SHEAR FLOCCULATION OF CHROMITE AND SERPENTINE FINES

A Ph.D Thesis

Presented by

Ünal AKDEMİR

to

the Graduate School of Natural and Applied Sciences

of Middle East Technical University

in Partial Fulfillment for the Degree of

DOCTOR OF PHILOSOPHY

in

MINING ENGINEERING

MIDDLE EAST TECHNICAL UNIVERSITY

ANKARA

January, 1995

Approval of the Graduate School of Natural and Applied Sciences

Prof.Dr. İsmail TOSUN

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

Prof.Dr. A. Günhan PAŞAMEHMETOĞLU

Chairman of the Department

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy in Mining Engineering

Assoc. Prof.Dr. Cahit HİÇYILMAZ

Supervisor

Examining Committee in Charge:

Prof.Dr. Mehmet CANBAZOĞLU
Prof.Dr. Çetin HOŞTEN
Prof.Dr. M. Ümit ATALAY Ü. Atalay
Assoc. Prof.Dr. Cahit HİÇYILMAZ
Assoc. Prof.Dr. A. İhsan AROL A. İhsan Arol

ABSTRACT

SHEAR FLOCCULATION OF CHROMITE AND SERPENTINE FINES

AKDEMİR, Ünal
Ph.D. in Mining Engineering
Supervisor: Assoc. Prof.Dr. Cahit Hiçyılmaz
January, 1995, 189 pages

In this study, shear flocculation of chromite and serpentine fines and selective shear flocculation of chromite from artificial mixtures of chromite and serpentine were investigated. The effect of pH, sodium oleate and dodecyl amine acetate concentration, stirrer speed, flocculation time and suspension concentration were examined. Electrokinetic potential and contact angle measurements were also carried out to interpret the flocculation in terms of surface charge and particle hydrophobicity.

Electrokinetic potential measurements indicated that chromite sample has i.e.p. of pH 5.2. Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} shifted the i.e.p. in the direction of their corresponding oxides. Adsorption of sodium oleate and dodecyl amine acetate shifted the i.e.p. to pH 3.1-3.8 and 9-9.5 depending on collector concentration, respectively.

Electrokinetic potential measurements with serpentine indicated that i.e.p. is obtained at pH 8.7. H^+, OH^- and Mg^{2+} are potential determining ions. Adsorption of sodium oleate and dodecyl amine acetate shifted the i.e.p. to pH 5.5-6.5 and 11.5-12, respectively depending on collector concentration.

Contact angle measurements carried out with chromite indicated that maximum contact angles are obtained at pH 9.0 and 10.0 for the sample conditioned with sodium oleate and dodecyl amine acetate. These values are 59.11° and 69.49° for sodium oleate and dodecyl amine acetate, respectively.

Maximum contact angle of serpentine conditioned with sodium oleate was 86.77° at pH 8.0. Conditioning the sample with dodecyl amine acetate gave a contact angle of 81.83° at pH 9.0.

Shear flocculation studies with chromite indicated that collector adsorption is necessary for aggregation. Optimum flocculation is obtained where zeta potential is minimum. Other factors influencing shear flocculation are collector concentration, stirrer speed, flocculation time and suspension

concentration. Shear flocculation of chromite with sodium oleate and dodecyl amine acetate increased the amount of settled material from 11.3 % to about 87 %. Turbidity of suspensions decreased from about 2100 NTU to about 120 NTU.

Hydrophobicity and zeta potential were found as most important parameters for shear flocculation of serpentine. Collector concentration, stirrer speed, flocculation time and suspension concentration are other factors affecting the flocculation. The experiments carried out at optimum conditions indicated that the amount of settled material increases from 8.63 % to about 92 % and turbidities decreased from 2900-3000 NTU to 200-300 NTU.

Selective shear flocculation of chromite from a chromite-serpentine mixture containing 29.47 % Cr_2O_3 yielded a concentrate assaying 44.60 % Cr_2O_3 with 81.06 % recovery.

Key Words: Shear Flocculation, Zeta Potential, Contact Angle, Selective Shear Flocculation, Settled Material, Turbidity.

Science Code:607.02.07
607.02.04

ÖZ

İNCE BOYUTTAKİ KROMİT VE SERPANTİNİN MAKASLAMA FLOKÜLASYONU

AKDEMİR, Ünal

Doktora Tezi, Maden Mühendisliği Anabilim Dalı

Tez Yöneticisi: Doç.Dr. Cahit Hiçyılmaz

Ocak, 1995, 189 sayfa

Bu çalışmada ince boyuttaki kromit ve serpantinin makaslama flokülasyonu incelenmiş, ayrıca yapay bir kromit-serpantin karışımından kromit seçimli makaslama flokülasyonu ile kazanılmaya çalışılmıştır. Bu amaçla, pH'ın, sodyum oleat ve dodesil amin asetat miktarının, karıştırma hızının, flokülasyon süresinin ve katı oranının etkileri incelenmiştir. Makaslama flokülasyonunu yüzey potansiyeli ve ıslanmazlık çerçevesinde yorumlayabilmek amacıyla zeta potansiyeli ve temas açısı ölçümleri de yapılmıştır.

Kromitin sıfır yük noktası pH 5.2 olarak bulunmuştur. Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} ve Cr^{3+} iyonları ise bu noktayı kendi oksitlerinin sıfır yük noktalarına doğru kaydırmaktadır. Kromit yüzeyinin sodyum oleat ve dodesil amin asetat ile kondisyonlanması ise sıfır yük noktasını kollektör miktarına bağlı olarak pH 3.1-3.8 ve pH 9-9.5'a çekmiştir.

Elektrokinetik potansiyel ölçümleri serpantinin sıfır yük noktasının pH 8.7'de olduğunu göstermiştir. H^+, OH^- ve Mg^{2+} iyonları ise potansiyel tayin eden iyonlardır. Ortama sodyum oleat eklenmesi ile sıfır yük noktası konsantrasyona bağlı olarak pH 5.5-6.5'da oluşmuştur. Dodesil amin asetat ise konsantrasyona bağlı olarak bu noktanın pH 11.5-12'de oluşmasını sağlamaktadır.

Sodyum oleat ve dodesil amin asetat ile şartlandırılmış kromitin en büyük temas açıları sırasıyla pH 9.0 ve pH 10.0'da alınmıştır. Bu değerler sodyum oleat için 59.11°, dodesil amin asetat içinse 69.49° dir.

Serpantinin sodyum oleat ile şartlandırılması sonucu ölçülen en büyük temas açısı pH 8'de ölçülen 86.77° dir. Dodesil amin asetatla ise pH 9.0'da ölçülen 81.83° en yüksek temas açısıdır.

Kromitin makaslama flokülasyonu çalışmaları, tanelerin biraraya gelebilmesi için kollektörün gerekli olduğunu göstermiştir. Optimum sonuçlar zeta potansiyelinin minimum olduğu noktalarda alınmıştır. Flokülasyonu etkileyen

diğer faktörler ise kollektör miktarı, karıştırma hızı, flokülasyon süresi ve katı oranı olarak belirlenmiştir. Kollektör olarak sodyum oleat ve dodesil amin asetat kullanarak yapılan çalışmalarda çöken malzeme miktarının % 11.3'den % 87'ye çıktığı, bulanıklığın ise yaklaşık 2100 NTU'dan 120 NTU'ya düştüğü görülmüştür.

Serpantinin makaslama flokülasyonunu etkileyen en önemli faktörler ıslanmazlık ve zeta potansiyeli olarak belirlenmiştir. Kollektör miktarı, karıştırma hızı, flokülasyon süresi ve katı oranı flokülasyonu etkileyen diğer faktörlerdir. Optimum koşullarda, kollektör olarak sodyum oleat ve dodesil amin asetat kullanarak yapılan deneylerde çöken malzeme miktarının % 8.63'den yaklaşık % 92'ye çıktığı, bulanıklığın ise 2900-3000 NTU'dan 200-300 NTU'ya düştüğü belirlenmiştir.

Kromitin seçimli makaslama flokülasyonu çalışmaları sonucu ise, % 29.47, Cr_2O_3 tenörlü bir kromit-serpantin karışımından % 44.60 Cr_2O_3 tenörlü bir konsantre % 81.06'lık bir verimle kazanılmıştır.

Anahtar Kelimeler: Makaslama Flokülasyonu, Zeta Potansiyeli, Temas Açısı, Seçimli Makaslama Flokülasyonu, Çöken Malzeme, Bulanıklık.

Bilim Dalı Sayısal Kodu : 607.02.07

607.02.04

ACKNOWLEDGEMENTS

I would like to express my appreciation to Assoc.Prof.Dr. Cahit Hiçyılmaz for his kind supervision, suggestions and discussions throughout this research.

I also want to express my gratitude to Dr. Sedat Bilgen for his valuable suggestions and discussions during the study.

Thanks are given to Mr. Süleyman Kırıcı, Mr. Tuncer Gençtan, Mr. Levent Önder and to the department staff for their help in various stages of this thesis.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

µm	Micronmeter
rpm	Revolution per minute
M	Moles per liter
mV	Millivolt
min.	Minutes
°C	Degrees centigrade
i.e.p.	Iso-electrical point
pzc	Point of zero charge
e.s.d.	Equivalent Stokes Diameter
mg/l	Milligram per liter
NTU	Nephelometric Turbidity Unit
flocc.	Flocculation
Conc.	Concentration

CHAPTER 1

INTRODUCTION

It is necessary to develop efficient methods for treating low-grade ores, which often involves handling and processing of fine particles, with the depletion of high grade ores. It was estimated that 1/3 of phosphate (Tyler and Waggman, 1953), 1/6 of copper (Goldberger, 1973), 1/10 of iron exploited in U.S., 1/2 of the tin produced in Bolivia and 1/5 of the tungsten mined in the world (Somasundaran, 1976) and millions of tons of other minerals are lost in the form of fines. The major problem of fine particles and the emergent necessity for suitable processing methods to recover the valuable components from fines have resulted in a large number of publications and symposia. Several papers (Fuerstenau et al., 1978; Sennett and Young, 1978; Somasundaran, 1978; Sastry, 1978; Stratton-Crawley, 1978; Yang, 1978) deal with fine particles processing. These methods of fine particles treatment are column flotation, oil flotation, liquid-liquid extraction, electroflotation, selective flocculation, shear flocculation, magnetic flocculation and carrier flotation.

Shear flocculation is the aggregation of fine particles by stirring after hydrophobization by a collector. A direct contact due to collision is favoured by an energy of hydrophobic assocation. For the formation of hydrophobic aggregates the hydrophobic interaction energy is a significant factor since it is a few times higher than the energy of molecular or electrostatic repulsive energy (Lu and Li, 1984).

Shear flocculation of scheelite (Warren, 1975a; Warren, 1975b; Jarrett and Warren, 1977; Koh and Warren, 1980; Warren, 1981; Koh et al., 1986; Sivamohan, 1988; Sivamohan and Cases, 1990), galena (Dippenaar, 1985; Subrahmanyam et al., 1990a; Subrahmanyan et al., 1990b), hematite (Li and Fuerstenau, 1987; Fuerstenau et al., 1988; Wang and Heiskanen, 1992), copper (Bulatovic and Salter, 1989), pentlandite (Bulatovic and Salter, 1989), rutile (Song and Lu, 1990), fluorite (Sivamohan, 1988; Sivamohan and Cases, 1990), quartz (Raju et al., 1991), wolframite (Yarui and Daxin, 1986), magnesite (Skvarla and Kmet, 1991), dolomite (Skvarla and Kmet, 1991), rhodochrosite (Lu et al., 1988), siderite (Lu et al., 1988), cassiterite (Warren, 1982; Bilgen, 1992), tourmaline (Warren, 1982), graphite (Raghavan et al., 1992) were investigated.

Shear flocculation of chromite and serpentine fines is a new subject. The aim of this research is to investigate the possibility of shear flocculation of chromite and serpentine fines. It is also aimed to recover chromite fines from chromite-serpentine mixture by selective shear flocculation which will contribute the recovering of chromite fines lost as slime in conventional techniques.

CHAPTER II

GENERAL CONSIDERATIONS

2.1. Theory of Shear Flocculation

Interparticular forces arising from electrostatic repulsion, van der Waals forces and specific chemical interactions lead to an energy barrier, and colloid stability depends on the magnitude of this barrier. The energy barrier is calculated by the theory known as DLVO, after DerJaguin-Landau and Verwey-Overbeek (1948). This deals with colloid stability for the conditions where van der Waals attraction and diffuse double layer repulsion are the sole operative factors. A typical interaction curve is shown in Figure 2.1.

For high dispersion stability, an energy barrier greater than about 20 kT (thermal energy) is considered to be necessary. This corresponds to surface potentials greater than 20-30 mV, depending on the particle size and the thickness of the electrical double layer. If the primary maximum is less than 15 kT, then the net force of attraction will pull the particles together into the primary minimum, resulting in irreversible coagulation. However, hydrophobic cassiterite particles with 40 mV potential and an energy barrier of up to 1200 kT (Warren, 1982), scheelite particles with a potential of 45 mV (Warren, 1975a) have been aggregated under high shear conditions.

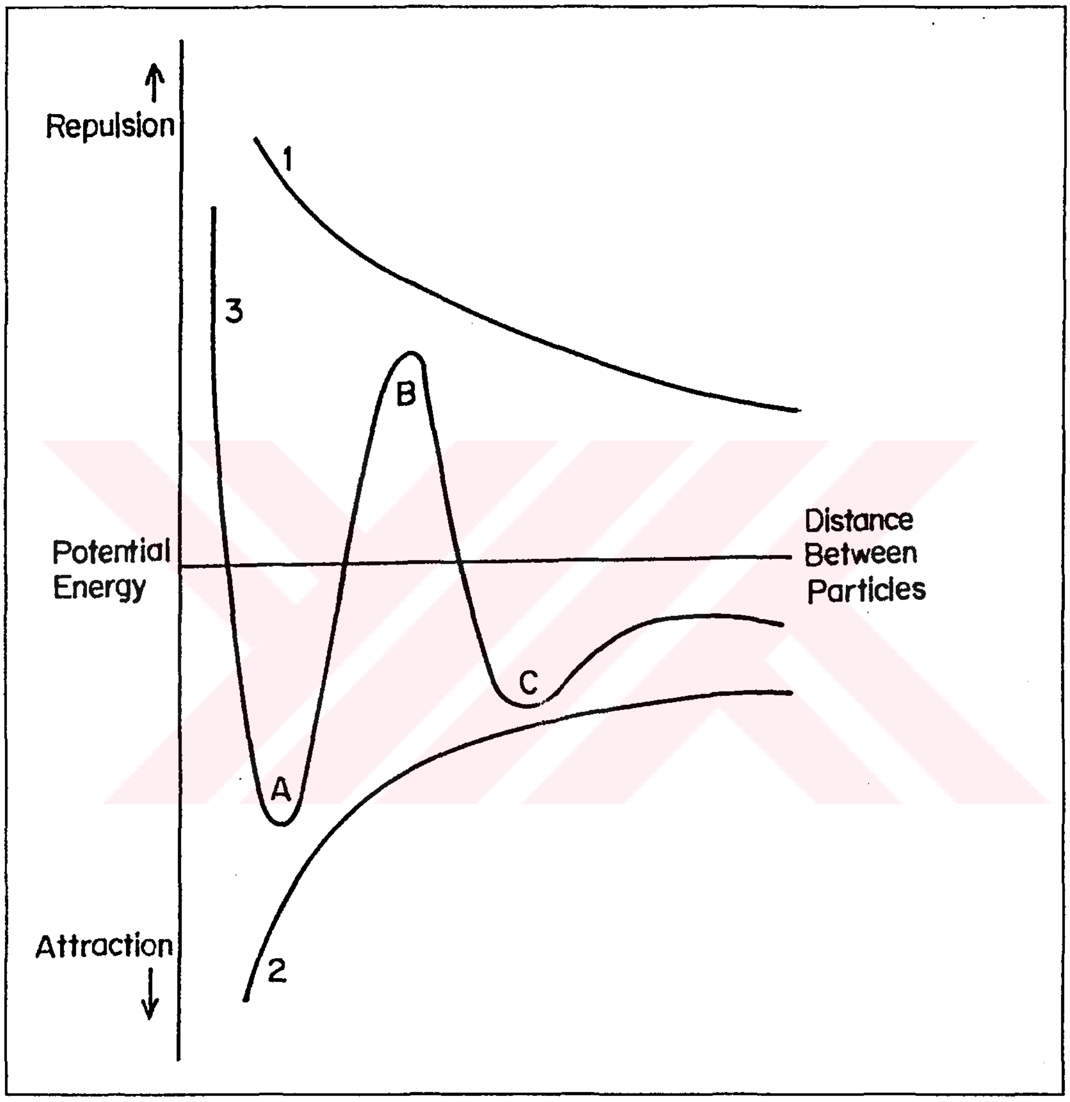

Figure 2.1. DLVO Interaction Curve: 1. Double Layer Repulsion, 2. van der Waals Attraction , 3. Resultant, A. Primary Minimum, B. Primary Maximum, C. Secondary Minimum

Since most minerals are hydrophobic or hydrophilic, one can expect that the DLVO forces are incomplete and that there is an additional third force of unknown origin and mechanism (Skvarla and Kmet, 1991). This additional force is smoothly varying repulsive or attractive structural force. The structural force is repulsive between the hydrophilic surfaces, and attractive between hydrophobic surfaces (Israelachvili, 1987). Pashley and Israelachvili (1981) have shown that the magnitude of the structural force between hydrophobic mica surfaces was three times that of the expected van der Waals force.

It has been demonstrated that (Lu and Li, 1984), apparent aggregation always occurs only with the surface hydrophobization of the mineral particles, and such aggregation can't be interpreted by DLVO theory. The calculation of the potential energy of hydrophobic interaction between particles shows that hydrophobic interaction energy is of 1-2 magnitude orders larger than that of electrostatic repulsion and van der Waals attraction.There are two reasons for the hydrophobic interaction: The first reason is the repelling action of water to force the hydrophobic particles to aggregate together. The other reason is the hydrophobic association of the outward extending hydrocarbon chains of the adsorbed collectors between two approaching particles. Claessen et al. (1986) reported that the hydrophobic forces on muscovite surfaces resulting from the adsorption of dimethyl dioctadecylammonium ions were considerably stronger than the expected van der Waals force.

Warren (1975a) has found that bare scheelite particles are likely to carry one or more layers of "bound" water at the surface and when such particles approach closely enough they will experience a repulsive force associated with desorbing the bound water. The desorption energy required will be too large to be supplied by shear forces and direct contact between surfaces will be difficult to establish. Even when coagulation is produced by the addition of electrolytes, particles in the resulting aggregates are still separated by one or two layers of water molecules. Such coagula tend to break up at high shear rates. In the case of oleate-covered particles the solvated layer opposing direct contact is replaced by the hydrocarbon tails of the adsorbed oleate ions and now there will be an additional attractive energy associated with interactions between the oleate layers. The following mechanism was proposed for the shear flocculation.

1. Under turbulent agitation the average energy of collision is much greater than thermal energy, allowing the colliding particles to approach more closely.

2. The formation of aggregates is favoured by an energy of "hydrophobic association" which comes into effect if the collision result in direct contact between the hydrophobic particles.

Since hydrophobic association takes place only in direct particle contact, it is necessary to bring highly charged particles together. This is achieved by throwing them towards each other with a force exceeding the energy barrier. The rate of shear flocculation depends on the rate at which particles collide with each other and on the number of those collisions which result in adhesion (Warren, 1981).

Collisions occur because of velocity gradients in the fluid flow for sufficiently large particles. For colloidal particles, collisions occur because of the random nature of Brownian motion. For fine particles in turbulent flow, Levich (1962) described particle movement by a chaotic turbulent diffusion similar to Brownian motion. There will be more collisions per unit time for particles larger than about 0.1 μm, due to turbulent flow than to Brownian motion. For 1 μm particles, the turbulent collision rate may be up to 1000 times the Brownian collision rate (Levich, 1962). And more contacts per unit time generally means more rapid floc formation.

According to Levich (1962), the collision rate is a function of particle size, particle concentration and the specific energy loss occuring in the flow, which is related to the stirrer speed. If the fluid flow velocity is directly proportional to the stirrer speed then the collision rate is proportional to the 3/2 power of the stirrer speed. However the measured extent of aggregation increased by much more according to Warren's findings (1975a) and therefore increase in the collision rate is not the only factor. The other factor related directly to the stirrer speed is the energy of impact of the colliding particles. Ultrafine particles will only adhere if the stirrer speed is high enough to provide a sufficient energy of impact . Larger particles, having a greater kinetic energy for the same velocity, adhere at speeds too low for the aggregation of ultrafines. Again, ultrafine particles will attach to larger particles at stirrer speeds under which they do not aggregate themselves. One is led to the simple hypothesis that shear flocculation only occurs when the energy of impact of the colliding particles is sufficient to overcome energy barrier preventing their spontaneous coalescence. When two particles approach on a collision course, the liquid separating them must be thinned and ultimately removed before physical contact can be made. In a high energy turbulent collision the resistance to thinning is likely to be greater, since the faster the rate of approach the more water per unit time must be removed (Warren, 1975a).

Warren (1975a) indicated that conditioning speed has great influence on shear flocculation. However the experiments carried out with fluorite and scheelite (Sivamohan, 1988) have shown that the effect of conditioning speed is not significant.

