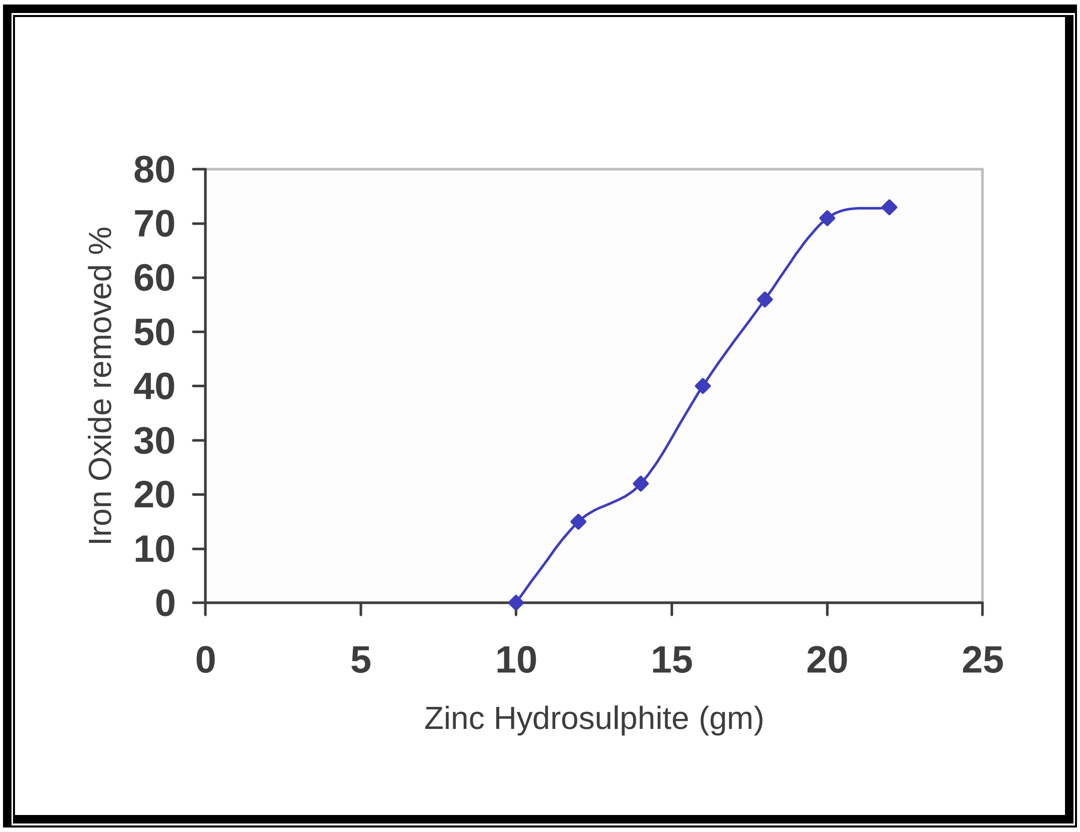

Figure (4-8) The relation between zinc hydrosulfite and iron oxide

Fig (4-9) shows the effect of sodium phosphate as a dispersant agent on the viscosity of kaolin and why we used the amounts of this dispersant agent from 2.0 gm in M_1 to 6.8 gm in M_6 with 10 gm of kaolin. The results mentioned above are based on using the kaolin clay with minimum value of viscosity after addition of sodium phosphate. The six samples (M_1 to M_6) which were prepared by the addition of 10 gm of kaolin with different amount of the dispersant agent, ranging from 2.0 gm in sample M_1 to 6.8 gm in sample M_6. We started the addition of dispersant agent from 2.0 gm, because it found before that using lower values (less than 2.0 gm) had no effect on the viscosity and most the particles of kaolin were sediment in the bottom of the cylinder without any dispersion in the colloidal system.