Raju et al. (1991) found that shear flocculation of quartz is optimum at a stirrer speed of 500 rpm and above this flocculation decreases. A stirrer speed range of 250-400 rpm has been found to be sufficient for the shear flocculation of cassiterite (Bilgen, 1992).

Higher speeds break up larger aggregates beacause the energy of impact exceeds the energy of hydrophobic association. It has also been found that optimum speed may probably depend on hydrophobicity, specific gravity and size of particles. Low stirrer speeds may be enough for the highly hydrophobic particles whereas higher speeds are required for partly hydrophobic particles. Also heavier minerals have higher kinetic energy at a given speed than the lighter ones, so lower speeds will be enough to bring them in contact.

It must be pointed out that the agitation speeds vary from system to system. Floc redispersion occurs mainly because of the factors such as attrition, breakage of flocs due to a high stirring speed, removal of the adsorbed reagent from the particle surface and consequently detachment of the adhered particles at higher speeds of stirring.

2.2. Previous Studies About Shear Flocculation

The first study on the shear flocculation is the aggregation of ultrafine scheelite particles (90% 0.75-1.4 μm) by sodium oleate. Aggregation occurred only at high stirring speeds. The extent of aggregation and the size of aggregates increased with increasing stirrer speed. Whereas coagulation with NaCl started immediately, aggregation with sodium oleate began slowly; during the first 20 minutes of stirring at 1700 rpm the turbidity hardly changed. Increasing suspension concentration and reducing the electrokinetic potential increased the extent of shear flocculation. D_{50} values of the particles increased from about 1 μm to 3 μm.

Jarrett and Warren (1977) investigated the selective flocculation of scheelite from artificial mixtures of scheelite and garnet using sodium oleate as collector. Stirrer speed, stirring time and initial weight ratio were found to have significant effects on both recovery and grade. The particle sizes also had an effect on the final grade. Optimum conditions for shear flocculation were established and under these conditions about 80 % of the scheelite could be recovered at a grade which depended upon the composition of the starting mixture. Starting with mixtures containing 10 % and 50 % scheelite, the best final grades were between 20 % and 50 % and between 70 % and 90 %, respectively; depending on the particular combination of the particle sizes.

A pilot plant study on the shear flocculation-flotation of ultrafine scheelite was carried out by Koh and Warren (1980). Scheelite ore, containing 0.83 % WO_3, was ground to give a high proportion of ultrafine material, up to 70 % -15μm. It was found that under continuous operating conditions 74 % of the scheelite could be recovered with a grade of 5.19 % WO_3, by using 5 kg/t sodium-oleate as collector at pH 10.2. Pre-treatment of the ultrafine pulp by shear flocculation at 420 rpm for 50 minutes improved subsequent flotation recovery of the scheelite to 83 % and concentrate grade increased from 5.19 % to 5.96 %

WO_3. The value of the extra tungsten recovered was as high as four times the incremental running cost of the shear flocculation tanks.

The separation of cassiterite from tourmaline by shear flocculation was shown to be possible (Warren, 1982). Increasing the concentration of S 3903 collector, a carboxylic acid derivative, increased the aggregation of both minerals up to certain levels but the concentrations above these levels decreased aggregation. Stirring speeds of 400-800 rpm provided maximum tourmaline aggregation. It was also found out that flocculation of tourmaline was slow; even after 90 minutes the equilibrium was still not established. The effects of increasing stirrer speed and stirring time on suspensions of cassiterite with S 3903 were similar to those observed for tourmaline. Tests on separate suspensions indicated that selective shear flocculation of cassiterite from tourmaline should be possible in mixtures of the two minerals. Sodium fluorosilicate was found to disperse tourmaline by selectively adsorbing on it. Optimum conditions for selective shear flocculation separation was found as follows: Collector (S 3903): 10 mg/l; dispersant: 300 mg/l; pH:6. An intermediate stirrer speed (400-800 rpm) and a fairly long stirring time (30-60 min.) were required for good flocculation.

The effect of shear flocculation on the flotation responses of galena and chalcocite was investigated by Dippenaar (1985). Shear flocculation of 1.5-5μm galena particles (d_{50} : 2.6 μm) using potassium hexyl xanthate at a stirrer speed of 1400 rpm increased the median size to 6.9 μm. Flocculation was rapid especially with potassium ethyl xanthate. A coarser galena sample with particle size 7-15 μm was treated with 10^{-5} M potassium amyl xanthate in a shear vessel of Couette-flow type at a shear rate of 300 rpm for 50 seconds. This application significantly improved the flotation rate and recovery from 30 % to about 70 %. When a 1:1 mixture of galena and quartz of roughly the same size distribution was subjected to shear force the subsequent flotation rate of galena was not affected as much as that of galena alone. Shear flocculation also improved the flotation rate of chalcocite particles with 10^{-4} M potassium amyl xanthate as collector.

Koh et al. (1986) have investigated the floc size distribution of 10 μm scheelite particles by sodium oleate. A simple kinetic model and a self-preserving distribution of log-normal form were proposed for the fine and coarse fractions, respectively. The predicted size distributions agreed reasonably well with experimental results.

The effects of various factors on the shear flocculation-flotation of ultrafine wolframite particles were investigated by Yarui and Daxin (1986). The recovery of ultrafine wolframite particles (-5μm) by shear flocculation-flotation was 80 % instead of 50 % in conventional flotation. For artificial mixtures of wolframite (-5μm) and quartz (-10μm) with a head grade of 12.18 % WO_3, the concentrate grade and recovery of wolframite in shear flocculation-flotation were 39.29 % WO_3 and 82.56 % respectively, instead of 30.14 % WO_3 and 58.92 %, respectively in conventional flotation. The d_{80} size of particles was increased from 4.1 μm to 8.5 μm and the rate of shear flocculation-flotation was 4.1 times the rate of conventional flotation. The suggested mechanism studied that the main aim of high speed stirring is to increase shear rate of fluid, causing high collision energy to overcome the repulsive energy barrier existing between wolframite particles. The van der Waals attractive interaction energy was increased remarkably by the hydrophobic association of sodium oleate on the surface of wolframite particles.

Li and Fuerstenau (1987) have studied the effects of pH and concentrations of sodium dodecyl sulfate on the stability of a fine hematite suspension, and on the zeta potential of hematite. Fine hematite particles having a high surface charge were destabilized in sodium dodecyl sulfate solution at high shear rates. The pH range of hematite flocculation increased by increasing the collector concentration. They concluded that the results could be used for the improvement of iron ore beneficiation by flocculation.

The effects of various factors such as pH, conditioning speed, conditioning time, and the effects of silicate, magnesium and carbonate ions on the shear flocculation of very fine fluorite and scheelite were investigated by Sivamohan (1988). It was found that pH had the greatest influence on the amount of shear flocculated particles under varying conditions. Experimental results showed that neither conditioning speed nor the conditioning time affects the shear flocculation. 5 minutes of stirring was sufficient to achieve shear flocculation, even up to 80-90 %. Shear flocculation of both minerals was not significantly affected in a temperature range of 20-45 °C. Silicate did have a pronounced influence on the amount shear flocculated for both minerals; whereas the effect of magnesium ion was only marginal.

Shear flocculation of -10 μm hematite and its effect on the flotation have been studied by Fuersteneau et al. (1988). Maximum flocculation of hematite was at a stirrer speed of 1200 rpm, using 10^{-4} M sodium dodecyl sulphate and at pH 3.0. Above this shear rate larger flocs began to break up. Shear flocculation prior to flotation improved the recovery from 80 % to about 85 %. The flotation recovery of hematite from a hematite-quartz mixture (1:1) also increased with increasing agitation time. This was attributed to the formation of flocs of hematite by shear flocculation. The grade however decreased slightly with increasing agitation time due to entrainment of quartz particles within the hematite flocs or due to the activation of quartz by hydroxy complexes and hydroxides of iron.

The hydrophobic aggregation of fine rhodochrosite particles with sodium oleate has been reported by Lu et al. (1988). The amount of flocculated material increased with increasing collector concentration. The reason for the aggregation of rhodochrosite was found to be the hydrophobization of the mineral surface. The extent of shear flocculation increased with increasing contact angle (in turn hydrophobicity) although zeta potential also increased to more negative values.

The separation of apatite from rhodochrosite by controlled dispersion-shear flocculation-flotation has been shown to be possible (Yongping and Mulong, 1988). The technique consists of dispersion of apatite and rhodochrosite with sodium silicate and HY-85, agitation for shear flocculation and finally flotation of rhodochrosite. Sodium oleate was used as collector. A rhodochrosite concentrate with a phosphorus content of 0.30 % P_2O_5 from a mixture of rhodochrosite-apatite (an impurity in rhodochrosite concentrate) containing 0.64 % P_2O_5 . The recovery of rhodochrosite was 66.02 %.

The effect of high intensity conditioning prior to flotation has been developed as a means of improving the flotation of ultrafine particles from massive sulphide ores that require a relatively fine-grind (Bulatovic and Salter, 1989). This technique can only be effective if high-intensity conditioning is done in the presence of collectors and modifiers. The froth after conditioning with collector is heavy and fine particles are aggregated and readily floatable. The selectivity between valuable minerals and gangue slimes is significantly improved so that a higher grade concentrate is obtained. Laboratory and pilot plant testwork have been carried on finely disseminated copper-zinc, copper-nickel, copper-lead-zinc-silver and copper ores. The recovery of copper increased from about 35 % to 80 % after high intensity conditioning with -10 µm material. Similar results were obtained for pentlandite. High intensity conditioning also improved the grade of copper concentrates from 19-22 % Cu to 25-26 % Cu for 0-10 µm and 10-15 µm materials, respectively. Grade of zinc concentrate was 56 % Zn with high intensity conditioning plus flotation instead of 48 % Zn in flotation without conditioning.

The dependence of shear flocculation on surface coverage and zeta potential was elucidated using a model system of fluorite-scheelite-oleate (Sivamohan and Cases, 1990). The experimental results showed well developed correlations between the surface coverage, the zeta potential and the amount shear flocculated. At a sufficiently high shear, both increasing the surface coverage and decreasing the zeta potential led to increased degree of aggregation of fluorite and scheelite with sodium oleate. Manipulation of these two factors permitted the turbidity to be reduced from 450 NTU to 40 NTU in the case of scheelite. With fluorite turbidity drop was from 120 NTU to 20 NTU.

Shear flocculation and flotation of galena and synthetic PbS were investigated by Subrahmanyam et al. (1990) with special emphasis to the effect of surface charge and the degree of hydrophobicity. -5 µm galena was subjected to shear flocculation at pH 7, at a stirrer speed of 1500 rpm. Sodium ethyl xanthate was used as collector. It was found that both the surface coverege (degree of hydrophobicity) and the surface potential were of utmost importance for shear flocculation. Partial flocculation in the absence of collector was attributed to the hydrophobic species formed as a result of surface oxidation. Flocculation increased with increasing collector concentration but at a very high concentration (6.94×10^{-4} M) where the corresponding zeta potential was about -60 mV, no aggregation occured. The absence of flocculation was probably due to high negative potential resulting in repulsion between the particles. It was also shown that 20-30 minute stirring was sufficient to reach equilibrium; the solution turbidity, then, hardly changed. Shear flocculation improved the flotation recoveries of galena which was higher in comparison to the conventional flotation recoveries. This was attributed to the better collision efficiencies of aggregates with bubbles.

The hydrophobic aggregation flotation of fine rutile particles (-20 µm) has been investigated by Song and Lu (1990). The rutile recovery raised gradually with the increase of agitation speed and time. Furthermore, a close correlation between the agitation speed and time was observed. If a high agitation speed like 3000 rpm was used, 5 minutes agitation time was sufficient to obtain a good recovery whereas about 60 minutes was necessary to obtain the same recovery at a stirrer speed of 700 rpm. When benzyl arsonic acid was used as collector, the hydrophobic aggregation prior to flotation increased rutile recovery from 30 % to 70-80 %, depending on agitation speed and time. Using benzyl arsonic acid and kerosene together in emulsion form improved the rutile aggregation and the subsequent flotation recovery. D_{50} of rutile particles increased from 5.73 µm to about 60 µm by shear flocculation. A rutile concentrate with a grade of 71.4 % TiO_2 was obtained with a recovery of 89.00 % from a mixture of rutile and amphibole with a head grade of 10.00 % TiO_2, whereas by conventional flotation the grade and recovery were 26.30 % TiO_2 and 45.09 %, respectively.

In another study, the effects of various factors on shear flocculation of quartz in aqueous solutions of dodecylamine chloride were investigated (Raju et al., 1991). It was found that aggregation was rapid nearly completing in 15 minutes and that there was a critical dodecylamine chloride concentration above which flocculation deteriorates. Flocculation first increased and then decreased with increasing particle size. Aggregation was best at 500 rpm stirrer speed and the amount flocculated decreased with increasing speed. It was shown that hydrophobicity and surface charge were the most important factors influencing the aggregation mechanism. Maximum flocculation being at pH 9.6 was attributed to very low surface charge and maximum contact angle of particles at this pH. It was emphasized that low surface charge or high contact angle alone was not sufficient for good flocculation instead these two conditions were required. The flocculation was found to be maximum for the conditions: pH 9.6; dodecylamine chloride concentration 9.02×10^{-5} M; stirrer speed 500 rpm; and the size of the coarse particle -38+20 μm.

The influence of wettability on the aggregation of fine magnesite and dolomite was studied by Skvarla and Kmet (1991). These particles aggregated strongly with an increasing concentration of sodium oleate above approximately 10^{-4} M. The aggregation efficiency was maximum at 3×10^{-4} M sodium oleate for magnesite and 5×10^{-4} M sodium oleate for dolomite. The next increase of the oleate concentration caused a decrease in the aggregation. The stability of magnesite and dolomite without collector was evoked by the hydration (hydrophillic) structural forces of repulsive character. On the other hand, the attractive hydrophobic structural force was responsible for the aggregation in the presence of sodium oleate.

Bilgen (1992) studied shear flocculation of fine cassiterite. The effects of pH, collector concentration, stirrer speed and stirring time were investigated. It was found that they all affect shear flocculation. Different amount of CA 540 (a sulphosuccinamate collector) was required for different pH values, varying from 1 to 5 mg/l. Aggregation decreased with increased CA 540 concentration above an optimum level. The reason was probably due to the bonding of non-polar part of "free" collector to the same part of the collector already adsorbed on the mineral, creating hydrophillic surfaces. A stirrer speed range of 250-400 rpm was found to be sufficient. This gentle speed was related to high specific gravity of cassiterite which provides sufficient kinetic energy to overcome the repulsive energy barrier. Higher speeds broke up larger aggregates. However the amount of fine particles remaining in the suspension was less at 800 rpm than at 250-400 rpm. It was also found that shear flocculation was a slow process requiring 30-45 minutes. However, the formation of initial flocs was rapid. pH did not affect the shear flocculation as much as collector concentration and stirrer speed. General trend was that aggregation increased when pH was increased from 3.0 to 4.0 which is close to the i.e.p. of cassiterite and remained roughly same through pH 6.0. D_{50} value increased from 4-5 μm to as high as 27-30 μm.

The flocculation and selective flocculation in the apatite-hematite system was studied with sodium oleate as collector and sodium pyrophosphate as dispersant. Sodium oleate was an effective collector for agglomeration for apatite over a wide range of pH but was a dispersant in alkaline media and collector for agglomeration in neutral to acidic media for hematite. Selective flocculation of minerals from their mixtures was also achieved (Wang and Heiskanen, 1992).

The effect of shear agitation on the removal of ultrafine graphite impurities from kaolinite by floc-flotation was investigated by Raghavan et al. (1992). It was shown that graphite particles flocculated to form macroflocs of the size suitable for conventional flotation whereas kaolinite particles remained non-aggregated, using 800 g/t kerosene as collector. The subsequent graphite flotation removed about 80 % of the graphite with total clay loss of 9.5 %.

2.3. Factors Affecting Shear Flocculation

2.3.1. Zeta Potential

The results of different studies indicate that low zeta potential of particles increases the extent of shear flocculation (Warren, 1975a; Sivamohan and Cases, 1990; Subrahmanyam et al., 1990; Raju et al., 1991). Sivamohan and Cases (1990) obtained well developed correlations between the zeta potential and the amount shear flocculated. The study of Raju et al. (1991) indicated that maximum flocculation occured at the point of zero charge of particles and this was explained by less electrostatic repulsion. When the particles hold high potentials it became necessary to apply higher stirrer speeds to overcome the repulsive energy barrier.

Contrastly, it was shown that zeta potential did not affect the hydrophobic aggregation of fine rhodochrosite particles by sodium oleate. The amount of flocculated material increased with increasing hydrophobicity although zeta potential also increased in the same range (Lu et al., 1988).

2.3.2. Hydrophobicity

Aggregation under high shear rate occurs only if the particle surfaces become hydrophobic with a suitable collector. The degree of aggregation increases with increase in collector concentration up to certain levels but beyond these levels aggregation decreased due to the bonding of the non-polar part of the collector already adsorbed on the mineral, creating hydrophillic surfaces (Bilgen and Wills, 1991).

Skvarla and Kmet (1991) obtained clear correlations between the aggregation, wettability and the surface energy of minerals. The evaluated surface energy parameters of magnesite particles show that the adsorption of oleate on the magnesite surface results in very dramatic changes in the surface properties of magnesite. The decrease in the electron-donor surface energy parameter, due to the shielding of the surface oxygens by oleate alkyl groups, as well as in the van der Waals surface energy parameter, clearly correlates with the aggregation increase.

Bilgen (1992) showed that the collector concentrations corresponding to maximum aggregation were different at each pH, and the amount of collector was lower near iso-electrical point.

2.3.3. Stirrer Speed

Since hydrophobic association takes place only in direct particle contact, it is necessary to bring particles together. This is achieved by throwing them towards each other with a force exceeding the energy barrier (Nemethy and Scheraga, 1962). However, too high shear rates may break up larger flocs.

The stirrer speeds vary from system to system: 1500 rpm in scheelite-sodium oleate (Warren, 1975a), 500 rpm in quartz-dodecylamine (Raju et al., 1991), 250-400 rpm in cassiterite CA 540 (Bilgen, 1992). The stirrer speed may depend on some factors like particle size, specific gravity and zeta potential. Higher stirrer speeds are usually required for finer and lighter particles and for the particles holding high surface charge.

2.3.4. Flocculation (Stirring) Time

The results of different studies on the effect of stirring time on shear flocculation are different. According to Warren (1975a), shear flocculation is a slow process. The slowness of floc growth is probably caused by a low probability of adhesion between the highly charged particles. This is consistent with the fact that if the zeta potential is deliberately reduced the rate of aggregation increases. Reducing the zeta potential from -45 mV to -25 mV reduced the equilibrium flocculation time to 20-30 minutes whereas equilibrium was not still attained after 90 minutes stirring with highly charged particles. The retarding effects of electrostatic repulsion become relatively less important as the size and the kinetic energy of the colliding particles increase. This aggrees with the observation that for 1 μm and 3 μm ultrafine scheelite particles the longer stirring time leads to higher recoveries whereas for 11 μm particles there is little change after 15 minutes.

Sivamohan (1988) showed that conditioning time did not in any way affect the amount of shear flocculated fluorite and scheelite. 5 minutes of conditioning was sufficient to achieve shear flocculation, even up to 80-90 %.

Bilgen and Wills (1991) suggested that to commence or accelerate the aggregation of fine particles with high surface charge it was probably necessary to form seed flocs initially as in the pelletizing process. Their experiments showed that aggregation started immediately but longer stirring was necessary to reach the equilibrium.

2.3.5. Particle Size

Most investigations indicate that the rate and extent of shear flocculation increases with increasing particle size up to certain levels. Coarser materials usually require lower speeds, shorter stirring time and they can be flocculated in a wider range of pH.

The size of the coarse particle is an important factor in shear flocculation since it influences the collision mechanism. Samygin et al. (1968) found that the adhesion rate of fines to coarse particles to be 10^3-10^4 as high as the rate of cohesion between the fines. Such effects was attributed to different mechanisms at work, i.e. diffusion between fines and inertia for collisions between fine and coarse particles.

The work of Raju et al. (1991) with quartz of different size fractions indicated that there was almost no flocculation with very fine (-5 μm) and very coarse (-75+53 μm) material. Maximum flocculation was observed with -38+20 μm material.

2.3.6. Suspension Concentration

Warren (1975a) showed that aggregation in more concentrated suspensions was more rapid and a ten-fold increase in suspension concentration increased the initial rate of aggregation about 50 times. More concentrated suspension contained less discrete particles than did the initially dilute suspension; also the d_{50} value was greater.

In another study, on the other hand, statistical analysis to investigate the effect of some factors on the selective shear flocculation of scheelite from garnet indicated that pulp density was not a significant factor at 95 % confidence level (Jarret and Warren, 1977).

2.4. Theory of Electrokinetics

2.4.1. Electrical Double Layer Formation and Zeta Potential

When solids are brought in contact with an aqueous medium, they will experience a surface charge. Ionisation, ion dissolution and ion adsorption are the possible charging mechanisms (Shaw, 1970). The reactions between the water molecules and various mineral surface ions are not uniform in energy. As a result, some mineral ions pass into solution in greater quantities than others and electrical neutrality of the surface is impaired. Under these conditions the surface acquires a charge opposite in sign to the ions which have principally passed into solution. The increase in the surface electric charge impedes the passage of ions of opposite sign into solution from the mineral crystal lattice. Finally, a state of equilibrium will be established between the solution and the solid surface, which will be surrounded by electrical double layer (Glembotskii et al., 1972; Leja, 1982). An electrical double layer is a system in which by definition there exists a separation of electrically charged ions at an interface; that is, there is a layer of positively charged ions and a layer of negatively charged ions with the whole system remaining electrically neutral.

The theory of electrical double layer deals with the distribution of counter-ions and co-ions in the locality of charged surface and hence with the magnitude of the electric potentials occurring in this region. This is important for interpreting many of the experimental observations concerning the electrokinetic properties, stability, ion-exchange, adsorption, corrosion, flocculation, flotation, etc. of charged colloidal systems. Figure 2.2 shows the structure of an electrical double layer.

It is mainly cations which pass into solution from the outer layer (between lines 1-1 and 2-2). The mineral surface then acquires a negative charge. After equilibrium has been established between the solution and the solid phase, mineral anions will predominate to the right of the line 1-1, which represents the boundary between the unaltered and altered layers of the mineral lattice; this layer will be negatively charged. This part of the double layer is designated as A.

The ions in the inner skin A of the double layer are firmly attached to the mineral crystal lattice in regular order, and move with the crystals as they themselves move in water. The line 2-2 is the physical boundary between the mineral and the aqueous solution. Immediately beyond this boundary is the next

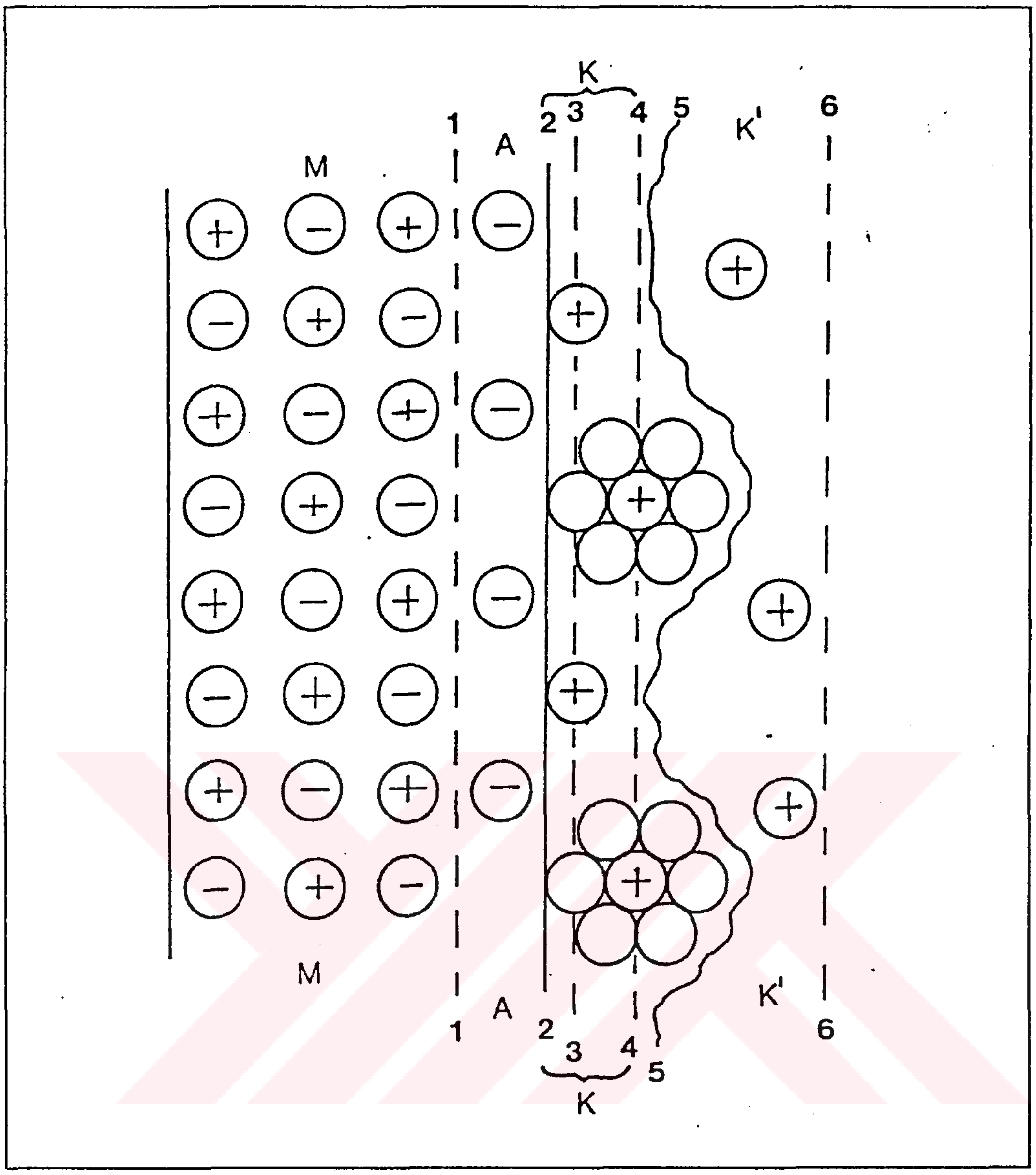

Figure 2.2 Structure of Electrical Double Layer (M-M: Part of the mineral crystal lattice; 1-1: Boundary between altered and unaltered lattice layers; A-A: Inner skin of double layer; 2-2: Physical boundary between mineral and aqueous solution; 3-3: Inner Helmholtz plane; 4-4: Outer Helmholtz plane; K-K: Stern layer; 5-5: Shear plane; K'-K': Diffused layer; 6-6: Boundary between diffused layer and solution).

layer of ions which is also regulary ordered and is charged positively, i.e. it is composed of cations (Layer K). Since Stern (1924) proposed a model for the inner part of the double layer, the layer K is termed the Stern layer. The Stern model for the inner part of the double layer was refined by Grahame (1947) who distinguished between the Stern layer, also called the Outer Helmholtz Plane (OHP) to indicate the closest distance of approach of hydrated ions in solution and an Inner Helmholtz Plane (IHP) to indicate the centers of ions which are specifically adsorbed on to the solid surface. These ions, together with water molecules which surround them, form the outer skin of the electrical double layer.

The cations in the Stern layer are only some of the total number of cations which passed into solution. The remaining cations are beyond the boundary of the Stern layer (4-4) and are in no regular pattern, forming the diffused layer K', having a gradually diminishing ion concentration as the distance from line 4-4 increases. The line 6-6 is the boundary between the diffused layer and the liquid, which contains practically no cations. The ions lying between lines 2-2 and 6-6 have an opposite charge to the ions in the inner skin of the double layer and are called counter ions. A distinction must be drawn between the counter ions in the Stern layer in a regular pattern and the counter ions in the diffused layer K'. When the mineral particles move in the liquid the counter ions in the Stern layer will move with the mineral while the counter ions in the diffused layer will lag behind them. For this reason the overall electrical neutrality of the system is upset and a potential difference is set up between the crystal surrounded by the ion layers A and K and the remaining part of the solution. This potential difference only occurs and can only be detected when the mineral with its ion layers A and K move relative to the liquid. Its conventional designation is therefore electrokinetic (zeta) potential. The counter ions in the Stern layer are therefore called fixed and those in the diffuse layer free counter ions; the surface 5-5 is called the shear plane, since it is the boundary which separates the mineral and ions which move with it from the remaining ions, which lag behind them in movement.

The exact position of the shear plane (5-5) within the diffuse layer of the electrical double layer is not known. In theoretical treatments of electrokinetic effects it is assumed that slippage occurs along, or close to, outer Helmholtz plane. Therefore the zeta potential measured by electrophoresis is the potential at the shear plane. The total charge of all the counter ions is equal to the charge of the ions of opposite sign in the inner skin of the double layer; the magnitude of the zeta potential is therefore described as the difference in potential between the ions in the diffused layer taken together and all the ions to the left of the shear plane (taking signs into account).

The sign and magnitude of the zeta potential indicate the nature of the adsorbed ions and the relative magnitude of the potential in the solid phase. For example, a high positive zeta potential means that the mineral surface is dominated by cations, a high negative zeta potential indicates dominations by anions, and a low zeta potential indicates that the surface is influenced almost equally by cations and anions (Gaudin and Sun, 1946).

De Bruyn and Agar (1962) state that the interface between the solid and the solution phase may be treated as a semi-permeable membrane which allows only charged species common to both the solid and solution to pass through. These species which affect the surface potential are called potential determining ions (pdi). Potential determining ions are specific for each solid. In general, the ions which build the crystal lattice as well as their hydroxy complexes are pdi for ionic solids and hydrogen and hydroxide ions are pdi for oxides (Parks, 1965). At a certain concentration of pdi in the solution, the electrical double layer will be absent, and the solid surface will show no net positive or negative charge, this point is called the point of zero charge (pzc) of the mineral. If hydrogen and hydroxy ions are potential determining ions, the pzc may be given the special name isoelectric point (i.e.p.). In other words, the i.e.p. is used to represent both the pH at which an immersed solid oxide surface has zero net charge and the pH resulting in equivalent concentration of positive and negative complexes. In the absence of specifically adsorbed ions, the pzc and i.e.p. are the same (De Bruyn and Agar, 1962).

2.4.2. Electrokinetic Phenomena and Measurement of Zeta Potential

There is a number of electrokinetic phenomena that have in common the feature that relative motion between a charged surface and the bulk solution is involved. Essentially, a charged surface experiences a force in an electric field and, conversely, a field is induced by the relative motion of such a surface (Adamson, 1967).

The four electrokinetic phenomena are as follows:

1. Electrophoresis: The movement of a charged surface plus attached material (i.e dissolved or suspended material) relative to stationary liquid by an applied electric field. Measurements of velocity of the particles under a known external field gives information about their net electric charge, or their surface potential with respect to the bulk of the suspending phase.

2. Electroosmosis: The movement of liquid relative to a stationary charged surface (e.g. a capillary or porous plug) by an applied electric field. The pressure necessary to counter-balance electroosmotic flow is termed the electroosmotic pressure.

3. Streaming Potential: The electric field which is created when liquid is made to flow a stationary charged surface. The development of a streaming potential when

an electrolyte is forced through a capillary or porous plug is a complex process. The liquid in the capillary or plug carries a net charge and its flow gives rise to a streaming current and consequently a potential difference. This potential opposes the mechanical transfer of charge by causing back-conduction by ion diffusion and, to a much lesser extent, by electroosmosis. The transfer of charge due to these two effects is called the leak current, and the measured streaming potential relates to an equilibrum condition when streaming current and leak current cancel one another.

4. Sedimentation Potential: The electric field which is created when charged particles move relative to stationary liquid.

Electrophoresis has the greatest practical applicability of these electrokinetic phenomena and has been studied extensively in its various forms, whereas electroosmosis and streaming potential have been studied to a moderate extent (Shaw, 1970).

2.5. Contact Angle

2.5.1. Contact Angle and Wetting

Hydrophobicity has to be imparted to the minerals for their aggregation by shear flocculation. This is done by addition of suitable collectors which convert the hydrophilic surface into a hydrophobic one by adsorbing with its head group towards the surface and its long hydrocarbon chain projects out into the solution. The degree of hydrophobicity of a mineral surface can be measured by contact angle between the surface, the solution and air bubble pressed against the solid (Wills, 1980).

When a drop of liquid is placed on a flat surface it may spread completely over the surface or, more likely it may remain as a drop having a definite angle of contact with the solid surface (Figure 2.3).

Assuming that the various surface forces can be represented by surface tensions acting in the direction of surfaces, then, equating the horizontal components of these tensions:

$$\gamma_{S/G} = \gamma_{S/L} + \gamma_{L/G} \cos\theta \qquad (2.1)$$

where $\gamma_{S/G}$, $\gamma_{S/L}$ and $\gamma_{L/G}$ are the surface tensions between solid-gas, solid-liquid and liquid-gas, respectively, and θ is the contact angle between the mineral surface and the bubble.

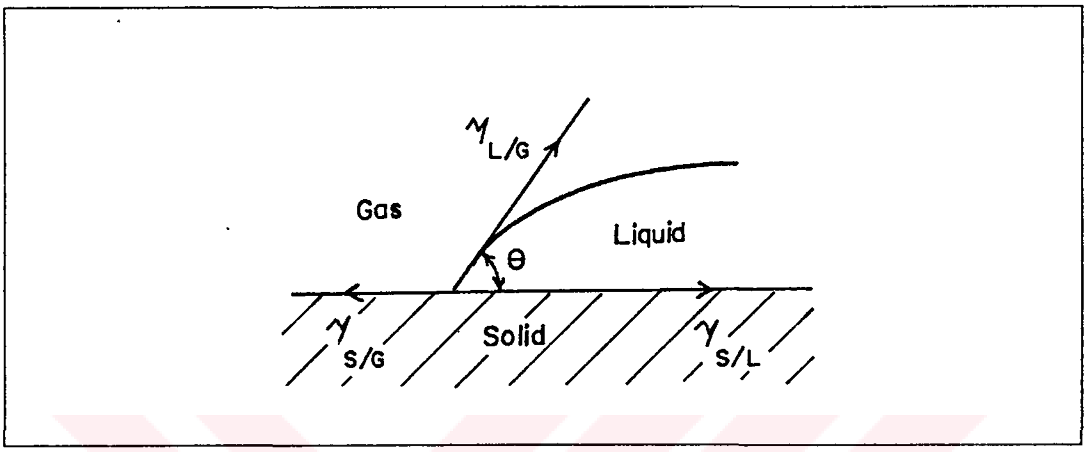

Figure 2.3. Contact Angle Between Solid and Bubble in an Aqueous Medium

The work of adhesion between the solid and liquid ($W_{S/L}$) is given by Dupre equation:

$$W_{S/L} = \gamma_{S/G} + \gamma_{L/G} - \gamma_{S/L} \qquad (2.2)$$

Combining these two equation,

$$W_{S/L} = \gamma_{L/G}\ (1 + \cos\theta) \qquad (2.3)$$

Indicating that the work of adhesion between solid and liquid decreases with increasing contact angle.

The wettability of mineral surfaces can be compared by the magnitude of the contact angles. Thus, if the contact angle is nill, the surface of the mineral is completely wetted by water. If the contact angle is 180°, the water will not spread on the mineral surface at all, corresponding to complete air-avidity by the surface. This extreme case does not occur in practice, hydrophobic surfaces are characterized by high contact angles ranging from 40 to 110 degrees (Zettlemayer, 1969).

2.5.2. Measurement of Contact Angles and Capillary Rise Method

The measurement of contact angles is complicated by the following factors:

1) Contamination of the liquid surface tends to reduce the contact angle.

2) Solid surfaces show great degree of heterogeneity even after careful polishing.

3) Contact angles are often not definite quantities but differ according to whether the liquid is advancing over a dry surface or receding from a wet surface. This hysteresis effect is most noticeable with impure surfaces; the difference between advancing and receding contact angles may be as much as 50° (Shaw, 1970).

The measurement of contact angle is usually facilitated when a moderately large and uniform solid surface is available. Tilting plate method, sessile drop method and captive bubble method are common techniques applied on such surfaces (Adamson, 1967).

The contact angles of solids in a finely divided form are technically important but are difficult to measure. Liquid penetration (capillary rise), compressed discs, and the Wilhelmy gravitational methods for powdered systems have been criticised by Buckton (1990). Bartell et al. (1928) have developed a method based on displacement pressures for measuring such contact angles (capillary rise method). It consisted of forcing a liquid through a previously compacted powder, measuring the pressure required to achieve this movement. A second powder bed was passed through this bed, the pressure required being ascertained.

The powder was assumed to resemble a bunch of equally size capillaries of radius "r" the pressure required to force the liquid through the powder (ΔP) being given by the Laplace equation:

$$\Delta P = \frac{2\gamma_{L/G} \cos\theta}{r} \qquad (2.4)$$

where θ is the advancing contact angle, $\gamma_{L/G}$ is the surface tension of liquid-gas interface and r is the radius of capillary. By substituting into the above equation for the liquid of known contact angle the value of "r" could be obtained, and hence substituted into the equation for the unknown angle, which could then be calculated.

This method is difficult to use and the following simpler method has been described by Crowl and Wooldridge (1967). The distance of penetration L in time t into horizontal capillary or in general when gravity may be neglected, is given by the Washburn equation (Allen, 1975).

$$\frac{L^2}{t} = \frac{r\gamma_{LG} \quad \cos\theta}{2\eta} \qquad (2.5)$$

where η is the viscosity of the liquid.

For a packed bed of powder this equation becomes;

$$\frac{L^2}{t} = \left(\frac{r}{K^2}\right) \frac{\gamma_{L/G} \quad \cos\theta}{2\eta} \qquad (2.6)$$

where K is an unknown factor dependent on the packing. To find the packing factor and the radius of pores, the contact angle is assumed to be zero when the powder is conditioned with a liquid that maintain the complete wetting of the mineral surface.

Reproducability of porosity in such systems is undoubtedly a problem. The limitation of these methods is the assumption of equal pore radii (Figure 2.4).

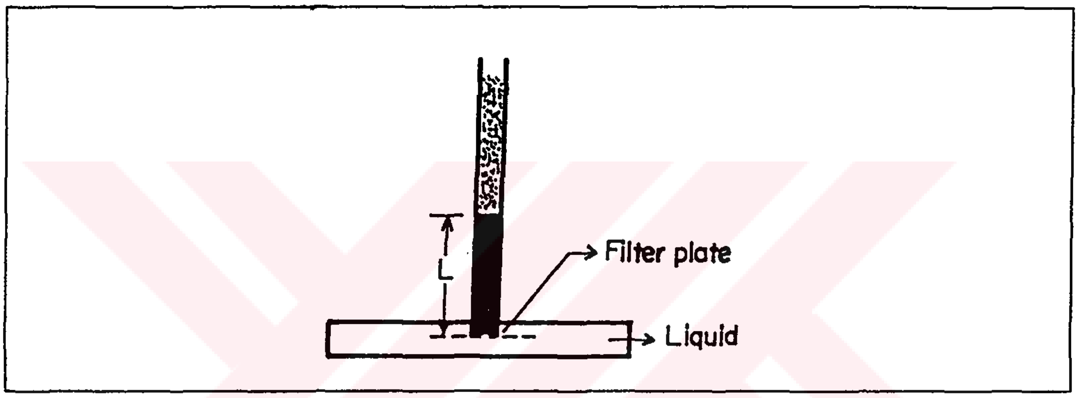

Figure 2.4. Capillary Rise Method

2.6. Sedimentation Technique

Sieving is rarely carried out on a routine basis below about 40 μm below this size the operation is referred to as sub-sieving. The most widely used procedures are sedimentation, elutriation, and microscopy, although a whole new field of electronic techniques is now in use (Wills, 1980).

In sedimentation techniques the material to be sized is dispersed in a fluid and allowed to settle under carefully controlled conditions. The particles are separated on the basis of resistance to motion in a fluid. This resistance determines the terminal velocity which the particles attain as they are allowed to settle in a fluid under the influence of gravity. The terminal velocity is given by Stoke's equation:

$$V = \frac{d^2 g\,(D_s - D_f)}{18\,\mu} \tag{2.7}$$

where V is the terminal velocity of the particle (cm/s), d is the particle diameter (cm), g is gravitational acceleration (cm/s^2), D_s is the particle density (gr/cm^3), D_f is the fluid density (gr/cm^3), and μ is the fluid viscosity in poise.

2.7. Nephelometry

The turbidity of a water sample is due to the presence of finely dispersed suspended matter. The abundance of these substances in the water is a measure of its degree of turbidity. The more the amount of suspended matter, the higher the turbidity (Rodier, 1957; Hunt and Wilson, 1986; Clesceri et al., 1989).

A distinction must be made between the turbidimetric and nephelometric methods. If the suspension is concentrated the amount of scattering will be large enough to cause an appreciable reduction in the intensity of the transmitted beam; the transmittance may be measured. This is called turbidimetric measurement. If the suspension on the other hand, is very dilute, the value of transmittance may be very small and the measurement is of no value. In this case the intensity at an angle to the incident beam must be measured. In most applications, the light scattered at 90° is measured; this is called nephelometric measurement (Kolthoff and Sandell, 1952).

The intensity of scattering is dependent upon the number of particles, their size and shape, refractive indices of medium and particles and wavelength. The relationship among these variables is complex. In fact most nephelometric and turbidimetric procedures tend to be highly empirical (Skoog and West, 1971).

CHAPTER III

MATERIALS AND METHODS

3.1. Sample Preparation

The chromite concentrate, taken from Üçköprü-MUĞLA plant and the hand-picked serpentine lumps obtained from Kavak-ESKİŞEHİR chromite concentrator were ground to -10 µm separately in a porcelain mill using pebbles as grinding media. -10 µm fractions were obtained by repeated beaker decantation in accordance with the Stoke's law. Finally, they were washed with dilute HCl and distilled water repeatedly to remove surface impurities. The dried samples were kept in nylon bags for the subsequent experiments.

3.2. Chemical Analyses and Size Distributions

The chemical analyses of chromite and serpentine samples are given in Table 3.1 and Table 3.2, respectively.