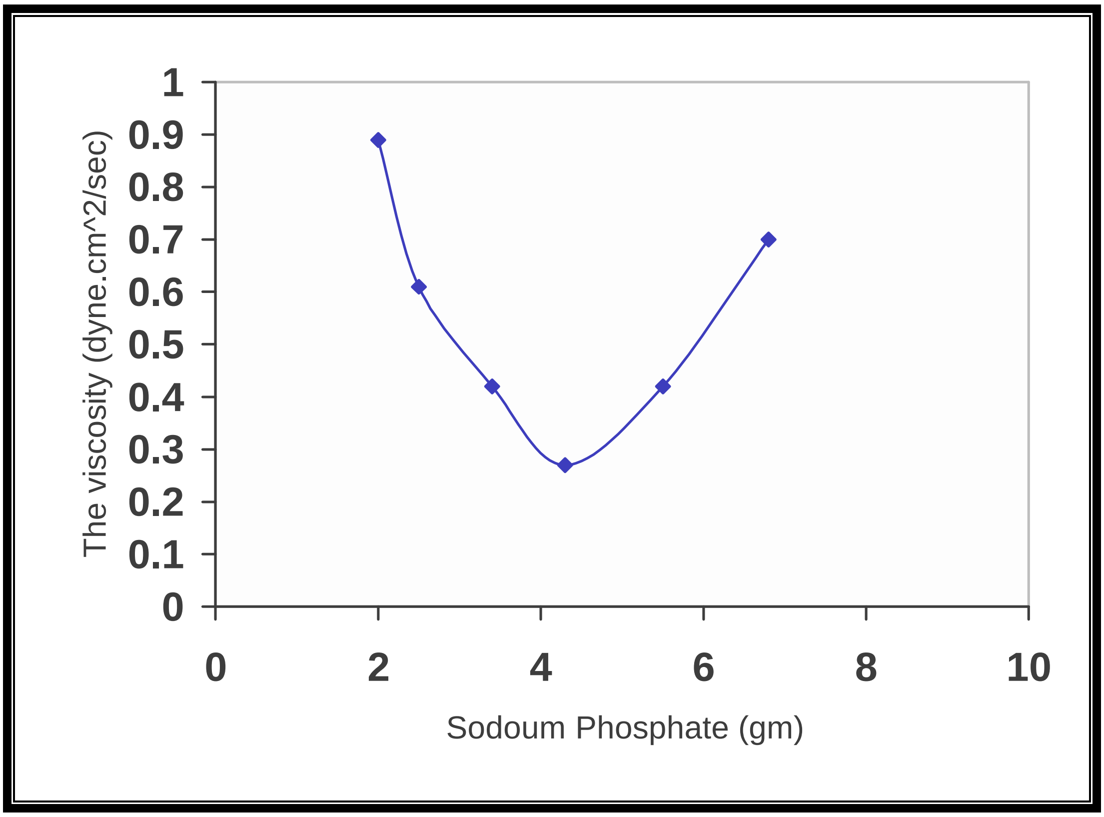

Figure (4-9) The effect of sodium phosphate on the viscosity of Duekhla kaolin

The addition of the dispersant agent with amount greater than 7.0 gm to 10 gm of kaolin will lead to the saturation and whenever we add the dispersant agent above 7.0 gm to the same amount of kaolin the viscosity will not affected strongly and there was a very slight increasing in viscosity that can be neglected.

The reason behind the using of the dispersant material with the kaolin is to reduce the mobility of kaolin particles and creates a stabilized suspension because of the well known electrolyte effects on charged kaolin particles. Reduced mobility of kaolin imparts a stabilized structure of suspension compared with fully deflocculated and flocculated systems.

This suspension stability is evidenced by greatly reduced settling rate of kaolin in our suspension. In this condition, adsorbed anatase impurities are released from the kaolin surface and gradually form visually observable flocs which are capable of penetrating and settling from the clay system. This process contrasts with ordinary classification in dispersed slurries, where the anatase impurities appear to remain attached to kaolin particles.

Thus the distribution of TiO_2 impurities in conventionally classified kaolin substantially reflects the degree that various size fractions of kaolin adsorb titanium impurities. In such suspensions anatase impurities are not fully librated and therefore are not free to settle in accordance with their size and mass.

4-1-2 X-ray and IR measurements

Figure (4-10) shows XRD pattern for Duekhla kaolin as raw material, and figure (4-11) shows XRD pattern for Duekhla kaolin treated with zinc hydrosulfite. By comparing these two figures with ASTM cards, the results show that the original Duekhla kaolin is composed of kaolinite and quartz, and it is not affected by all the processes of the treatments carried out on kaolin, but only we reduce the percentage of the removed impurities from kaolin and it becomes ready to be used as filler in the paper industry.

IR absorption bands curves for Duekhla kaolin as raw material is shown in fig (4–12) and for Duekhla kaolin which was treated with zinc hydrosulfite is shown in fig (4–13), this resulting from the present investigation is listed in table (4–2) are comparable with data listed by Marel **[66].** The study of the two figures showed that the original kaolin Duekhla is not affected by all the process of the treatments carried out on kaolin, but only we reduce the percentage and it become ready to be used as filler in the paper industry.