Table 3.1. Chemical Analysis of Chromite Sample

Constituent	%
Cr_2O_3	53.93
FeO	14.40
Al_2O_3	15.14
MgO	13.40
SiO_2	2.79
CaO	0.22

Table 3.2. Chemical Analysis of Serpentine Sample

Constituent	%
MgO	38.75
SiO_2	36.30
FeO	7.68
Fe_2O_3	7.90
Al_2O_3	1.66
H_2O	5.00
Cr_2O_3	0.90
CaO	0.34

Size distributions of chromite and serpentine samples, determined by Coulter counter, are given in Figure 3.1 and 3.2, respectively.

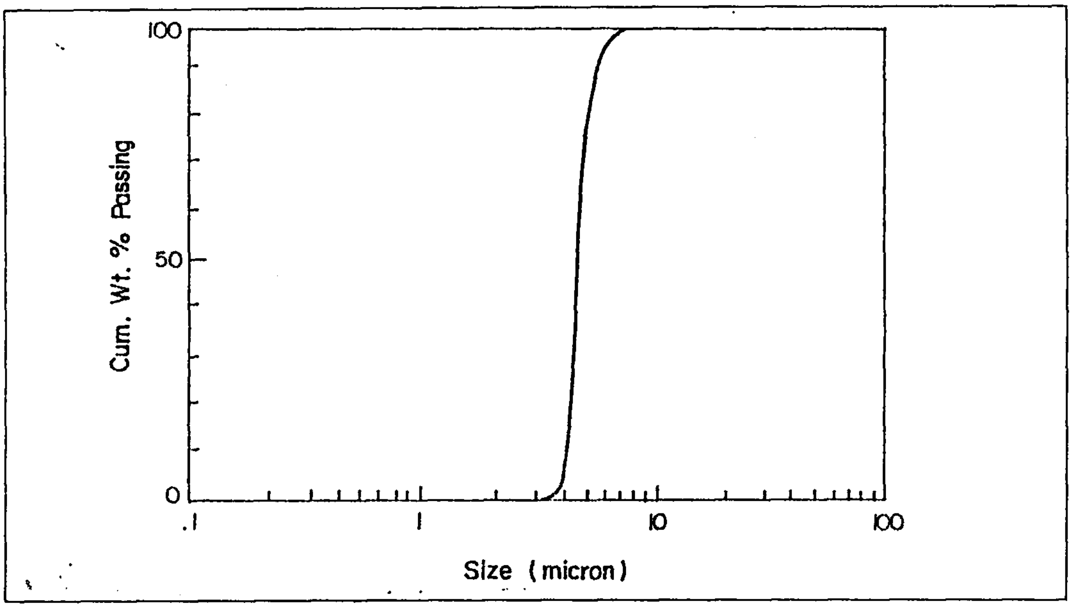

Figure 3.1. Size Distribution of Chromite Sample Determined by Coulter Counter

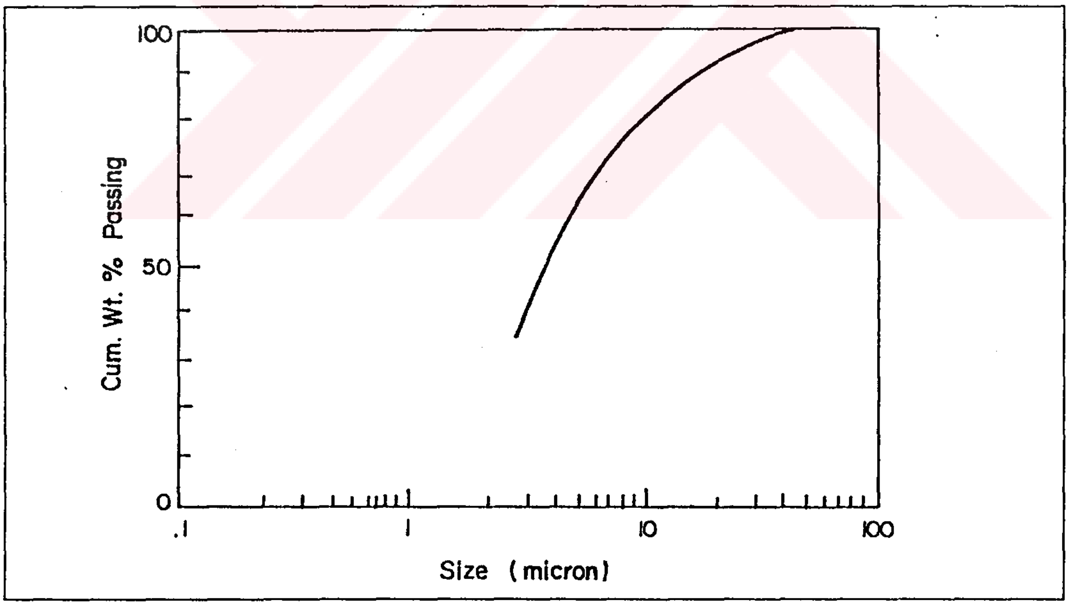

Figure 3.2. Size Distribution of Serpentine Sample Determined by Coulter Counter

3.3. Electrokinetic Potential Measurements

3.3.1. Sample Preparation

The sample prepared for shear flocculation experiments were washed with double-distilled water. Then diluted suspension were allowed to settle for a predetermined time calculated according to settling rate of ≈ +10 micron e.s.d. particles in accordance with the Stoke's law. ≈ -10 micron e.s.d. particles were siphoned off into another beaker; dried at 105°C and kept for zeta potential measurements.

3.3.2. Equipment

Rank Brothers Micro-Electrophoresis apparatus Mark II was used to measure the electrophoretic mobilities of chromite and serpentine particles. A quartz flat cell of rectangular cross section was used during the measurements. Palladium electrodes were used to eliminate "gassing" at high electrolyte concentrations and high field strenghts. The electrodes were charged with hydrogen by using them as cathodes in the electrolysis of dilute (10^{-3}M) H_2SO_4 solution, using a platinum anode and a current of 3 mA for one hour. The charging was repeated once a day. The cell was immersed in a thermostated tank whose temperature was controllable. The instrument was equipped with a stabilized DC power supply. Another connected part is the voltmeter and ampermeter together with an electromagnetic digital timer. Figure 3.3 shows the apparatus.

Figure 3.3. Rank Brothers Micro-Electrophoresis Apparatus

3.3.3. Calibrations

The correct alignment of the micro-electrophoresis cell relative to the microscope was made by adjustment of screw clamps so that the flat plane of the cell was adjusted horizontally and perpendicular to the optical path of the microscope. Focusing was made on minute stratches which occured on the front and back walls of the cell windows by adjusting the vernier on the microscope.

The eye-piece of the microscope was provided with a square grid graticule which was used to determine the velocities of the particles. The apparent distance between the graticules was 50.8 μm.

The determination of inter-electrode distance was described by Özbayoğlu (1977) and Atalay (1986). First, the cell is filled with a solution of known electrical conductivity "K" and then the electrical resistance between electrodes "R" is determined by a digital voltmeter. The digital voltmeter was used to measure the potential difference across the cell and across a standard resistance "r" which was placed in series with it. If these potential differences are "V_c" and "V_r", respectively then the cell resistance "R" is given by;

$$R = r\left(\frac{V_c}{V_r}\right) \qquad (3.1)$$

The cross-sectional area “A” of the cell can be determined by using the apparatus itself. The microscope is focused on mark on the inside near and far faces of the cell and micrometer readings are noted. The difference between the two readings is the apparent thickness of the cell. The real thickness of the cell can be found by multiplying the refractive index of water with the apparent thickness of the cell. The height of the cell was measured with the upper micrometer by raising the whole cell until the edges of the cell came into view. The effective interelectrode distance “L” is, then, calculated as follows:

$$L = R \, . \, K \, . \, A \tag{3.2}$$

Where L is the interelectrode distance (cm), R is resistance across the cell (ohm) and A is the cross-sectional area of the cell (cm^2). The width and thickness of the flat cell and the interelectrode distance were measured as 10.3 mm, 0.992 mm and 7.900 cm by Özbayoğlu (1977).

3.3.4. Procedure

Suspensions of 0.1 % solid by weight were used for measurements. The cell was washed with chromic acid and double-distilled water before every experiment.

The clean cell was flushed several times with the solution before the measurements. After filling the cell with the solution, the electrodes were inserted carefully, taking care not to trap any air bubble. Time was allowed to attain thermal equilibrium at 25 °C in the flat cell. Then a sufficient potential (usually 80 V) was applied across the cell to get the particles moving with a measurable speed.

The velocities of particles were measured both at the front and back stationary levels in the cell. Positions of these levels depend on the thickness of the cell at the observed point (Figure 3.4).

The Stationary levels of the cell were calculated from Komagata's equation:

$$\frac{S}{d} = 0.500 - \left(0.0833 + \frac{32}{\Pi^5} * \frac{d}{H}\right)^{1/2} \qquad (3.3)$$

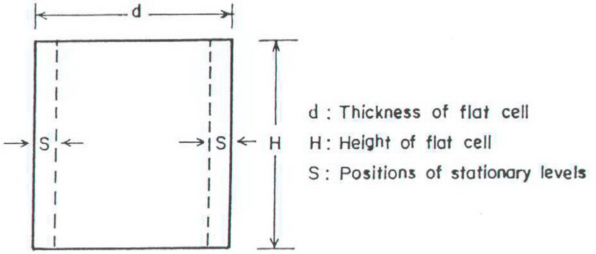

Figure 3.4. Positions of Stationary Levels

When apparent thickness and height of the cell are 0.992 mm and 10.3 mm respectively, from Komagata's equation.

$$\frac{S}{d} = 0.194433219 \tag{3.4}$$

The velocities of particles were measured at both the front and back stationary levels. Polarization effects were minimized by altering the direction of current after each measurement. The mobility of particles, defined as the velocity of migration under a constant potential gradient was computed after taking the averages of readings at the front and back levels. Each reported mobility was the mean of the mobilities of 20 particles, 10 in each direction.

$$\text{Mobility} = U = \frac{v}{E} = \frac{v}{V/L} \qquad (3.5)$$

where, v is particle velocity, V is the applied voltage and L is the inter-electrode distance. Zeta potential of particles were then calculated according to Smoluchowski equation at 25°C:

$$\delta = 12.83\ U \qquad (3.6)$$

3.4. Contact Angle Measurement

Capillary rise method was used to determine the contact angles of chromite and serpentine in sodium oleate and dodecyl amine acetate solutions. The measurements were carried out in a 3.3 mm diameter graduated cylinder with one end closed with a filter disc.

The graduated cylinder was cleaned with chromic acid and double-distilled water before every experiment. 3 grams of chromite or 1 gram of serpentine sample was conditioned with collector solution at required pH for about 40-60 minutes until solids settled to the bottom of a beaker. The supernatant was siphoned off into another beaker and the surface tension was measured with a "Fisher" surface tensiometer Model 20. Solids, dried at 45 °C in an oven, were filled to the graduated cylinder and the packing of the powders was provided by tapping the pipette 300 and 100 times for chromite and serpentine, respectively. The tip of the cylinder was immersed into the prepared solution and the rising distance of solution versus time was recorded. The contact angles were calculated by using the modified Washburn equation as follows:

$$\cos\theta = \frac{L^2 2\eta}{(r/K^2)\,\gamma_{L/G}\,t} \qquad (3.7)$$

where θ is the contact angle in degrees, L is the rising distance of solution through the powder bed in cm, η is the viscosity of the solution in poise, $\gamma_{L/G}$ is the surface tension of the solution in dyn/cm, t is the rising time in seconds, r is the pore radius in cm and K is the unitless packing factor. The value of r/K^2 was found by assuming contact angle zero when the powder was conditioned with a wetting agent namely Aerosol OT 75.

3.5. Shear Flocculation Tests

3.5.1. Shear Flocculation Cell and Stirrer

Shear flocculation experiments were carried out in a cell, 15 cm height and 1400 ml capacity in hexagonal shape. The cell was equipped with 4 baffles to prevent vortex formation and to create turbulence.

1 g. of sample (chromite and serpentine) was first mixed with 1400 ml double distilled water and then was poured into the flocculation cell. The suspension was then agitated for 3 minutes for wetting and dispersion. Then the pH was adjusted with HCl or NaOH. After the conditioning of the suspension for 5 minutes at 630 rpm, collector (sodium oleate or dodecyl amine acetate) was added and the mixture was stirred for 5 more minutes. Finally, the speed of the stirrer was adjusted to predetermined value for shear flocculation.

3.5.2. Turbidimeter and Turbidity Measurement

A LaMotte Model 2008 turbidimeter was used to measure the turbidities. It is acceptable for turbidity measurements reportable under the National Primary Drinking Water Regulations (NPDWR) or the National Pollutant Discharge Elimination System (NPDES) compliance monitoring program. The unit may be operated from line power via an AC adaptor or from self-contained rechargable batteries. The instrument is a true nephelometer measuring the amount of light scattered at right angles from a beam of light passing through the test sample. Test results were read directly in NTU (Nephelometric Turbidity Unit) on a digital readout.The instrument could measure the turbidity values up to 200 NTU and above this dilution were made. The calibration was made with a secondary standard manufactured by Advanced Polymer System, Inc. It is a suspension of uniformly sized plastics, " microspheres " requiring no preparation, and is stable for long periods. The turbidimeter was operated with a tungsten lump, operated at a color temperature of 2300 °K. Distance traversed by incident light and scattered light was 2.5 cm. Figure 3.5 shows the LaMotte Model 2008 turbidimeter.

Figure 3.5. LaMotte Model 2008 Turbidimeter

Turbidity drop (change) was used as a criterian to evaluate the degree of flocculation. The suspension was allowed to settle for 5 minutes at the beginning and at the end of each experiment and the supernatant was siphoned off at 7 cm from the bottom of the shear flocculation cell into a beaker. Turbidities were measured and turbidity drop in percent was calculated as follows:

$$\text{Turbidity Drop (\%)} = (T_i - T_f) / T_i \times 100 \; \ldots\ldots\ldots \qquad (3.8)$$

where T_i and T_f are the initial and final turbidities, respectively. The better the aggregation the lower the final turbidity and the higher the % turbidity drop (change). The values of initial and final turbidities for each experiment are given in Appendix A.

3.5.3. Sedimentation Tests

Sedimentation tests were intended to determine the amount of "settled material", at the end of a pre-determined time. Andreasen pipette was used to find the amount of settled material.

The apparatus was filled with the pulp immediately after each shear flocculation experiment. 10 ml samples were withdrawn immediately (t=0) and at the end of 18.5 or 40 minutes for chromite and serpentine, respectively which were the times necessary for ~ +10 μm chromite and serpentine particles to settle a height of 20 cm. These samples were then dried at 105 °C. The amount of "settled material" was calculated as follows:

$$\text{Settled Material (\%)} = 100 - \frac{W_i}{W_o} \times 100 \qquad (3.9)$$

where W_o and Wi are the weights of samples withdrawn immediately and at the end of 18.5 or 40 minutes, respectively. The higher the amount of settled material, the better the shear flocculation.

3.6. Selective Shear Flocculation Tests

Selective shear flocculation experiments were carried out in the same cell for shear flocculation of chromite and serpentine. The purpose was to flocculate chromite from a chromite-serpentine mixture. 1.00 g. chromite and 1.00 g. serpentine was mixed artificially and put into the cell with 1400 ml. double distilled water. pH adjustment and collector addition were made in the same manner described in Section 3.5.1. Sodium oleate was used as collector.

At the end of each selective shear flocculation experiment, the material was allowed to settle for a certain time and the supernatant was siphoned off at 4 cm. from the bottom of the cell. Supernatant (dispersed) and settled portions were dried separately at 105 °C, weighed and analysed for their Cr_2O_3 content.

The grades and recoveries of settled portion were used to evaluate the results. In addition, selectivity indeces for each separation (Gaudin, 1930) were calculated as follows:

$$SI = \frac{C_s S_D}{S_s C_D} \tag{3.10}$$

where SI is the selectivity index, C_S is the chromite content in settled portion, S_D is the serpentine content in dispersed portion, S_S is the serpentine content in settled portion and C_D is the chromite content in dispersed portion. These contents were found by using the weights and recoveries of each portion.

CHAPTER IV

EXPERIMENTAL RESULTS

4.1. Electrokinetic Potential Measurements

4.1.1. Electrokinetic Potential Measurements of Chromite

The effect of pH, sodium oleate, dodecyl amine acetate and K^+, Fe^{2+}, Al^{3+}, Cr^{3+}, Mg^{2+} and Fe^{3+} ions on the zeta potential of chromite are given in Tables 4.1 to 4.9.

Table 4.1. Zeta Potential of Chromite as a Function of pH

pH	Zeta Potential (mV)
3.0	29.24
3.5	21.46
4.2	16.50
5.0	5.58
5.3	-8.96
5.5	-14.08
6.1	-18.76
6.8	-25.38
7.3	-28.06
8.0	-31.70
9.0	-36.76
10.0	-40.97
11.0	-46.13

Table 4.2. Zeta Potential of Chromite in the Presence of Supporting Electrolyte KCl

pH	Zeta Potential (mV)	
	10^{-2} M	10^{-3} M
3.0	20.95	23.67
4.0	13.72	14.80
5.0	11.60	10.00
6.0	-19.63	-20.06
7.0	-23.99	-22.89
8.0	-24.81	-26.16
9.0	-27.39	-28.99
10.0	-29.98	-30.35
11.0	-31.27	-33.28

Table 4.3. Variation of Zeta Potential of Chromite in the Presence of Different Concentrations of Sodium Oleate

pH	Zeta Potential (mV)		
	10 mg/l	30 mg/l	70 mg/l
3.0	11.74	10.52	8.86
3.2	-	-	-9.72
3.3	-	8.17	-
3.6	6.84	-	-
3.7	-	-7.41	-12.51
4.1	-7.41	-	-
4.2	-	-15.18	-
4.3	-	-	-17.12
4.4	-16.93	-	-
5.1	-21.74	-24.96	-
5.3	-	-	-
5.8	-23.72	-	-25.54
6.1	-	-	-
6.2	-	-29.90	-31.81
6.8	-25.38	-	-
7.0	-	-31.67	-
7.1	-	-	-34.62
7.8	-29.55	-	-
8.0	-	-35.36	-35.07
8.8	-33.21	-	-
9.0	-	-36.45	-
9.1	-	-	-37.31
9.4	-38.17	-	-
10.0	-	-39.03	-37.90
10.2	-45.64	-	-
11.0	-49.66	-48.74	-46.22

Table 4.4. Variation of Zeta Potential of Chromite in the Presence of Different Concentrations of Dodecyl Amine Acetate

pH	**Zeta Potential (mV)**		
	10 mg/l	**20 mg/l**	**70 mg/l**
3.0	46.77	40.88	42.85
3.5	40.57	-	-
3.6	-	-	40.51
3.7	-	39.83	-
4.6	33.70	34.49	-
4.8	-	-	31.90
5.5	27.49	-	-
5.7	-	24.08	24.74
6.3	21.46	-	-
6.8	-	18.48	20.19
7.4	9.85	-	-
7.7	-	15.80	13.49
8.5	4.36	-	8.61
8.7	-	9.76	-
9.1	-	-	4.98
9.4	-	-10.99	-
9.5	-15.81	-	-
9.6	-	-	-9.44
10.3	-23.02	-21.05	-
11.0	-34.17	-33.33	-17.80

Table 4.5. Zeta Potential of Chromite in Different Concentrations of Fe^{2+}

pH	**Zeta Potential (mV)**	
	10^{-4} M	**10^{-5} M**
3.0	29.74	26.08
4.0	25.10	23.81
5.0	21.07	16.22
6.0	19.56	9.43
7.0	-10.81	-15.38
8.0	-19.30	-21.15
9.0	-20.51	-22.51
10.0	-27.65	-26.25
11.0	-33.68	-34.31

Table 4.6. Zeta Potential of Chromite in Different Concentrations of Al^{3+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	24.34	19.54
4.0	21.55	17.70
5.0	21.26	15.95
6.0	16.04	12.39
7.0	10.81	9.95
8.0	-12.14	-13.62
9.0	-27.87	-25.10
10.0	-30.51	-32.27
11.0	-34.46	-34.89

Table 4.7. Zeta Potential of Chromite in Different Concentrations of Cr^{3+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	28.87	25.15
4.0	16.71	15.57
5.0	11.16	11.04
6.0	10.12	8.61
7.0	9.85	7.94
8.0	-17.51	-16.90
9.0	-22.35	-25.14
10.0	-28.89	-32.60
11.0	-30.35	-38.81

Table 4.8. Zeta Potential of Chromite in Different Concentrations of Mg^{2+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	24.62	18.73
4.0	14.83	17.11
5.0	9.71	14.20
6.0	-14.16	-13.57
7.0	-18.85	-18.99
8.0	-26.53	-17.99
9.0	-18.34	-12.80
10.0	10.82	9.63
11.0	9.50	10.88

Table 4.9. Zeta Potential of Chromite in Different Concentrations of Fe^{3+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	33.41	29.53
4.0	27.71	25.74
5.0	21.09	20.53
6.0	16.65	16.08
7.0	-9.33	-10.21
8.0	-15.68	-16.28
9.0	-19.44	-22.60
10.0	-29.82	-31.18
11.0	-35.36	-37.40

4.1.2. Electrokinetic Potential Measurements of Serpentine

The effect of pH, sodium oleate, dodecyl amine, acetate and K^+, Fe^{2+}, Al^{3+}, Cr^{3+}, Mg^{2+}, Fe^{3+} ions on the zeta potential of serpentine are presented in Tables 4.10 to 4.18.

Table 4.10. Zeta Potential of Serpentine as a Function of pH

pH	Zeta Potential (mV)
3.0	44.08
4.0	43.84
5.0	33.00
6.0	27.46
7.0	23.89
8.0	15.49
8.5	9.17
9.0	-16.49
10.0	-21.52
11.0	-23.91

Table 4.11. Zeta Potential of Serpentine in the Presence of Supporting Electrolyte KCl

pH	Zeta Potential (mV)	
	10^{-2} M	10^{-3} M
3.0	34.00	37.86
4.0	32.64	34.51
5.0	26.13	30.87
6.0	25.28	27.94
7.0	20.97	22.15
8.0	15.70	16.46
9.0	-14.46	-13.80
10.0	-16.09	-17.56
11.0	-17.36	-18.06

Table 4.12. Variation of Zeta Potential of Serpentine in the Presence of Different Concentrations of Sodium Oleate

pH	Zeta Potential (mV)		
	10 mg/l	30 mg/l	70 mg/l
3.0	39.16	33.45	31.53
4.0	35.15	26.97	25.45
5.0	20.90	15.93	9.19
6.0	8.62	-10.10	-11.60
7.0	-15.14	-24.61	-26.87
8.0	-22.76	-26.64	-30.17
9.0	-28.65	-31.99	-33.92
10.0	-30.41	-34.50	-34.71
11.0	-32.28	-37.95	-39.93

Table 4.13. Variation of Zeta Potential of Serpentine in the Presence of Different Concentrations of Dodecyl Amine Acetate

pH	**Zeta Potential (mV)**		
	10 mg/l	**50 mg/l**	**70 mg/l**
3.0	46.82	47.78	49.75
4.0	44.02	43.91	44.16
5.0	43.37	43.04	42.35
6.0	40.33	41.68	41.97
7.0	37.86	39.10	40.36
8.0	30.51	35.13	34.55
9.0	21.11	24.56	24.15
10.0	17.38	18.82	18.80
11.0	12.81	11.90	14.41
11.5	-3.16	6.72	8.52
12.0	-16.97	-9.24	-8.30

Table 4.14. Zeta Potential of Serpentine in Different Concentrations of Al^{3+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	43.99	45.08
4.0	41.87	42.55
5.0	31.60	32.38
6.0	24.96	26.81
7.0	22.49	23.70
8.0	12.61	15.52
9.0	-15.67	-16.25
10.0	-17.02	-20.14
11.0	-18.41	-21.39

Table 4.15. Zeta Potential of Serpentine in Different Concentrations of Fe^{3+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	41.63	44.51
4.0	38.76	40.27
5.0	34.14	36.18
6.0	24.82	24.40
7.0	17.39	20.38
8.0	12.25	16.50
9.0	-15.84	-17.22
10.0	-18.61	-20.61
11.0	-20.09	-22.34

Table 4.16. Zeta Potential of Serpentine in Different Concentrations of Mg^{2+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	43.90	40.58
4.0	41.47	37.16
5.0	30.86	31.47
6.0	25.66	23.17
7.0	19.90	12.21
8.0	12.47	11.74
9.0	11.66	7.12
10.0	7.81	6.90
11.0	6.13	5.09
12.0	-5.25	-5.18

Table 4.17. Zeta Potential of Serpentine in Different Concentrations of Cr^{3+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	38.81	39.19
4.0	35.34	37.11
5.0	29.57	30.03
6.0	22.98	22.55
7.0	18.74	19.59
8.0	13.12	13.58
9.0	-11.46	-13.06
10.0	-15.08	-19.36
11.0	-18.77	-21.54

Table 4.18. Zeta Potential of Serpentine in Different Concentrations of Fe^{2+}

pH	Zeta Potential (mV)	
	10^{-4} M	10^{-5} M
3.0	39.63	43.22
4.0	35.15	39.70
5.0	32.27	36.18
6.0	29.85	29.14
7.0	25.14	26.07
8.0	15.80	16.23
9.0	-12.26	-15.51
10.0	-16.28	-18.30
11.0	-18.95	-22.17

4.2. Contact Angle Measurements

4.2.1. Contact Angle of Chromite

The effect of sodium oleate and dodecyl amine acetate on the contact angle of chromite is given in Table 4.19.

Table 4.19. Contact Angle of Chromite in Distilled Water, Sodium Oleate and Dodecyl Amine Acetate Solutions

pH	**Contact Angle (Degrees)**		
	No Collector	**Sodium Oleate (30 mg/l)**	**Dodecyl Amine Acetate (20 mg/l)**
3.0	16.64	22.94	42.34
4.0	16.46	22.23	46.33
5.0	13.87	23.91	60.45
6.0	11.61	35.81	61.38
7.0	9.72	56.88	61.36
8.0	12.71	56.64	65.37
9.0	15.02	59.11	64.31
10.0	15.50	35.25	69.49
11.0	17.88	30.12	68.76

4.2.2. Contact Angle of Serpentine

The effect of sodium oleate and dodecyl amine acetate on the contact angle of serpentine is given in Table 4.20.

Table 4.20. Contact Angle of Serpentine in Distilled Water, Sodium Oleate and Dodecyl Amine Acetate Solutions

pH	**Contact Angle (Degrees)**		
	No Collector	**Sodium Oleate (30 mg/l)**	**Dodecyl Amine Acetate (20 mg/l)**
3.0	53.91	63.88	78.39
4.0	34.73	77.66	75.02
5.0	24.29	82.96	75.95
6.0	46.80	84.73	76.98
7.0	54.18	84.78	76.71
8.0	62.38	86.77	81.46
9.0	67.69	84.43	81.83
10.0	62.51	83.85	80.04
11.0	47.68	38.39	78.01
12.0	-	-	79.69

4.3. Shear Flocculation of Chromite

4.3.1. Coagulation Behaviour of Chromite Fines at Different pH Values

The coagulation of chromite fines in the absence of collector was investigated by a set of experiments carried out at different pH values. The results are shown in Table 4.21.

Table 4.21. Coagulation of Chromite Fines at Various pH Values

pH	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
3.0	2.08	11.11	Collector : No
5.0	15.14	17.74	Stirrer Speed : 630 rpm
6.0	17.38	20.75	Stirring Time : 30 min.
7.0	13.44	14.55	
9.0	13.06	14.75	
11.0	00.00	12.31	

4.3.2. Shear Flocculation of Chromite Fines at Different pH Values

The results of experiments carried out to investigate the shear flocculation of chromite fines at different pH values by sodium oleate and dodecyl amine acetate are given in Tables 4.22 and 4.23, respectively.

Table 4.22. Shear Flocculation of Chromite Fines at Different pH Values with Sodium Oleate

pH	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
2.3	54.62	50.00	Collector : 30 mg/l
3.0	91.88	69.49	Stirrer Speed : 630 rpm
3.5	91.52	72.22	Flocculation Time : 60 min.
4.0	48.33	39.22	
4.5	23.24	41.82	
5.0	14.76	49.05	
6.0	7.64	11.48	
7.0	2.86	20.34	
9.0	0.00	12.70	
11.0	0.00	18.75	

Table 4.23. Shear Flocculation of Chromite Fines at Different pH Values with Dodecyl Amine Acetate

pH	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
3.0	26.62	22.58	Collector : 20 mg/l
4.0	61.63	34.69	Stirrer Speed : 630 rpm
5.0	68.86	54.17	Flocculation Time : 30 min.
6.0	69.22	57.63	
7.0	71.81	57.41	
8.0	83.14	74.58	
8.5	88.25	78.85	
9.0	94.16	82.00	
10.0	53.58	35.09	
11.0	45.98	26.42	

4.3.3. Shear Flocculation of Chromite in Various Concentrations of Sodium Oleate and Dodecyl Amine Acetate

Table 4.24 and 4.25 show the test results made by using various concentrations of sodium oleate and dodecyl amine acetate, respectively.

Table 4.24. Shear Flocculation of Chromite in Various Sodium Oleate Concentrations

Sodium Oleate Conc. (mg/l)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0	10.75	21.92	pH : 3.0
10	69.36	63.04	Stirrer Speed : 630 rpm
30	91.88	69.49	Flocculation Time : 60 min.
55	95.86	65.91	
65	93.69	70.45	
90	88.40 .	76.79	
105	95.31	78.67	

Table 4.25. Shear Flocculation of Chromite in Various Dodecyl Amine Acetate Concentrations

Dodecyl Amine Acetate Conc. (mg/l)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0	13.06	14.75	pH : 9.0
10	84.02	52.78	Stirrer Speed : 630 rpm
20	94.16	82.00	Flocculation Time : 30 min.
30	92.20	78.95	
50	95.79	88.89	
75	95.56	88.24	
100	95.52	87.50	

4.3.4. Shear Flocculation of Chromite as a Function of Flocculation Time

The turbidity drops and the amount of settled materials for chromite fines stirred for different times are tabulated in Tables 4.26 and 4.27 for oleate and amine flocculation, respectively.

Table 4.26. Shear Flocculation of Chromite Fines as a Function of Flocculation Time With Sodium Oleate

Flocculation Time (min.)	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
10	78.55	57.58	pH : 3.0
20	81.95	75.51	Collector : 30 mg/l
30	91.01	77.46	Stirrer Speed : 630 rpm
45	91.09	78.00	
60	91.88	69.49	
90	94.14	68.97	
100	91.30	64.71	

Table 4.27. Shear Flocculation of Chromite Fines as a Function of Flocculation Time with Dodecyl Amine Acetate

Flocculation Time (min.)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
10	74.53	62.00	pH : 9.0
20	89.93	71.43	Collector : 20 mg/l
25	95.08	80.39	Stirrer Speed : 630 rpm
30	94.16	82.00	
35	92.92	77.36	
45	88.81	66.04	
60	83.99	52.27	
90	82.26	56.25	
120	79.62	52.94	

4.3.5. Shear Flocculation of Chromite Fines Stirred at Various Speeds

A set of experiments were carried out to investigate the effect of stirrer speed on the aggregation of fines. The results for the oleate and amine flocculation are given in Tables 4.28 and 4.29, respectively.

Table 4.28. Shear Flocculation of Chromite Fines as a Function of Stirrer Speed with Sodium Oleate

Stirrer Speed (rpm)	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
0	38.67	61.76	pH : 3.0 Collector : 30 mg/l Flocculation Time : 30 min.
140	74.57	66.67	
360	85.26	69.57	
490	93.20	78.00	
580	89.39	78.32	
630	91.01	77.46	
870	90.39	69.39	
1200	-	23.08	

Table 4.29. Shear Flocculation of Chromite Fines as a Function of Stirrer Speed with Dodecyl Amine Acetate

Stirrer Speed (rpm)	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
0	34.47	49.35	pH : 9.0 Collector : 20 mg/l Flocculation Time : 30 min.
140	68.11	57.63	
360	89.65	73.91	
490	91.13	72.34	
580	94.46	82.69	
630	94.16	82.00	
870	81.83	57.14	
1200	-	28.07	

4.3.6. Effect of Suspension Concentration

The results of experiments carried out to see the effect of suspension concentration on the shear flocculation of chromite with sodium oleate and dodecyl amine acetate are shown in Table 4.30 and Table 4.31, respectively.

Table 4.30. Effect of Suspension Concentration on Shear Flocculation of Chromite with Sodium Oleate

Solid Concentration (g/l)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0.35	78.27	43.90	pH : 3.0
0.53	83.31	74.47	Collector : 30 mg/l
0.7	91.01	77.46	Stirrer Speed : 630 rpm
1.4	89.24	77.61	Flocculation Time : 30 min.
2.1	84.44	85.31	
3.5	88.40	87.40	

Table 4.31. Effect of Suspension Concentration on Shear Flocculation of Chromite with Dodecyl Amine Acetate

Solid Concentration (g/l)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0.35	87.99	73.58	pH : 9.0
0.53	92.59	78.95	Collector : 20 mg/l
0.7	94.46	82.69	Stirrer Speed : 580 rpm
1.4	93.99	85.15	Flocculation Time : 30 min.
2.1	92.07	85.14	
3.5	90.99	86.92	

4.4. Shear Flocculation of Serpentine

4.4.1. Coagulation of Serpentine Fines at Different pH Values

The coagulation of serpentine fines in the absence of collector at different pH values are shown in Table 4.32.

Table 4.32. Coagulation of Serpentine Fines at Different pH Values

pH	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
3.0	0.94	12.86	Collector: No
4.0	1.19	11.43	Stirrer Speed: 360 rpm
5.0	0.87	10.29	Flocculation Time: 20 min.
6.0	0.00	10.96	
7.0	0.20	11.27	
8.0	2.27	14.06	
9.0	20.38	30.00	
10.0	17.72	33.33	
11.0	19.35	32.89	
12.0	13.98	26.47	

4.4.2. Shear Flocculation of Serpentine Fines at Different pH Values

Table 4.33 and 4.34 indicate the results of experiments carried out to investigate the effect of pH on shear flocculation of serpentine with sodium oleate and dodecyl amine acetate, respectively.

Table 4.33. Shear Flocculation of Serpentine Fines at Different pH Values with Sodium Oleate

pH	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
3.0	1.14	16.47	Collector: 30 mg/l Stirrer Speed: 630 rpm Flocculation Time: 30 min.
4.0	30.97	56.16	
5.0	80.23	83.10	
6.0	78.08	85.14	
7.0	61.70	77.61	
8.0	65.63	76.06	
9.0	64.47	76.47	
10.0	60.20	73.33	
11.0	61.47	69.44	
12.0	49.29	65.33	

Table 4.34. Shear Flocculation of Serpentine Fines at Different pH Values with Dodecyl Amine Acetate

pH	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
3.0	0.91	10.84	Collector: 30 mg/l Stirrer Speed: 630 rpm Flocculation Time: 30 min.
4.0	2.32	11.54	
5.0	0.44	9.21	
6.0	0.00	13.51	
7.0	2.39	14.29	
8.0	3.17	14.08	
9.0	2.49	8.82	
10.0	10.77	25.30	
11.0	21.78	41.18	
11.5	42.44	58.97	
12.0	40.43	56.96	
12.4	39.30	52.81	

4.4.3. Shear Flocculation of Serpentine in Various Concentrations of Sodium Oleate and Dodecyl Amine Acetate

The effect of amount of sodium oleate on the shear flocculation of serpentine is tabulated in Table 4.35.

Table 4.35. Shear Flocculation of Serpentine in Various Sodium Oleate Concentrations

Sodium-Oleate Conc. (mg/l)	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
10	34.45	69.74	pH: 6.0 Stirrer Speed: 630 rpm Flocculation Time: 30 min.
20	61.43	73.53	
30	78.08	85.14	
50	80.37	85.25	
75	80.01	86.79	
100	80.40	88.52	

Table 4.36 shows the effect of dodecyl amine acetate concentration on the shear flocculation of serpentine fines.

Table 4.36. Shear Flocculation of Serpentine in Various Dodecyl Amine Acetate Concentrations

Dodecyl Amine Acetate Conc. (mg/l)	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
0	13.45	8.33	pH: 11.5 Stirrer Speed: 630 rpm Flocculation Time: 30 min.
10	18.41	45.61	
30	42.44	58.97	
50	53.94	71.67	
75	53.91	69.49	
100	54.35	69.35	
150	48.68	63.79	

4.4.4. Effect of Flocculation Time on Shear Flocculation of Serpentine

The turbidity drops and the settling rates of serpentine fines flocculated for different times are given in Tables 4.37 and 4.38 for oleate and amine flocculation, respectively.

Table 4.37. Effect of Flocculation Time on Shear Flocculation of Serpentine with Sodium Oleate

Flocculation Time (min.)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
5	74.66	79.17	pH: 6.0
10	76.84	84.62	Collector: 30 mg/l
20	80.00	85.37	Stirrer Speed: 630 rpm
30	78.08	85.14	
45	73.86	81.48	
60	73.63	80.33	
90	72.02	80.77	

Table 4.38. Effect of Flocculation Time on Shear Flocculation of Serpentine with Dodecyl Amine Acetate

Flocculation Time (min.)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
5	68.89	81.08	pH: 11.5
10	59.43	81.82	Collector: 50 mg/l
15	57.14	79.41	Stirrer Speed: 630 rpm
20	55.00	79.69	
30	53.94	71.67	
45	23.57	65.22	
60	18.90	57.33	
90	19.02	62.12	
120	14.94	44.78	

4.4.5. Shear Flocculation of Serpentine Stirred at Various Speeds

The results of experiments made to observe the flocculation behaviour of serpentine fines stirred at different rates with sodium oleate are presented in Table 4.39.

Table 4.39. Shear Flocculation of Serpentine Stirred at Various Speeds with Sodium Oleate

Stirrer Speed (rpm)	**Turbidity Drop (%)**	**Settled Material (%)**	**Experimental Conditions**
0	42.05	36.51	pH: 6.0
140	67.69	63.64	Collector: 30 mg/l
360	80.76	87.93	Flocculation Time: 20 min.
490	76.22	86.15	
630	80.00	85.37	
870	64.29	73.97	
1200	-	48.53	

Table 4.40 shows the results of experiments carried out to investigate the effect of stirrer speed on the flocculation of serpentine with dodecyl amine acetate.

Table 4.40. Shear Flocculation of Serpentine Fines Stirred at Various Speeds with Dodecyl Amine Acetate

Stirrer Speed (rpm)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0	49.48	45.59	pH: 11.5 Collector: 50 mg/l Flocculation Time: 10 min.
140	64.68	80.65	
360	72.43	85.71	
490	67.71	83.78	
630	59.43	81.82	
870	47.73	72.58	
1200	-	36.67	

4.4.6. Effect of Suspension Concentration

The turbidity drops and the settling rates of serpentine particles with suspension concentration are tabulated in Tables 4.41 and 4.42.

Table 4.41. Effect of Suspension Concentration on Shear Flocculation of Serpentine with Sodium Oleate

Solid Conc. (g/l)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0.35	48.81	48.00	pH: 6.0
0.53	70.00	72.50	Collector: 30 mg/l
0.7	80.76	87.93	Stirrer Speed: 360 rpm
1.4	88.09	88.64	Flocculation Time: 20 min.
2.1	90.89	90.34	
3.5	93.67	92.06	

Table 4.42. Effect of Suspension Concentration on Shear Flocculation of Serpentine with Dodecyl Amine Acetate

Solid Conc. (g/l)	Turbidity Drop (%)	Settled Material (%)	Experimental Conditions
0.35	70.81	75.00	pH: 11.5
0.53	66.58	78.72	Collector: 50 mg/l
0.7	72.43	85.71	Stirrer Speed: 360 rpm
1.4	85.67	86.99	Flocculation Time: 10 min.
2.1	90.38	92.42	
3.5	90.03	91.30	

4.5. Selective Shear Flocculation of Chromite

In this part, the results of experiments carried out to flocculate the chromite selectively from chromite-serpentine mixture (usually 1:1) at different levels of pH, sodium oleate concentration, flocculation time and stirrer speed were given. The effects of NaF, Na_2SiF_6, Na_2SiO_3 and feed grade (% Cr_2O_3) on selective flocculation of chromite were also presented.

4.5.1. Selective Shear Flocculation of Chromite at Different pH Values

The effect of pH on selective flocculation of chromite from serpentine was investigated with a series of experiments. The results, given in terms of concentrate (settled material) and tailing (dispersed) grades (% Cr_2O_3), recoveries and selectivity indices are tabulated in Table 4.43.

Table 4.43. Selective Shear Flocculation of Chromite at Different pH Values

pH	**Material**	**Grade (% Cr_2O_3)**	**Recovery (%)**	**Selectivity Index**	**Experimental Conditions**
3.0	Concentrate	39.84	59.42	4.97	Collector: 30 mg/l Sodium Oleate Stirrer Speed: 630 rpm Flocculation Time: 30 min. Settling Time: 5 min.
	Tailing	19.33	40.58		
3.3	Concentrate	42.88	64.05	8.04	
	Tailing	17.41	35.95		
3.5	Concentrate	42.56	68.99	7.28	
	Tailing	16.90	31.01		
4.0	Concentrate	35.60	85.84	5.52	
	Tailing	13.19	14.16		
5.0	Concentrate	32.15	80.88	2.24	
	Tailing	20.68	19.12		
6.0	Concentrate	34.43	85.63	3.70	
	Tailing	16.22	14.37		
7.0	Concentrate	32.83	82.19	2.76	
	Tailing	18.92	17.81		
8.5	Concentrate	31.65	83.48	3.19	
	Tailing	16.59	16.52		
10.0	Concentrate	34.07	84.25	3.12	
	Tailing	18.11	15.75		
11.0	Concentrate	29.15	68.42	1.37	
	Tailing	25.45	31.58		

4.5.2. Selective Shear Flocculation of Chromite with Different Concentrations of Sodium Oleate

The results of selective flocculation experiments carried out with different amounts of sodium oleate are given in Table 4.44.