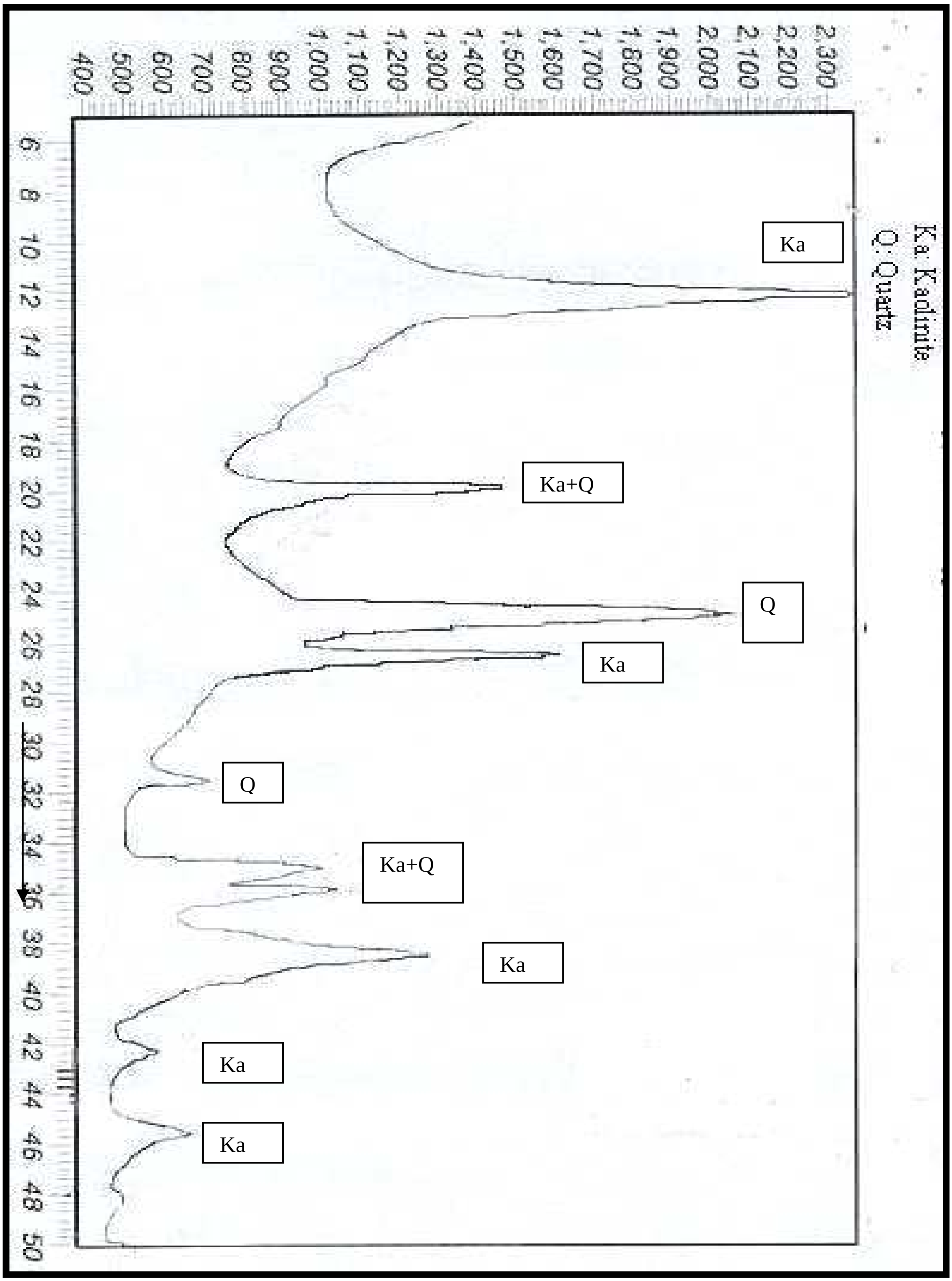

Figure (4-10) XRD pattern for Duekhla kaolin raw material

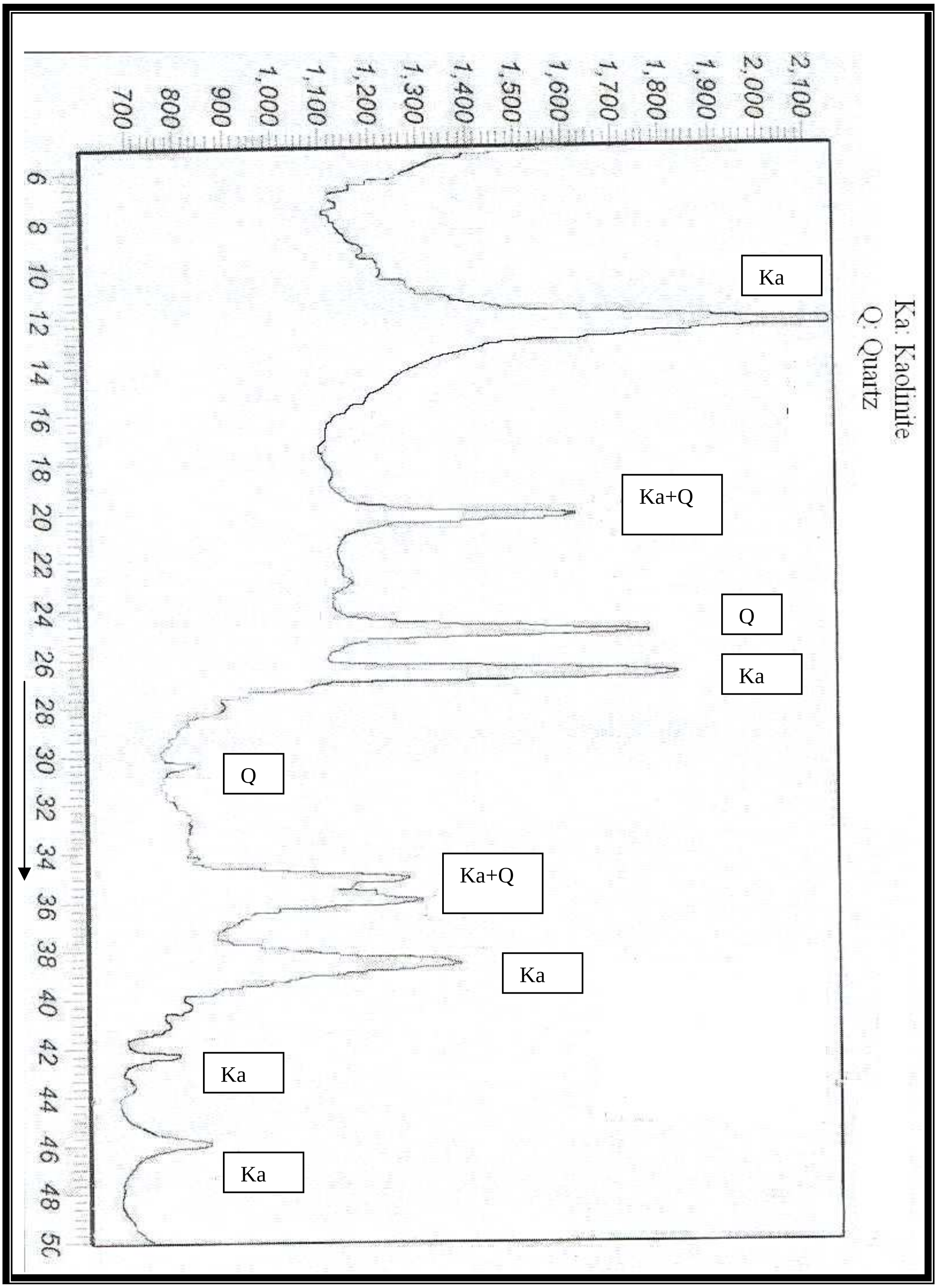

Figure (4-11) XRD pattern for Duekhla kaolin treated with zinc hydrosulfite

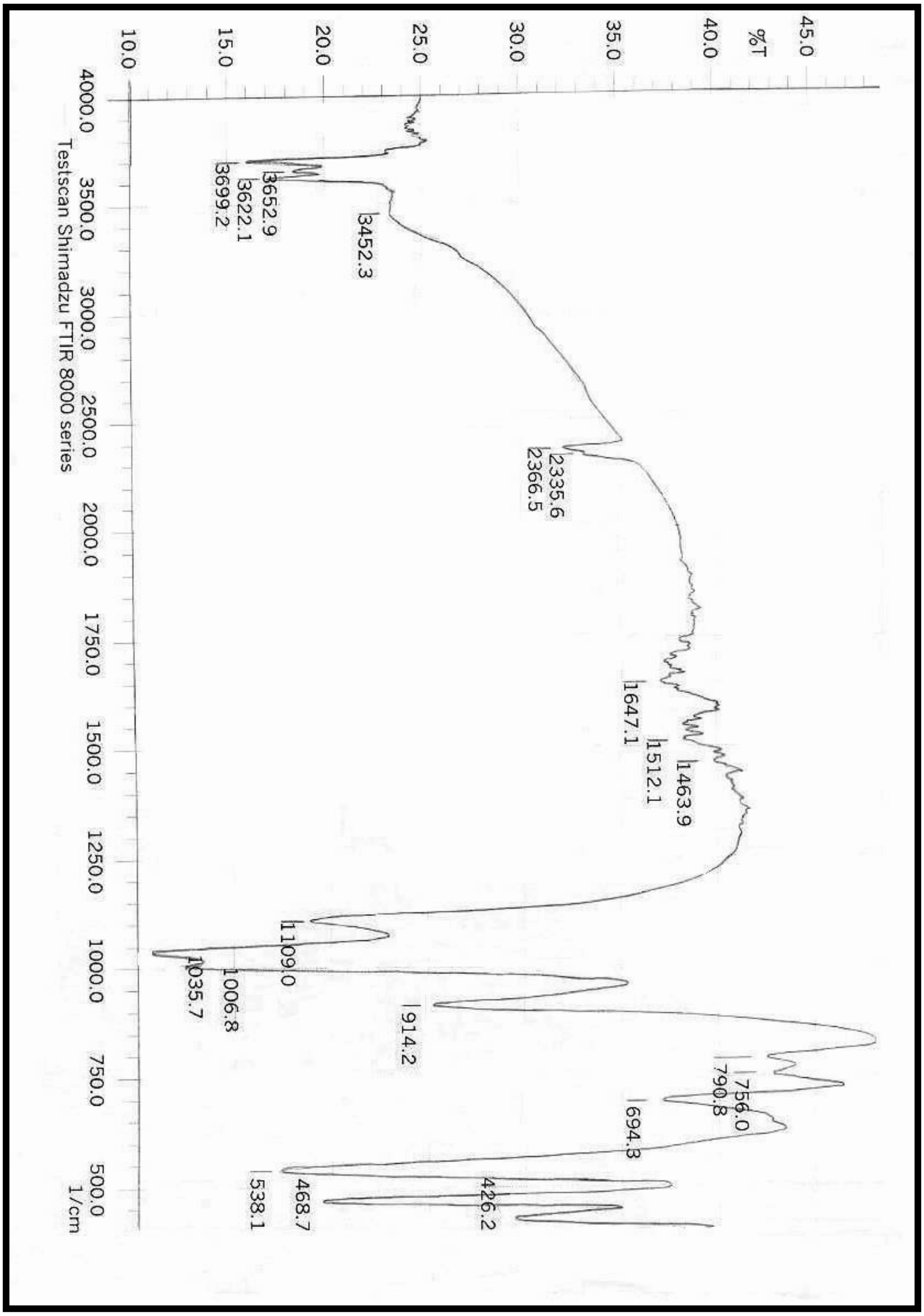

Figure (4-12) IR analysis for Duekhla kaolin as raw material

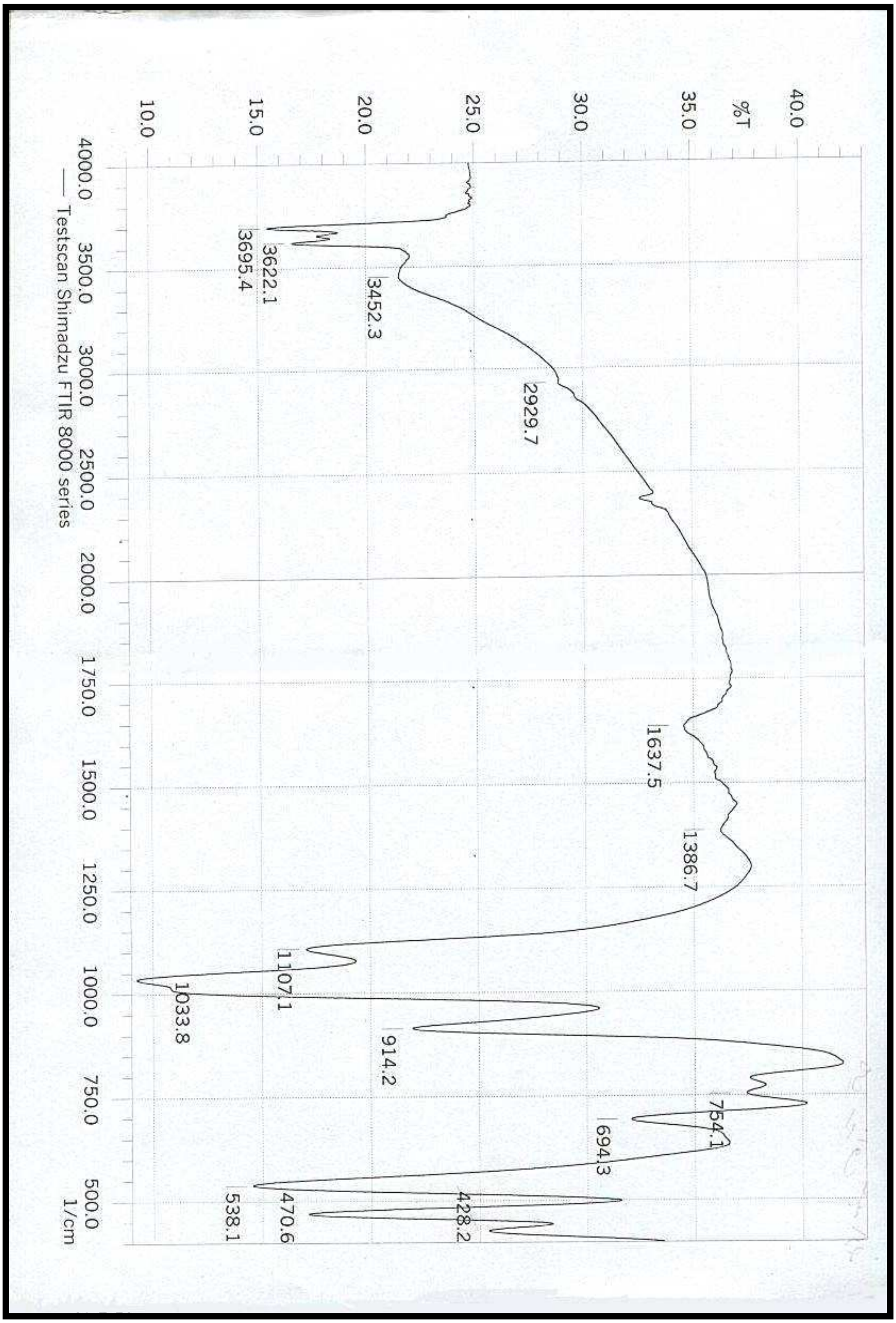

Figure (4-13) IR analysis for Duekhla kaolin treated with zinc hydrosulfite

Table (4–2) Absorption bands in Duekhla kaolin

Material	Bands (1/cm)				
	O – H	H_2O	Minerals		
			Si-O	Al-OH	SiO-Al
Duekhla Kaolin	3699.2 3622.1 3652.9	1512.1	1109.0 1035.7 1006.8	914.2	790.8 756.0 694.3
Duekhla Kaolin treated with zinc hydrosulfite	3695.4 3622.1	—	1107.1 1033.8	914.2	754.1 694.3 538.1

4-2 Conclusions:-

1- The measured value for minimum viscosity parameter is equal to 0.31 dyne.cm^2/sec. which required for dispersing Duekhla kaolin was obtained by using 4.3 gm of Na_2PO_3 in sample M_4.

2- The conditions of preparing and treatment which give the maximum removing for oxides (TiO_2, Fe_2O_3, and free SiO_2) are presented in sample G_7.

4-3 The Future Work:-

1- Using other dispersant material (sodium dithionite) at different temperature, different percentage of mass and different settling time to optimize the required value of viscosity.

2- Studying the effect of other bleaching agents such as $Na_2SO_4.7H_2O$, or $CaSO_4.7H_2O$.

3- Study other properties such as (brightness measurement) under these above conditions.