Table 4.44. Selective Shear Flocculation of Chromite with Different Sodium Oleate Concentrations

Sodium Oleate Conc. (mg/l)	Material	Grade (% Cr_2O_3)	Recovery (%)	Selectivity Index	Experimental Conditions
0	Concentrate	36.82	40.54	2.10	pH: 3.5 Stirrer Speed: 630 rpm Flocc. Time: 30 min. Settling Time: 5 min.
	Tailing	26.17	59.46		
10	Concentrate	43.26	59.25	5.87	
	Tailing	20.01	40.75		
20	Concentrate	43.86	62.45	6.45	
	Tailing	19.14	37.55		
30	Concentrate	42.56	68.99	7.28	
	Tailing	16.90	31.01		
50	Concentrate	39.27	70.28	4.80	
	Tailing	18.03	29.72		
75	Concentrate	35.71	72.24	2.18	
	Tailing	18.91	27.76		
100	Concentrate	33.01	84.63	3.33	
	Tailing	16.71	15.37		

4.5.3. Selective Shear Flocculation of Chromite at Different Stirring Times

The grades and recoveries of concentrates (settled material) and tailings (dispersed material) and selectivity indices obtained by selective shear flocculation of the chromite at different stirring times are given in Table 4.45.

Table 4.45. Selective Shear Flocculation of Chromite at Different Flocculation Times

Flocculation Time (min.)	**Material**	**Grade (% Cr_2O_3)**	**Recovery (%)**	**Selectivity Index**	**Experimental Conditions**
10	Concentrate	37.67	73.34	3.64	pH: 3.5 Collector: 30 mg/l Sodium Oleate Stirrer Speed: 630 rpm Settling Time: 5 min.
	Tailing	19.21	26.66		
20	Concentrate	41.91	64.72	5.18	
	Tailing	19.55	35.28		
30	Concentrate	42.56	68.99	7.28	
	Tailing	16.90	31.01		
45	Concentrate	42.67	68.05	6.81	
	Tailing	17.36	31.95		
60	Concentrate	43.18	71.58	7.61	
	Tailing	16.45	28.42		
90	Concentrate	42.74	68.64	6.14	
	Tailing	18.16	31.36		
120	Concentrate	42.19	67.76	5.93	
	Tailing	17.93	32.24		

4.5.4. Selective Shear Flocculation of Chromite Stirred at Various Speeds

A set of experiments were carried out to investigate the effect of stirrer speed on selective shear flocculation of chromite. The results are shown in Table 4.46.

Table 4.46. Selective Shear Flocculation of Chromite Stirred at Various Speeds

Stirrer Speed (rpm)	**Material**	**Grade (% Cr_2O_3)**	**Recovery (%)**	**Selectivity Index**	**Experimental Conditions**
140	Concentrate	39.39	52.09	3.15	pH: 3.5 Collector: 30 mg/l Sodium Oleate Flocc. Time: 60 min. Settling Time: 5 min.
	Tailing	23.34	47.91		
360	Concentrate	41.51	58.46	4.16	
	Tailing	21.79	41.54		
490	Concentrate	44.12	70.48	7.37	
	Tailing	17.03	29.52		
580	Concentrate	44.36	72.65	8.44	
	Tailing	16.19	27.35		
630	Concentrate	43.18	71.58	7.61	
	Tailing	16.45	28.42		
870	Concentrate	43.43	64.14	7.11	
	Tailing	18.10	35.86		
1200	Concentrate	39.39	53.87	3.86	
	Tailing	21.51	46.13		

4.5.5. Effect of NaF, Na_2SiF_6 and Na_2SiO_3 on Selective Shear Flocculation of Chromite

It is known that fluoride ions are used to activate the chromite in chromite-serpentine flotation separations (Abido, 1971). The effect of fluoride ions on selective shear flocculation of chromite were tested by adding varying amounts of NaF and Na_2SiF_6. The results are given in Table 4.47 and 4.48, respectively.

Table 4.47. Effect of NaF on Selective Shear Flocculation of Chromite

NaF Conc. (mg/l)	Material	Grade (% Cr_2O_3)	Recovery (%)	Selectivity Index	Experimental Conditions
20	Concentrate	43.34	65.90	6.58	pH: 3.0 Collector: 30 mg/l Sodium Oleate Stirrer Speed: 630 rpm Flocc.Time: 60 min. Settling Time: 5 min.
	Tailing	18.41	34.10		
40	Concentrate	42.81	63.16	6.44	
	Tailing	18.67	36.84		
80	Concentrate	44.26	70.13	8.09	
	Tailing	16.82	29.87		
120	Concentrate	44.10	70.86	7.38	
	Tailing	16.88	29.14		

Table 4.48 Effect of Na_2SiF_6 on Selective Shear Flocculation of Chromite

Na_2SiF_6 Concentration (mg/l)	**Material**	**Grade (% Cr_2O_3)**	**Recovery (%)**	**Selectivity Index**	**Experimental Conditions**
0	Concentrate	43.18	71.58	7.61	pH: 3.5 Collector: 30 mg/l Sodium Oleate Stirrer Speed: 630 rpm Flocc.Time: 60 min. Settling Time: 5 min.
	Tailing	16.45	28.42		
20	Concentrate	38.79	62.27	5.11	
	Tailing	18.37	37.73		
40	Concentrate	36.82	59.56	3.19	
	Tailing	21.39	40.46		
80	Concentrate	39.19	55.43	4.33	
	Tailing	20.87	44.57		
120	Concentrate	38.85	55.28	3.78	
	Tailing	21.51	44.72		

The dispersing effect of Na_2SiO_3 were also tested at different concentrations. The results are shown in Table 4.49.

Table 4.49 Effect of Na_2SiO_3 on Selective Shear Flocculation of Chromite

Na_2SiO_3 Concentration (mg/l)	Material	Grade (% Cr_2O_3)	Recovery (%)	Selectivity Index	Experimental Conditions
0	Concentrate	44.80	81.06	9.70	pH: 3.5 Collector: 30 mg/l Sodium Oleate Stirrer Speed: 580 rpm Flocc.Time: 60 min. Settling Time: 10 min.
	Tailing	13.85	18.94		
20	Concentrate	43.76	83.41	10.93	
	Tailing	12.14	16.49		
40	Concentrate	43.49	82.17	10.13	
	Tailing	12.47	17.83		
80	Concentrate	42.76	85.75	9.48	
	Tailing	12.18	14.25		
120	Concentrate	42.79	85.44	9.64	
	Tailing	12.39	14.56		

4.5.6. Effect of Settling Time on Selective Shear Flocculation of Chromite

A series of experiments were made to see the effect of settling time on the grades and recoveries of settled and dispersed particles after selective shear flocculation. Table 4.50 shows the experimental results.

Table 4.50 Effect of Settling Time on Selective Shear Flocculation of Chromite

Settling Time (min.)	**Material**	**Grade (% Cr_2O_3)**	**Recovery (%)**	**Selectivity Index**	**Experimental Conditions**
1	Concentrate	40.92	45.28	2.96	pH: 3.5 Collector: 30 mg/l Sodium Oleate Stirrer Speed: 580 rpm Flocc.Time: 60 min.
	Tailing	25.11	54.72		
2	Concentrate	42.16	53.33	4.36	
	Tailing	22.08	46.67		
3	Concentrate	44.80	62.57	7.92	
	Tailing	18.41	37.43		
5	Concentrate	44.36	72.65	8.44	
	Tailing	16.19	27.35		
8	Concentrate	44.30	73.13	9.63	
	Tailing	15.15	26.87		
10	Concentrate	44.60	81.06	9.70	
	Tailing	13.85	18.94		
12	Concentrate	42.11	83.23	9.91	
	Tailing	12.19	16.77		
15	Concentrate	41.74	86.52	9.32	
	Tailing	11.23	13.48		

4.5.7. Effect of Feed Grade on Selective Shear Flocculation of Chromite

The grades and recoveries of the settled and dispersed particles and selectivity indices obtained by stirring the chromite-serpentine mixtures of different ratios are tabulated in Table 4.51.

Table 4.51. Selective Shear Flocculation of Chromite with Different Chromite Content

Chromite/ Serpentine	**Material**	**Grade (% Cr_2O_3)**	**Recovery (%)**	**Selectivity Index**	**Experimental Conditions**
1/3	Concentrate	16.43	40.56	1.46	pH: 3.5 Collector: 30 mg/l Sodium Oleate Stirrer Speed: 580 rpm Flocc.Time: 60 min. Settling Time: 10 min.
	Tailing	13.31	59.44		
	Feed	14.42	100.00		
1/2	Concentrate	27.81	67.82	3.54	
	Tailing	12.02	32.18		
	Feed	19.55	100.00		
1/1	Concentrate	44.60	81.06	9.70	
	Tailing	13.85	18.94		
	Feed	29.47	100.00		
2/1	Concentrate	47.40	85.86	19.02	
	Tailing	16.33	14.14		
	Feed	37.19	100.00		

CHAPTER V

DISCUSSION OF RESULTS

5.1. Electrokinetic Potential Measurements

5.1.1. Electrokinetic Potential Measurements of Chromite

The electrokinetic potential measurements of chromite were performed by examining the effect of pH and different concentrations of sodium oleate and dodecyl amine acetate. The effect of divalent and trivalent cations namely Fe^{2+}, Mg^{2+}, Cr^{3+}, Al^{3+} and Fe^{3+} on the zeta potential of chromite were also examined.

5.1.1.1. Effect of pH on Zeta Potential of Chromite

The variation of zeta potential of chromite with pH, tabulated in Table 4.1, is given in Figure 5.1. It is seen that the iso-electrical point (i.e.p.) is pH 5.2

and the mineral has positive zeta potential at pH values lower than 5.2 and negative zeta potential above pH 5.2. The i.e.p. did not coincide with the i.e.p. of Üçköprü chromite which had been found as 5.8 (Atalay, 1986). This difference is probably due to the difference in the chemical compositions between the samples used in the electrokinetic study.

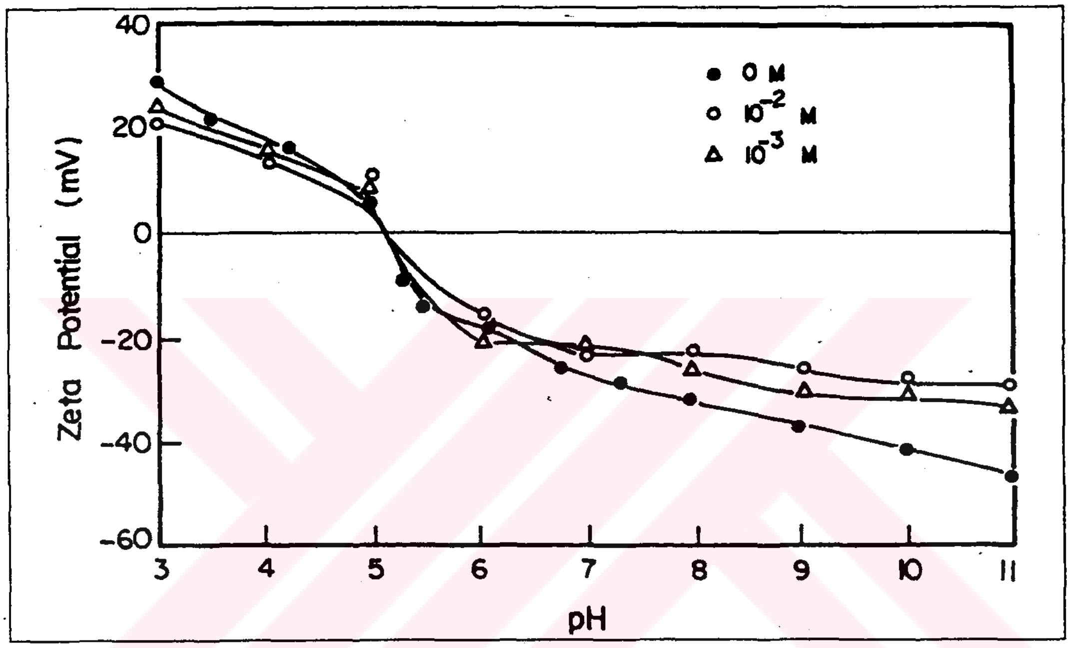

Figure 5.1. Zeta Potential of Chromite as a Function of pH and Effect of KCl

The shape of the curve (Figure 5.1) is similar to those found for SiO_2, Fe_2O_3, TiO_2, FeOOH, and Cr_2O_3 (TarJan, 1986; Wiese and Healy, 1975; Iwasaki et al., 1960; Atalay et al., 1988; Palmer et al., 1975) and are characteristics of oxide-solution interfaces for which H^+ and OH^- are potential determining ions.

The addition of supporting electrolyte KCl did not change the i.e.p. of chromite as it is seen from Figure 5.1. Only the magnitudes of positive or negative zeta potentials decreased by compression of electrical double layer. Therefore, KCl is an indifferent electrolyte for chromite.

5.1.1.2. Effect of Sodium Oleate and Dodecyl Amine Acetate on Zeta Potential of Chromite

Figures 5.2. and 5.3 show the zeta potential of chromite conditioned with different concentrations of sodium oleate and dodecyl amine acetate, respectively. The addition of sodium oleate shifted the i.e.p. from pH 5.2 to pH 3.1-3.8 depending on the collector concentration. Adsorption of negative oleate on chromite surface increases the negative charge in neutral and alkaline environment.

The adsorption of RNH^{+}_{3} ion from dodecyl amine acetate made the chromite surfaces more positive; i.e. it increased the magnitude of positive potential in neutral and acidic media. The i.e.p. of the mineral shifted from pH 5.2 to pH 9-9.5, depending on the concentration of dodecyl amine acetate.

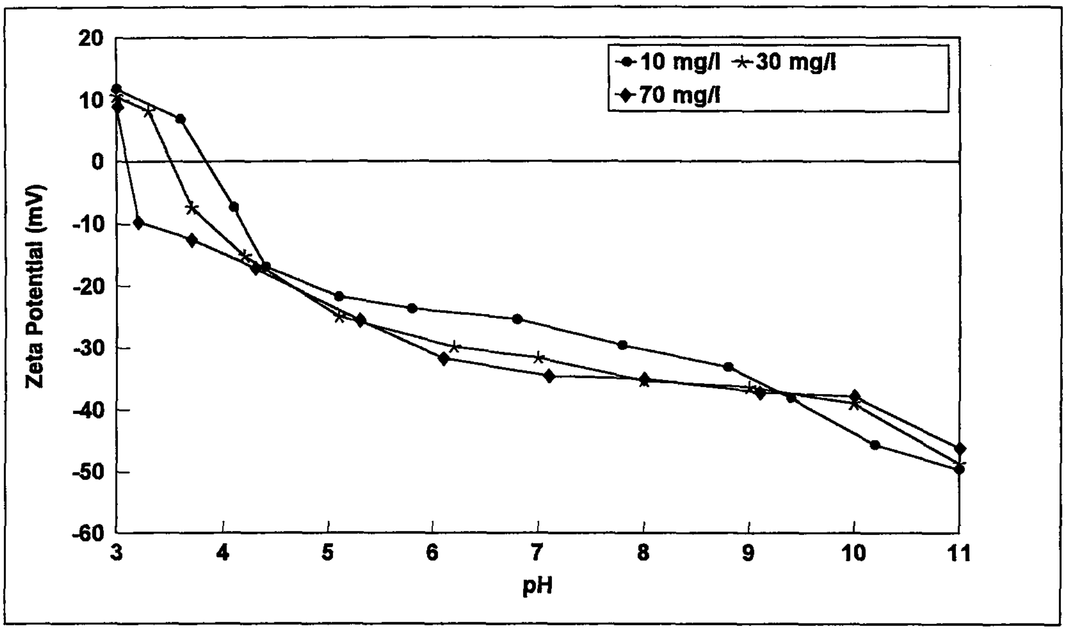

Figure 5.2. Variation of Zeta Potential of Chromite in the Presence of Different Concentrations of Sodium Oleate

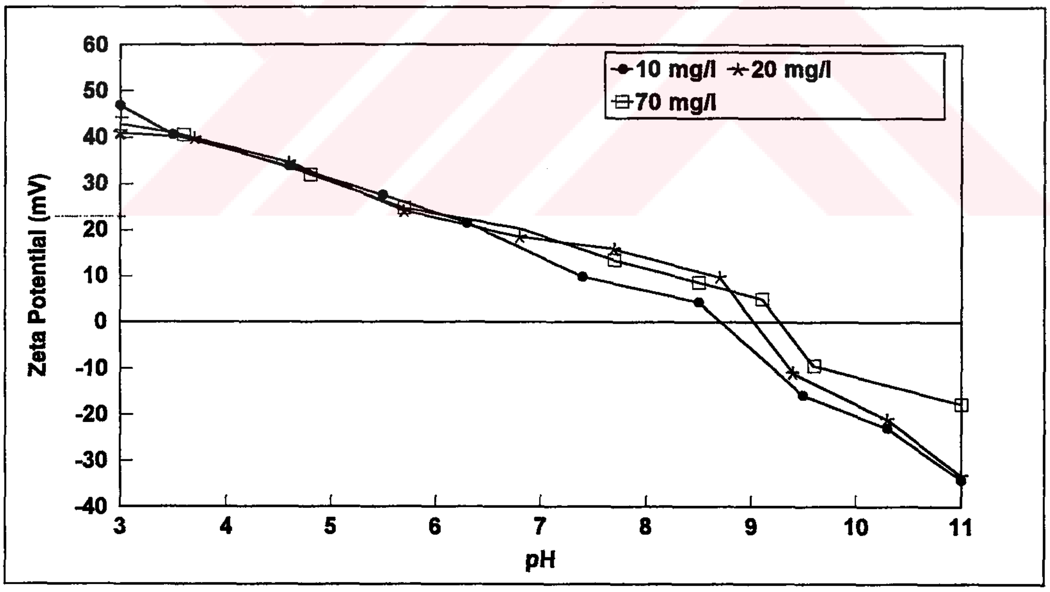

Figure 5.3. Variation of Zeta Potential of Chromite in the Presence of Different Concentrations of Dodecyl Amine Acetate

5.1.1.3. Effect of Divalent and Trivalent Cations on Zeta Potential of Chromite

Electrokinetic potential measurements were carried out with Cr^{3+} and Fe^{2+}. Fe^{3+}, Al^{3+} and Mg^{2+} were also tested since they substitute for Cr^{3+} and Fe^{2+} in crystal lattice (Cornelius, 1959).

Figures 5.4 and 5.5 show the effect of these ions on the zeta potential of chromite. The results indicate that i.e.p. of chromite shifts towards the i.e.p. of metal oxides in consistent with Parks (1965) who stated that the cations would be expected to shift the i.e.p. in the direction of their appropriate oxides. The i.e.p. of chromite shifted from pH 5.2 to 6-6.5 in the presence of Fe^{2+} and Fe^{3+} whose oxide has i.e.p. of pH 8.2. Presence of Al^{3+} and Cr^{3+} whose oxides have i.e.p. of pH 9.1 and 7, respectively shifted the i.e.p. of chromite from pH 5.2 to pH 7-7.5. Presence of Mg^{2+} ion whose oxide has i.e.p. of pH 12.4 shifted the i.e.p. of chromite to pH 9.5. This was explained by hydrolysis of metal ions in aqueous solution.

When metal ion is placed in an aqueous environment, the ions react with water and various hydrolysis products are formed. The hydrolysis reactions of Al^{3+}, Cr^{3+}, Fe^{3+}, Fe^{2+} and Mg^{2+} ions are as follows (Latimer, 1952; Butler, 1964).

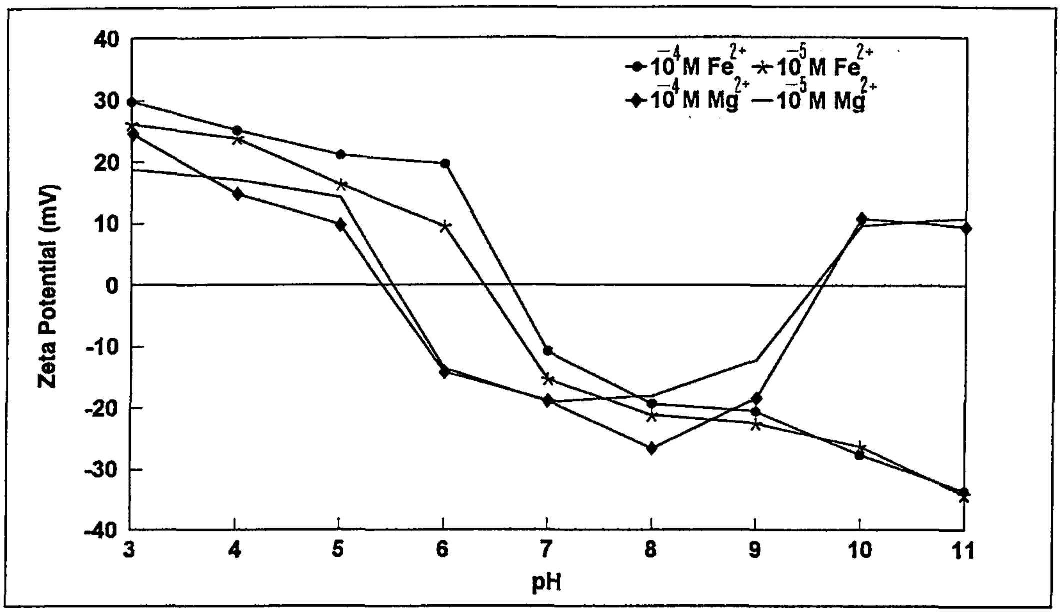

Figure 5.4. Variation of Zeta Potential of Chromite in Different Concentrations of Fe^{2+} and Mg^{2+}

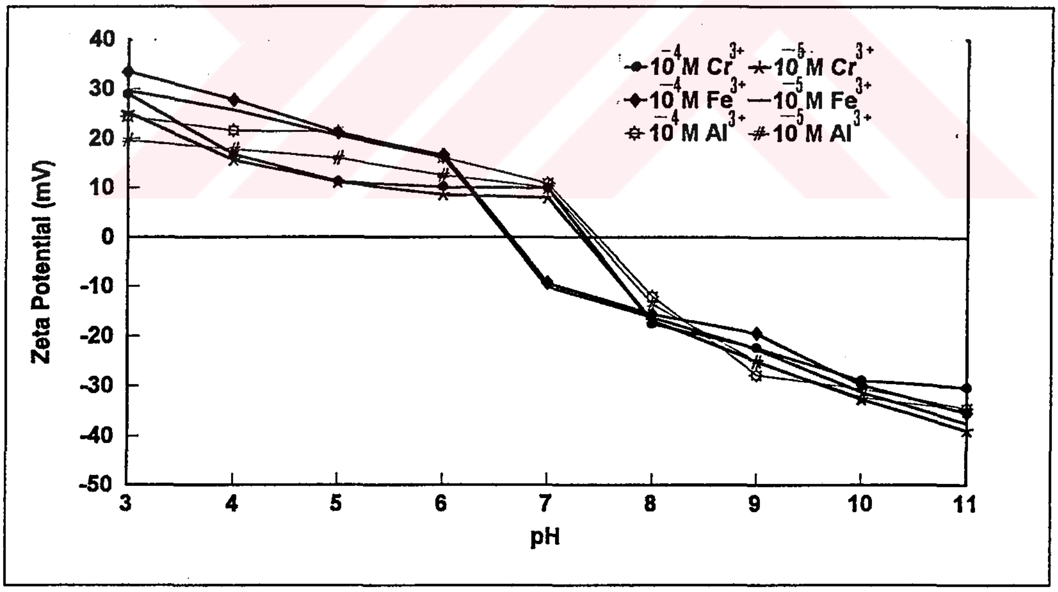

Figure 5.5. Variation of Zeta Potential of Chromite in Different Concentrations of Fe^{2+} , Al^{3+} and Cr^{3+}

$$Al^{3+} + H_2O \rightleftharpoons Al\,(OH)^{++} + H^+$$

$$AlOH^{++} + H_2O \rightleftharpoons Al(OH)^{+}_{2} + H^+$$

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3(s)$$

$$Al(OH)_3(s) + H_2O \rightleftharpoons Al(OH)^{-}_{4} + H^+$$

$$Cr^{3+} + H_2O \rightleftharpoons CrOH^{++} + H^+$$

$$Cr(OH)_3(s) \rightleftharpoons Cr^{3+} + 3OH^-$$

$$Cr(OH)_3(s) + OH^- \rightleftharpoons 2H_2O + CrO^{-}_{2}$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{++} + H^+$$

$$Fe^{2+} + OH^- \rightleftharpoons FeOH^+$$

$$Fe(OH)_2\,(s) \rightleftharpoons Fe^{2+} + 2OH^-$$

$$Mg^{2+} + OH^- \rightleftharpoons MgOH^-$$

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+} + 2OH^-$$

The concentration of first hydroxy complexes in these systems is of particular importance. Hydrolysis of surface of mineral leads to adsorption of hydrogen ion on mineral surface. Adsorbed hydrogen ion is capable of reacting with the hydroxy complex yielding a metal ion adsorbed on the oxide surface with the subsequent formation of water. This event deposits an excess of positive charge on the oxide surface and increases the zeta potential.

The charge-reversal of chromite surfaces from negative to positive at pH 9.5 in the presence of Mg^{2+} was explained by the coverage of chromite surface with $Mg(OH)^+$ ions which is formed by the hydrolysis of Mg^{2+} ions (Latimer, 1952; Butler, 1964).

5.1.2. Electrokinetic Potential Measurements of Serpentine

In this section, zeta potential of serpentine at different pH values and the effect of various concentrations of sodium oleate and dodecyl amine acetate on the electrokinetic behaviour of serpentine were discussed. The electrokinetic potential measurements of particles in the presence of divalent and trivalent cations, Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} were also discussed.

5.1.2.1. Effect of pH on Zeta Potential of Serpentine

The experimental results, tabulated in Table 4.10 and shown in Figure 5.6, indicate that the zeta potential of serpentine is pH dependent and the i.e.p. is pH 8.7, below which particles carry positive charge. Above this pH they are negatively charged. The variation of zeta potential from positive to negative with increasing pH shows that H^+ and OH^- ions are potential determining ions for the mineral.

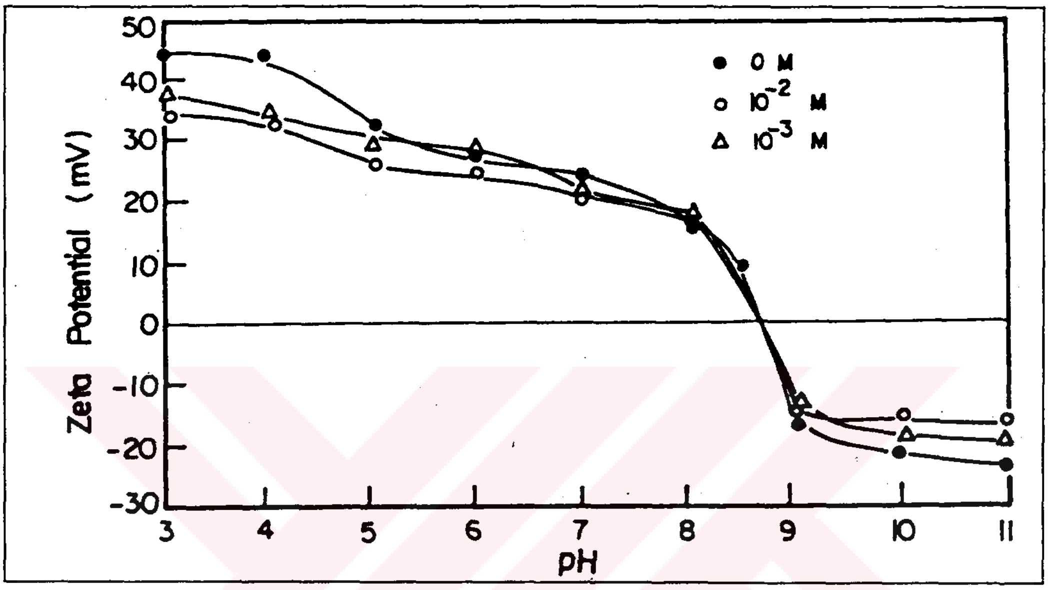

Figure 5.6. Variation of Zeta Potential of Serpentine as a Function of pH and the Effect of KCl

Although there is few electrokinetic studies with serpentine in literature the i.e.p. of pH 8.7 correlates well with the studies which have shown that the serpentine particles carry a positive charge in a neutral or weakly acidic medium and the charge is reversed to negative in an alkaline solution, i.e.p. being pH 7.5-8 (Eitel, 1954).

The addition of a supporting electrolyte KCl did not cause a charge reversal, i.e, i.e.p. remained the same, but the magnitudes of potentials decreased by electrical double layer compression (Figure 5.6). That is, it is an indifferent electrolyte for serpentine.

5.1.2.2. Effect of Sodium Oleate and Dodecyl Amine Acetate on Zeta Potential of Serpentine

The zeta potential values of serpentine conditioned with different concentrations of sodium oleate and dodecyl amine acetate are shown in Figure 5.7 and 5.8, respectively.

The adsorption of $C_{17}H_{33}COO^-$ ion shifted the i.e.p. of particle from pH 8.7 to pH 5.5-6.5, depending on the oleate concentration.

A comparison of Figure 5.8 and 5.6 shows that the uptake of amine ions, by the serpentine surface increases the magnitude of positive zeta potential and the i.e.p. of particles shifts to pH 11.5-12, depending on the amine concentration.

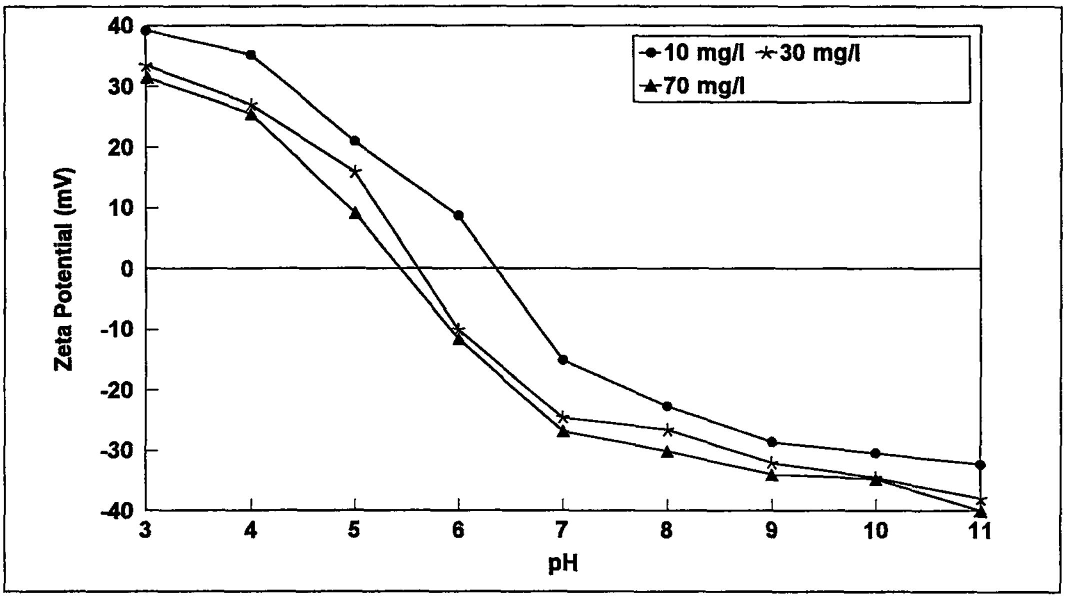

Figure 5.7. Variation of Zeta Potential of Serpentine in the Presence of Different Concentrations of Sodium Oleate

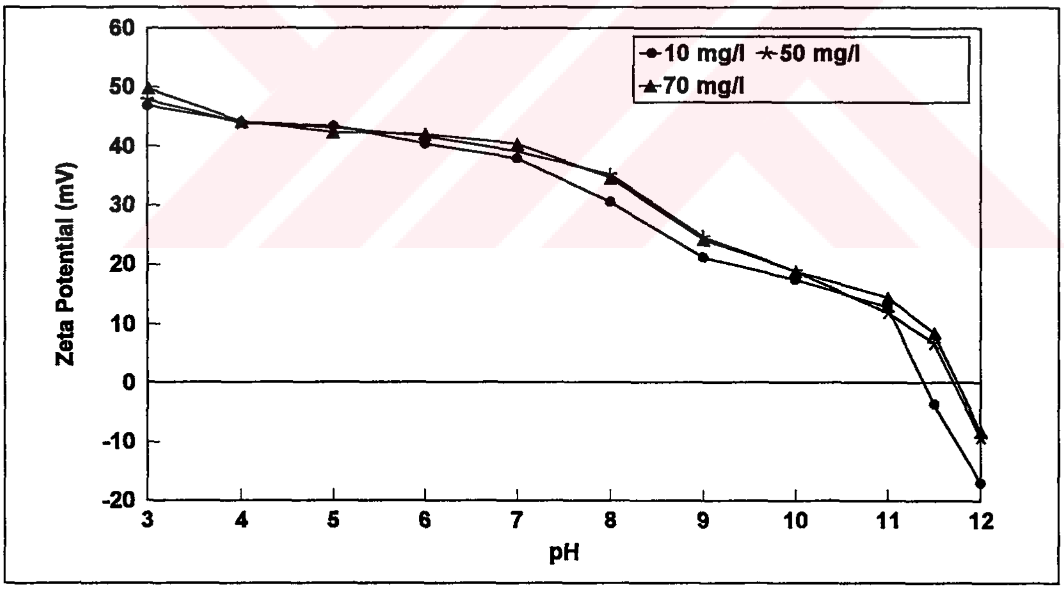

Figure 5.8. Variation of Zeta Potential of Serpentine in the Presence of Different Concentrations of Dodecyl Amine Acetate

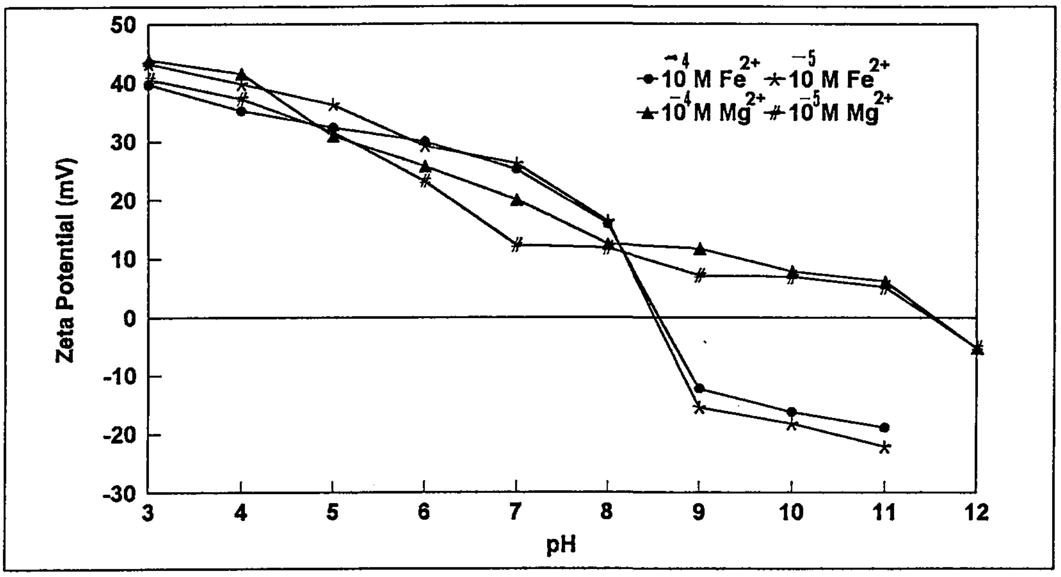

Figure 5.9. Variation of Zeta Potential of Serpentine in Different Concentrations of Fe^{2+} and Mg^{2+}

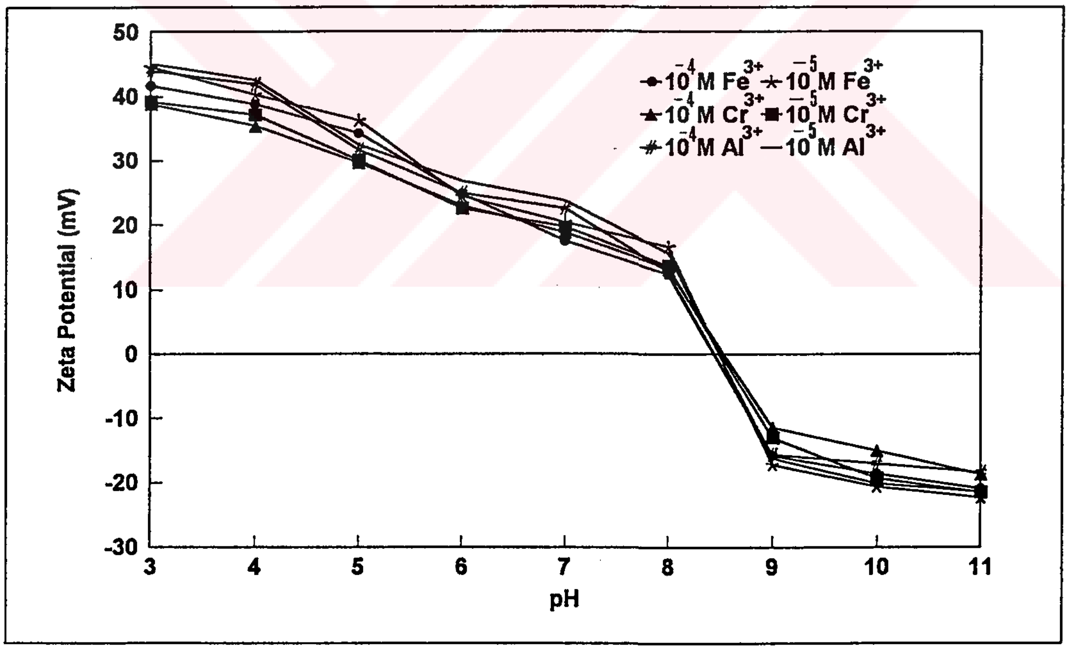

Figure 5.10. Variation of Zeta Potential of Serpentine in Different Concentrations of Fe^{3+}, Cr^{3+} and Al^{3+}

5.1.2.3. Effect of Divalent and Trivalent Cations on Zeta Potential of Serpentine

Figures 5.9 and 5.10 present the electrokinetic potential of serpentine conditioned with 10^{-4} and 10^{-5} M of Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+}. Non-of these ions changed the i.e.p. of serpentine except Mg^{2+} whose uptake from the solution changed the i.e.p. from pH 8.7 to pH 11.5. Therefore, Mg^{2+} is a potential-determining ion for serpentine in addition to H^+ and OH^-.

5.2. Contact Angle Measurements

5.2.1. Contact Angle Measurements of Chromite

The contact angle of chromite, conditioned with 30 mg/l sodium oleate and 20 mg/l dodecyl amine acetate and without any collector are plotted in Figure 5.11.

It is seen from Figure 5.11 that both sodium oleate and dodecyl amine acetate increase the contact angle; maximum contact angle being obtained at pH 9.0 and 10.0 for the particles conditioned with sodium oleate and dodecyl amine acetate, respectively. It is also seen that high contact angle values are obtained at a wide pH range (5-11) with dodecyl amine acetate while this is restricted to a narrower pH range (7-9) with sodium oleate.

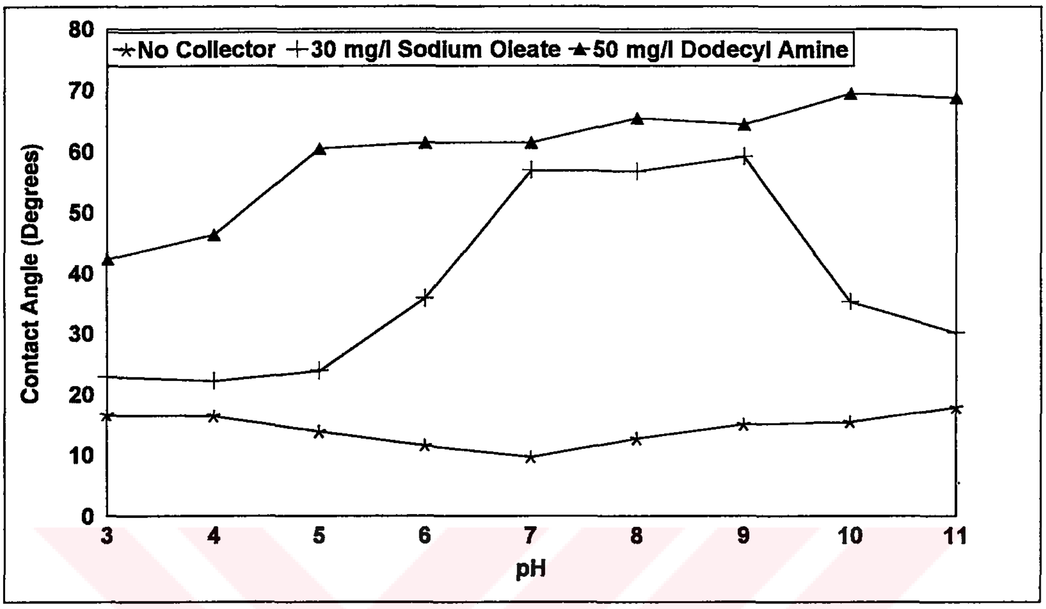

Figure 5.11. Contact Angle of Chromite in Distilled Water and Sodium Oleate and Dodecyl Amine Acetate Solutions

The results are in aggreement in trend with the measurements of Atalay (1986) who found that maximum contact angles are 50° and 40° obtained at pH 9.2 and 10.5 with sodium oleate and dodecyl amine acetate, respectively. However, higher contact angles were measured by using dodecyl amine acetate in this research in contrast to Atalay's findings where higher contact angles were obtained with sodium oleate. This is probably due to the differences in the compositions of the minerals and to measurement methods.

5.2.2. Contact Angle Measurements of Serpentine

Figure 5.12 shows the contact angle of serpentine, conditioned with 30 mg/l sodium oleate, 50 mg/l dodecyl amine acetate and without any collector.