Republic of Iraq
Ministry of Higher Education and
Scientific Research
Nahrain University
College of Science
Department of Physics

A STUDY OF USING KAOLIN DUEKHLA AS FILLER IN THE PAPER INDUSTRY

A Thesis

Submitted to the College of Science
Nahrain University
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in
Physics

By

Ali Razzaq Abdul Rida

(B.Sc. 2003)

Supervised by
Dr.Azhar J.Dawod

Rabi'a Al - Awal	**1427 A.H**
April	**2006 A.D.**

Examination Committee Certificate

We certify that we have read the thesis entitled
"A Study of Using Duekhla Kaolin as Filler in the Paper Industry"
and as Examining Committee, examined the student
Ali Razzaq Abdul Rida
in its contents and what is related to it, and that in our opinion it is adequate as standard of thesis, with ***Very Good*** standing of
Degree of Master of Science
in ***Physics***

Signature:
Name:
Title: Assist. Professor (Chairman)
Address: University of Baghdad
Date: / /2006

Signature:
Name:
Title: Assist. Professor (Member)
Address: University of Baghdad
Date: / /2006

Signature:
Name:
Title: Lecture (Member)
Address: Al-Nahrain University
Date: / /2006

Signature:
Name:
Title: Lecture (Supervisor)
Address: Al-Nahrain University
Date: / /2006

Approved by the University Committee of Postgraduate Studies

Signature:
Name: **Dr. Laith A. Al-Ani**
(Dean of the college of science)
Date: / / 2006

Supervisor's Certification

I certify that this thesis was prepared under my supervision at the 'AL-Nahrain University' as a partial requirement for the degree of Master of Science in Physics.

Signature:
Name: Dr. Azhar J. Dawod
Title: Lecturer
Address: Dept. of Physics
College of Science
Nahrain University
Date: / /2006

In the view of the recommendation. I forward this thesis for debate by the examination committee.

Signature:
Name: Dr. Ahmad K. Ahmad.
Title: Assist Professor
Address: Head of the Department of Physics
College of Science
AL - Nahrain University.
Date: / /2006

Acknowledgement

I wish to extend my appreciation to my supervisor ***Dr. Azhar Juad Dawod*** for her kind guidance and encouragement, which make this research possible.

I would like to express my thanks to ***Dr. Ahmad K. Ahmad*** the head of Physics department and all the staff of physics department, for their assistance during to preparing of the thesis.

I would like thank to ***Dr. Fadhil A. Rasin*** for helping me to solve many problems.

Deep thanks to my father, my mother, my brother Dr. Firas, my sisters, Dr. Khamayl, Noor, and my friends, Mustafa ,Mohammed, Raad, Ali, Safaa, Wissam, Usama, &Yousif; for their help during the work.

Ali
April 2006.

[1] Norton, F.H "**Fine Ceramic Technology & Application**," McGraw–Hill, Inc. (1970).

[2] Tamer Agha, M.Y. **"Exploration and Prospecting in the Ga'ara Deposition"** General Geology, Report No. 1899, Geosurvey, Baghdad, (1990), **PP. 183.**

[3] Grim, R. E "**Applied Clay Mineralogy**" 1st edition, McGraw-Hill, book company, New York, (1962).

[4] Norton, F. H "**Element of Ceramic**" McGraw-Hill, Inc, (1974)

[5] Fernand, W. L "**Ceramic Corporation**" 2nd, McGraw-Hill, Inc, (1953).

[6] Murray, H. H & Lyons. S, C "**Correlation of Paper Coating with Degree of Crystal Perfection of Kaolin**" Natl. Acad. Sci. Publ. 456. (1955).

[7] Lyons, S. C "**Paper Coating Pigment**" U. S. Patent 2,524, (1958)

[8] Uzbaki, K. T"**دراسة جيوكيميائية و معدنية الحديد المتواجد مع الترسبات الطينية**" M.Sc Thesis, College of Science, Mussel University, (1989).

[9] Sathy, B." **Removal of Ultra Fine Graphite Impurities From China Clay** "Int.j. Miner. Process, **36**, (1994), **pp. 55-56**.

[10] Weissen Born, P. K" **Behavior of Amylopectin & Amylose Component of Ultra fine Iron Ore**" Int. J. Miner. Process, **47**, (1992), **pp. 197-211**.

[11] Raghavan, P." **Value Addition of Paper Coating Grade Kaolin by the Removal of Ultra Fine Coloring Impurities**" int. j. miner. Process, **50**, (1996), **pp. 307-316**.

[12] Suito, E. & Arakawa, M. "**Bull. J. Chem. Res.**" Kyoto University, **23**, (2005), **pp. 7-10**.

[13] Kassim, S. A."**Ph.D. Thesis**" Mousul University, (1996).

[14] Brindly, G. W. & Robinson, K. "**The Structure of Kaolin**" Inc. Mag., **27**, (1965), **pp. 242-253**.

[15] Nordel, E."**Water Treatment for Industrial & Other Uses**" Reinhold Publishing Corporation, Inc, New York, (1951).

[16] Norton, F. H. "**Rfractories**" 4th edition, Mc Graw-Hill Inc, New York, (1968), **pp. 164-167**.

[17] King, M. E. "**Physical-Chemical Properties & Engineering Performance of Clays**" Mines Bull, **16**, (1979), **pp. 153-157**.

[18] David. C. C "**Chemistry & Technology of Rubber**" Am. Society Monograph, **74**, (1970), **pp. 71-81**.

[19] Rodnkov, P. P "**The Technology of Ceramic & Refractories**" M. I. T. Press Cambridge, (1964).

[20] Kumari, P. J.; Pilla, P. K., J. "**Matter Sci. Lett**"., (1986).

[21] Smith, E. F., & Deines, G. J., "**ASTM-Bull**", **154**, (1987), **pp. 46-56**.

[22] Saboo, D. P., "**Chem. Abst.**", **110**, (1989).

[23] Mehra, O. P.,& Jakson, M. L. "**7th National Conference on Clays & Clay Minerals"**, **18**, (1976), **pp. 71-97**.

[24] Lyons, S. C.,"**Paper Coating Pigment**" U. S. Patent, **1,062**, (1958)**, pp. 982.**

[25] Miller, C. F. "**The Structure of Kaolin & its Relation to Acid Treatment**" U. S. Patent **2,278,695**, (1963).

[26] Norton, F. H. "**Fundamental of Ceramic**" by Mc Graw-Hill (1971).

[27] Mahasin, J. A. **"Reducing of Free Silica from the Duekhla Kaolin Clay"**, M.Sc Thesis, Extractive Metallurgical Engineering, University of Technology, (2000)

[28] Rand, B., & Melton, I. E., "**Effect of pH up on the Made of Particle Interaction in Kaolin Suspension**" J. Colloid Interface Sci., **60**, (1977), **pp. 303-320.**

[29] Dana, J. D. "**Manual of Mineralogy**" 2nd ed. John Wiley & Sons, Inc. (1977).

[30] Grim Show, R. W. "**The Chemistry & Physics of Clays**" 4th Ed. London, (1971).

[31] Allen, T., "**Particle Size Measurement**" 3rd ed. London, (1981).

[32] Yono, T., & Sato,M. "**Resent Work in Japan on the Mixing of Solids**" Powder Technology, **20**, (1978), **pp. 9-14**.

[33] Petrzzelli, G., & Sequi, P., "**Electro-Optical Measurements Clay**" Clays &Clay Minerals, **11**, (1976), **pp. 81-84.**

[34] Farad, R. W., "**Ceramic Drying**" Pergamon Press; Oxford, New York, (1989).

[35] Brownell, W. E. "**Structure Clay Product**" Spring-Verlag, New York, (1976).

[36] Olphen, H. V. "**An Introduction to Clay Colloid chemistry**" 2nd ed. John Wiley & Sons. (1977).

[37] Gray, D. H. "**Formation Damage in Sand Stone Caused by Clay Dispersion**" Clays & Clay Minerals, **14**, (1966), **pp. 365-366**.

[38] La Mer, V. K. & Smellie, R. H." **Theory of Flocculation & Filtration Rates of Colloidal Dispersion**" Clays & Clay Minerals, **9**, (1962), **pp. 295-314.**

[39] Alberty, R.A. "**Physical Chemistry**" 2nd Ed. By John Wiley & Sons, Inc. New York, (1997).

[40] Bongiovanni R., Ottewill R. H., Rennie A. R., Laughlin R. G. Langmuir**,12**, (1996), **pp. 4681-4690**.

[41] John, O.F. **"Physical Phenomena in Clays"** publishing in physic **A270,** (1999)**, pp. 270 – 277.**

[42] Jianzhoug, Wu. And Huagao, G. **"Journal of Chemical Physics" ,120**, (2004)**, pp. 15**.

[43] B. Chun and A.J.C. Ladd. **"Journal of Colloid and Interface Science", 274**, (2004)**, pp. 687–694**.

[44] Toylor, J. R. & Bull, A. C. **"Ceramic Glaze Technology"** pergamon press, New York, (1986).

[45] Worral, W.E. "**Clays & Ceramic Raw Material**", Applied Sci. Publ. Ltd. London, (1987).

[46] Folk, R. L. "**Petrology of Sedimentary Rocks**" 1st Ed. John Wiley & Sons, Inc. New York, (1980).

[47] Carver, R. E. "**Procedure in Sedimentary Petrology**", John Wiley & Sons, Inc. New York, (1971).

[48] Harwell, J. M. "**The Divers Uses of Kaolin**" Clays and Clay Minerals, **6**, (1965), **pp. 111-118.**

[49] Hamaker, H. C. "**The Role of the Forces between the Particle in Electro deposities & other Phenomena**" Trans Faraday Soc., **36**, (1980), **pp. 180-185.**

[50] Imris, P., and Landspersky, H." **Clay Minerals,**" **9**, (1956)**, pp. 372-380**.

[51] Stainmand, C. J." **Symp. Particle Size Analysis**" Inst. Chem. Eng., **25**, (1953), **pp. 110-114**.

[52] Olphen, H. V. "**An Introduction to Clay Colloid chemistry**" 1st ed. John Wiley & Sons. (1963).

[53]Tullera, M., Dani Orb,**" Journal of Hydrology" 272**, (2003)**,** **pp. 50–71**.

[54] Dolocator, D. L. & Syers, J. K. "**Titanium as Free Oxide & substituted Forms in Kaolin**" Clays & Clay Minerals, **18,** (1965)**, pp. 71-74**.

[55] Rengasamy, P. & Murti, G. S. "**Introduction Substitution of Iron in Some Soil Kaolin**" Clays & Clay Minerals, **23,** (1975)**, pp. 211-214**.

[56] Alpert, N. L. & Keiser, W. E. **"IR Theory &Practice of Infrared Spectroscopy"** 2 nd by plenum press, New York, (1970).

[67] Sarasota, J. M. **"Dehydration Rehydration Studies of Clay Minerals by Infrared Absorption Spectra"** by pergmon press, New York, (1962).

[58] Miller, J. G. **"J. Phys. Chem." 65**, (1961), **pp. 800– 804**.

[59] Grim, R. E. **"Clay Mineralogy"** 2 nd edition, MC Geaw Hill book Company, New York, (1968).

[60] Farmer, V. C. **"Infrared Spectroscopy"**. Data Handbook for Clay materials and other Non – Metallic Material, (H.V. Olephen &J.J.Fripiat ed.)pregamon press, Oxford,(1979).

[61] Rasin, F.A.. **"The Use of Iraqi Siliceous Rocks as Electrical Insulators Industry"**, Ph.D Thesis College of science, Nahrain University, (1998).

[62] Jansen, L. "**Phys. Rev.**" **112**, (1958)**, pp. 434-444**.

[63] Berry, R. S. & Flynn, G. P**. "Physical Chemistry "**by john wiely &Sons, Inc. New York (1980).

[64] McDonald, J. A., & Rennie, A. R. "**Progress in Colloidal & Polymer Science**" **98**, (1995), **pp. 75-78.**

[65] Van der Marel, H. W. and Spacher **"Atlas of Infrared Spectroscopy of Clay Minerals and their Admixed"**. Elsever Scientific publishing company, New York, (1976).

[66] Maynard, R. N., & Millman, N." **A Method for Removing Titanium Dioxide Impurities from Kaolin**" Clays and Clay Minerals, **17**, (1969), **pp. 59-62.**

CHAPTER ONE

GENERAL REVIEW

CHAPTER TWO

THEORETICAL CONCEPT

CHAPTER THREE

PRACTICAL PART

CHAPTER FOUR

DISCUSSION & RESULTS, CONCLUTION & FUTURE WORK

REFERENCES

DEDICATION

TO
MY FAMILY

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين/كلية العلوم
قسم الفيزياء

دراسة تحضير مادة كاؤلين دويخله كمالأت في صناعة الورق

رسالة

مقدمة إلى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الفيزياء

من قبل
علي رزاق عبد الرضا
بكالوريوس٢٠٠٣ (جامعة النهرين)

بأشراف
د.أزهار جواد داوود

ربيع الأول
نيسان

١٤٢٧هـ
٢٠٠٦م

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ ربِ أَوَزعني أَن أَشكَر نعمتكَ التي أَنعَمتَ عليَّ
وعَلى والدي وأن أَعمَل صَالحاً ترضاهُ وأَدخِلني
برَحمَتك في عِبادكَ الصَّالحينَ ﴾

صدق اللَّهِ العظيم

﴿ النمل: ١٩ ﴾

الخلاصة

يتناول البحث دراسة تأثير خفض نسبة اكاسيد الحديد و التيتانيوم السيليكا الحرة من أطيان كاؤولين دويخله لغرض استخدامها كمالأت في صناعه حشوه الورق.لما لهذه المكونات من تأثير على خواص الحشوه. يحتوي خام الكاؤولين المستخدم في هذا البحث على حوالي ١,٧% من أوكسيد الحديد و ١,٢% من أكسيد التيتانيوم و ٥١,١٦% من أوكسيد السيلكون من ضمنه١٢% من السيليكا الحرة. و يعتبر وجود هذه النسب من اوكسيد الحديد والتيتانيوم و السيليكا الحره ضمن الخام غير مرغوب في صناعة الورق ، لقد أجريت معامله كيميائية لكاؤولين دويخله بهدف تنقيته من الشوائب التي يمكن أن تذوب بحامض الهيدروكلوريك حيث ثم الاستمرار بغسل الكاؤولين بالماء المقطر لتصل درجةpH إلى قيمة خمسة . ثم تجفيفه لمدة ٣ ساعات بدرجة حرارة من (٤٠-٦٠) م^0 وبعدها تم طحن المسحوق بالمطحنة البورسلينيه لمدة ٥ ساعات. ثم نخل المسحوق بمنخل ذو حجم حبيبي ٦٥ مايكرون ليتم استخدامه في الدراسة. استخدمت في هذا البحث طريقة الترسيب، وقد اعتمد في طريقة الترسيب على فصل الأكاسيد المذ كوره من الأطيان استخدام ماده مشتته هي فوسفات الصوديوم. كما تم دراسة تأثير ألماده المشتتة على لزوجة الخليط حيث تبين إن بزيادة ألماده ألمشتته تقل نسبه اللزوجة إلى أن تصل إلى اقل قيمه. كما تم دراسة تأثير كبريتات الخارصين المائية كماده قاصرة على نموذج ألمجموعه M_4 وبأوزان تراوحت(بين١٠ إلى ٢٢ غم) من ألماده القاصرة كخطوه ثانيه لتقليل نسبه الشوائب المذكورة والتي بالنتيجة تؤدي إلى زيادة نصوعيه كاؤولين دويخله حيث تم إزالة حوالي ٧٣% من أوكسيد الحديد،٩١% من أكسيد التيتانيوم، ١٥% من أوكسيد السيلكون، و ٥٠% من السيليكا الحرة في نموذج ألمجموعه G_7. النتائج المستحصله تبين كفاءة هذه الطريقة في فصل الشوائب الغير مرغوب فيها إذ انخفضت نسبة أوكسيد الحديد المتبقي في ألماده ألمعالجه (من ١,٧١% الى٠,٣%)، و أكسيد التيتانيوم (من١,٢% إلى ٠,٠٩%)، و أوكسيد السيلكون (من ٥١,١٦% إلى ٣٩,٧%). وكون الطريقة ألمتبعه في الفصل هي طريقة فيزيائيه فلم يلحظ حدوث تغير في خواص الخام بعد ألمعالجه، مما يمكنا استخدام الخام المعالج بهذه ألطريقه في صناعات أخرى.