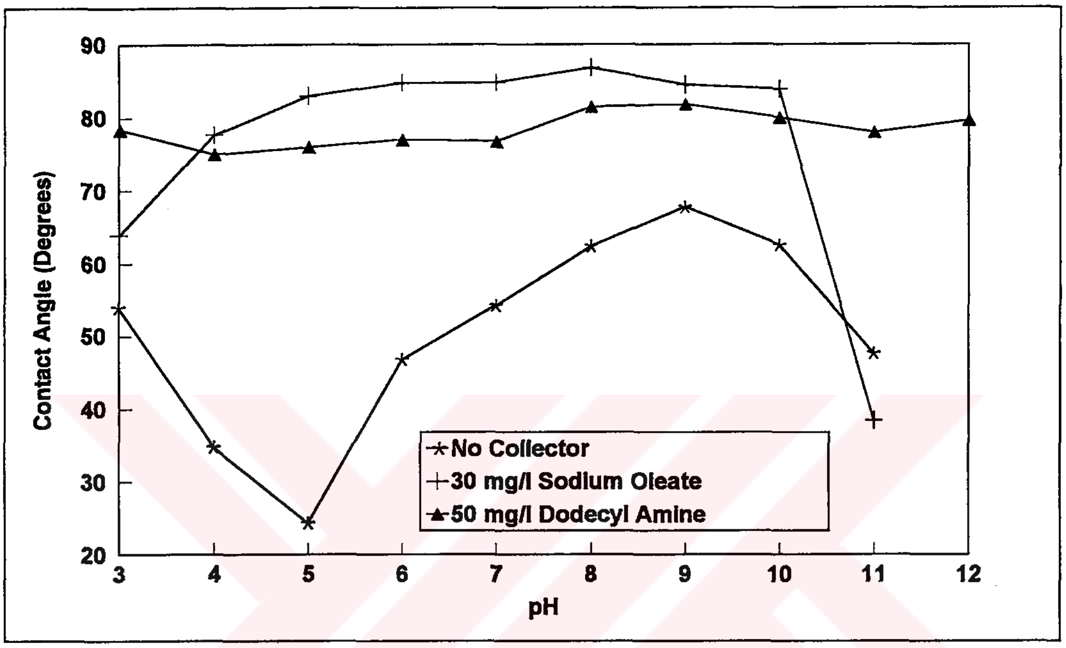

Figure 5.12. Contact Angle of Serpentine in Distilled Water and Sodium Oleate and Dodecyl Amine Acetate Solutions

A survey of the figure indicates that serpentine exhibits higher hydrophobic character than chromite. The contact angle values obtained in double distilled water especially in the pH range of 6-11 are quite high.

It is also seen from Figure 5.12 that both collectors increase the contact angle of serpentine. High contact angle was recorded with sodium oleate in a wide pH range from 5 to 10, giving a maximum of 86° at pH 8. Slightly smaller contact angles were measured with dodecyl amine acetate in a wider pH range of 3-11 with a maximum value of 82° at pH 9.

5.3. Shear Flocculation Studies

5.3.1. Shear Flocculation of Chromite

In this part, the results of shear flocculation experiments were discussed with a special emphasis to zeta potential and contact angle. The effect of sodium oleate and dodecyl amine acetate concentration, flocculation time, stirrer speed and suspension concentration are also discussed.

5.3.1.1. Coagulation of Chromite Particles in the Absence of Collector and the Role of Collector

The results of experiments carried out to investigate the coagulation properties of chromite by stirring in a collectorless medium at different pH values were plotted in Figure 5.13. It is seen that maximum coagulation is at pH 5-6 where the zeta potential is minimum. The turbidity drop is 15-17 % and amount of settled material is 18-20 % at these pH values.

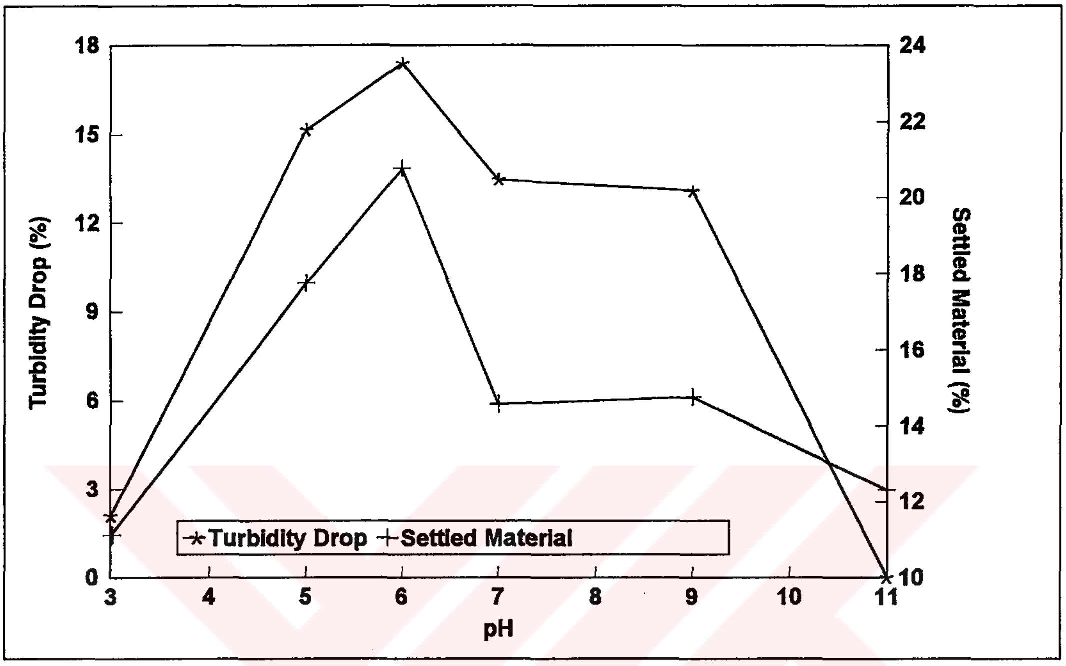

Figure 5.13. Coagulation of Chromite Fines at Various pH Values (No Collector; Stirrer Speed: 630 rpm; Stirring Time: 30 min.)

A survey of Table 5.1 indicates that the effect of stirring is very limited on the particle aggregation. On the other hand, when the particles are conditioned with sodium oleate and dodecyl amine acetate at suitable pH values the extensive flocculation starts. Great reductions in turbidity are observed and the amount of settled material increases about 7 times.

Table 5.1. Role of Collector on the Aggregation of Chromite Fines (Flocculation Time: 30 min.)

pH	Collector	Stirrer Speed (rpm)	Turbidity Drop (%)	Settled Material (%)
6	No	No	0.00	11.30
6	No	630	17.38	20.75
3	No	630	2.08	11.11
3	Sodium Oleate (30mg/l)	630	91.01	77.46
9	No	630	13.06	14.75
9	D.Amine Acetate (20 mg/l)	630	94.16	82.00

According to DLVO theory, which is a well-known theory in colloid chemistry, aggregation should occur in the pH range 5-6 without collector addition, because the repulsive energy is minimum due to low zeta potential (Figure 5.2). However, this is not the case in our results. So, DLVO theory is not able to interpret this kind of aggregation. At this point, the hydrophobic interaction theory (Lu and Li, 1984), proposing that apparent aggregation always occurs only with the surface hydrophobization, should come into consideration. Our results are also in aggreement with Warren's findings (1975a) that bare particles can't come together even when coagulation is produced by the addition of electrolytes due to “bound” water layers and that aggregation occurs only between the collector covered particles since solvated layer opposing direct contact is replaced by the hydrocarbon tails of the collector.

5.3.1.2. Effect of pH on Shear Flocculation of Chromite

The results of experiments, carried out at different pH values, where the particles have different zeta potentials and contact angles were plotted in Figures 5.14 and 5.15 for shear flocculation with sodium oleate and dodecyl amine acetate, respectively.

As it is seen from the Figures, aggregation is maximum at a pH range 3-3.5 with sodium oleate and pH 8.5-9 with dodecyl amine acetate. Combining Figures 5.14 and 5.15 with Figures 5.2 and 5.3 indicates clearly that apparent aggregation of chromite occurs only when particles have low zeta potential not exceeding 15-20 mV and the best results are obtained when the zeta potential is smaller than 10 mV. As the negative zeta potential increases from 5-10 mV to 25-30 mV, the amount of settled material decreases from 70 % to 10-15 % when using sodium oleate. Similarly the amount of settled material decreases from 82 % to 35 % when raising the pH from 9 to 10 with dodecyl amine acetate.

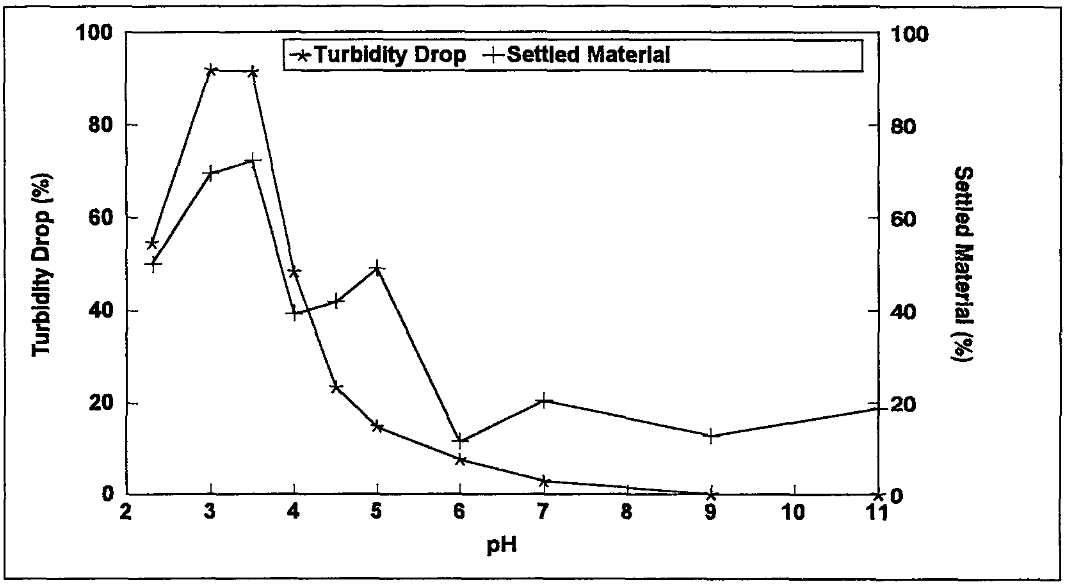

Figure 5.14. Effect of pH on Shear Flocculation of Chromite with Sodium Oleate (Collector: 30 mg/l; Stirrer Speed: 630 rpm; Flocc. Time:60 min.)

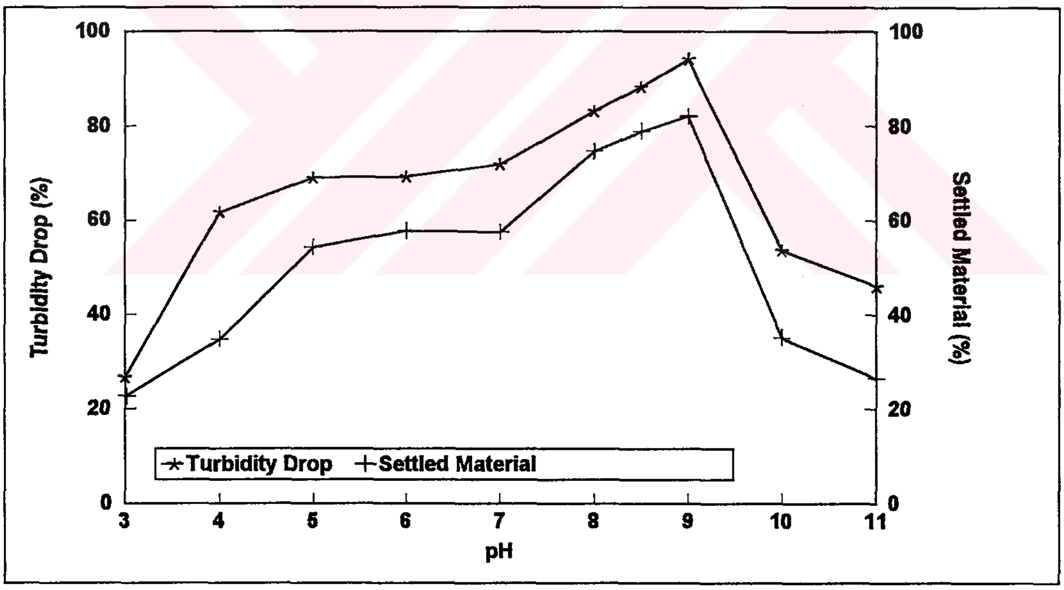

Figure 5.15. Effect of pH on Shear Flocculation of Chromite with Dodecyl Amine Acetate (Collector: 20 mg/l; Stirrer Speed: 630 rpm; Flocc.Time: 30 min.)

An important point is that the pH values, where the most apparent aggregation occurs with both sodium oleate and dodecyl amine acetate do not coincide with the pH values where maximum contact angles are recorded. Comparison of Figure 5.14 and Figure 5.15 with Figure 5.11 shows this clearly, especially when using sodium oleate as collector for which optimum aggregation occurs at pH 3-3.5 where the particles have a contact angle of 23°, a very low contact angle compared with 59.11° obtained at pH 9. No flocculation is seen at pH 9 with sodium oleate due to high zeta potential although the contact angle is maximum. Similarly; only partial aggregation is observed at pH 10, where the maximum contact angle is attained, by dodecyl amine acetate. These figures indicate that zeta potential is more dominant factor than the contact angle, i.e. hydrophobicity for the shear flocculation of chromite fines. However, this can't decrease the importance of surface hydrophobization without which no flocculation occurs.

Finally, it can be concluded that the most extensive shear flocculation of chromite particles are obtained at pH values where zeta potential is minimum although the contact angles at these points are not maximum.

5.3.1.3. Effect of Collector Concentration on Shear Flocculation of Chromite

The results of experiments carried out to investigate the effect of sodium oleate and dodecyl amine acetate concentrations on the shear flocculation of chromite, tabulated in Tables 4.24 and 4.25 were plotted in Figures 5.16 and 5.17, respectively.

It is seen that the degree of aggregation increases with the collector dosage up to certain level and then remains almost constant for both sodium oleate and dodecyl amine acetate as indicated by percent turbidity drops and the amount of settled material. The critical concentrations are 30 mg/l sodium oleate and 20 mg/l dodecyl amine acetate and higher concentrations than these levels do not increase the extent of flocculation at all.

The results are consistent with the work of Raju et al. (1991) which obtained similar results in the shear flocculation of quartz using dodecylamine chloride as collector.

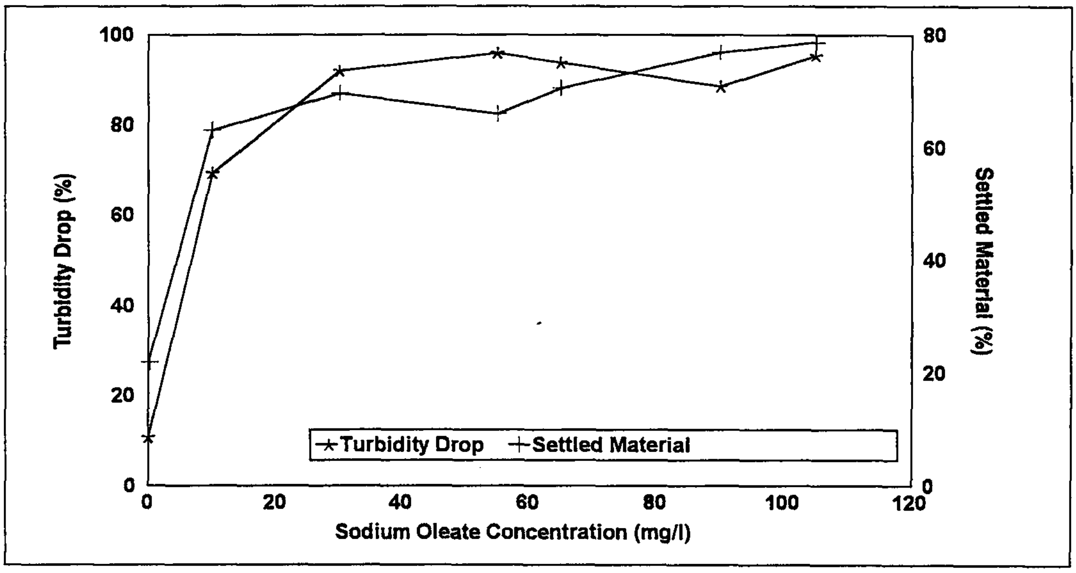

Figure 5.16. Effect of Sodium Oleate Concentration on Shear Flocculation of Chromite (pH: 3.0; Stirrer Speed: 630 rpm; Flocc. Time: 60 min.)

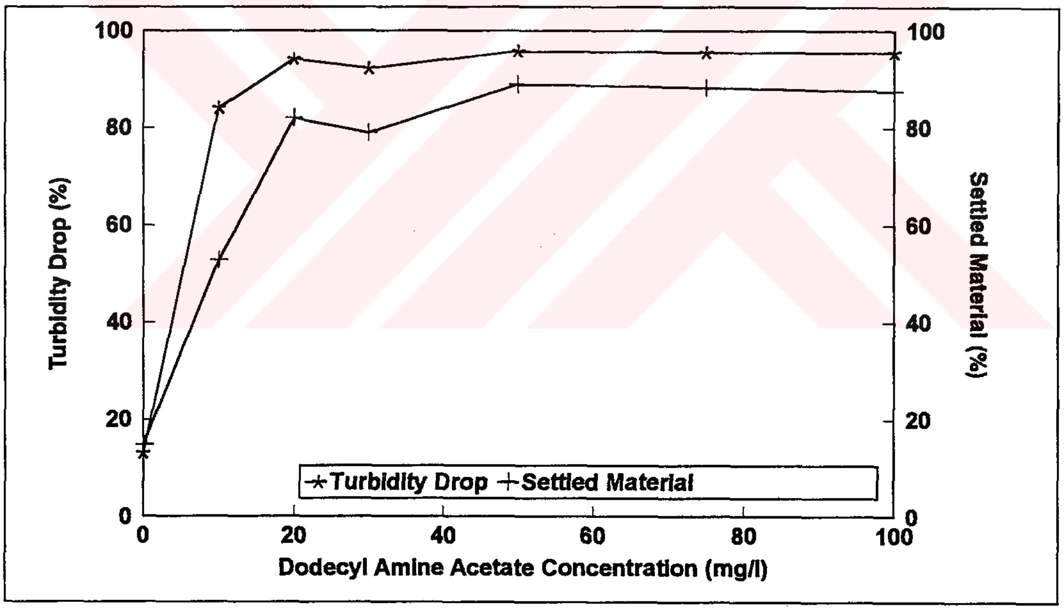

Figure 5.17. Effect of Dodecyl Amine Acetate Concentration on Shear Flocculation of Chromite (pH: 9.0; Stirrer Speed; 630 rpm; Flocc.Time: 30 min.)

5.3.1.4. Effect of Flocculation Time on Shear Flocculation of Chromite

The change in turbidity and in the amount of settled material in the shear flocculation of chromite with flocculation (stirring) time are shown in Figures 5.18 and 5.19.

It is observed from the figures that the initation of aggregation is rapid, starting immediately and reaching equilibrium in 30 minutes after which the degree of flocculation decreases. This deterioration for the stirring longer than 30 minutes is more significant with dodecyl amine acetate; the amount of settled material decreasing from 82% to 53% with increasing flocculation time from 30 to 120 minutes.

The figures also show that flocculation starts immediately and almost 80% flocculation is obtained in 10 minutes. In this respect, our results are similar to those of Sivamohan (1988) who showed that 80-90 % of shear flocculation was completed in 5 minutes. The results are also in aggreement with the work of Raju et al. (1991) where flocculation was nearly completed in 15 minutes.

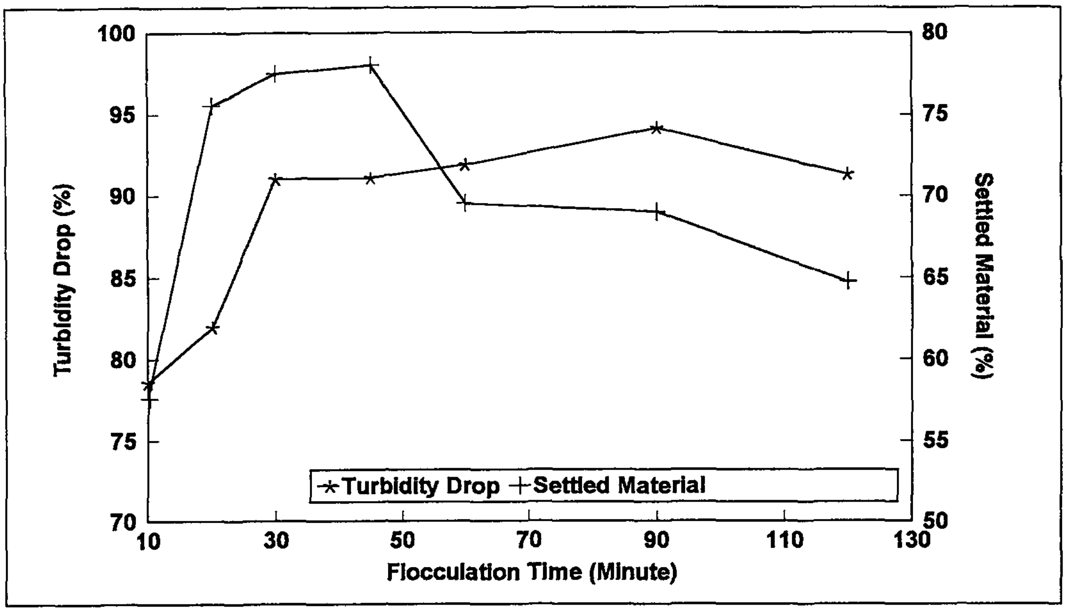

Figure 5.18. Effect of Flocculation Time on Shear Flocculation of Chromite with Sodium Oleate (pH:3.0; Collector: 30 mg/l; Stirrer Speed: 630 rpm)

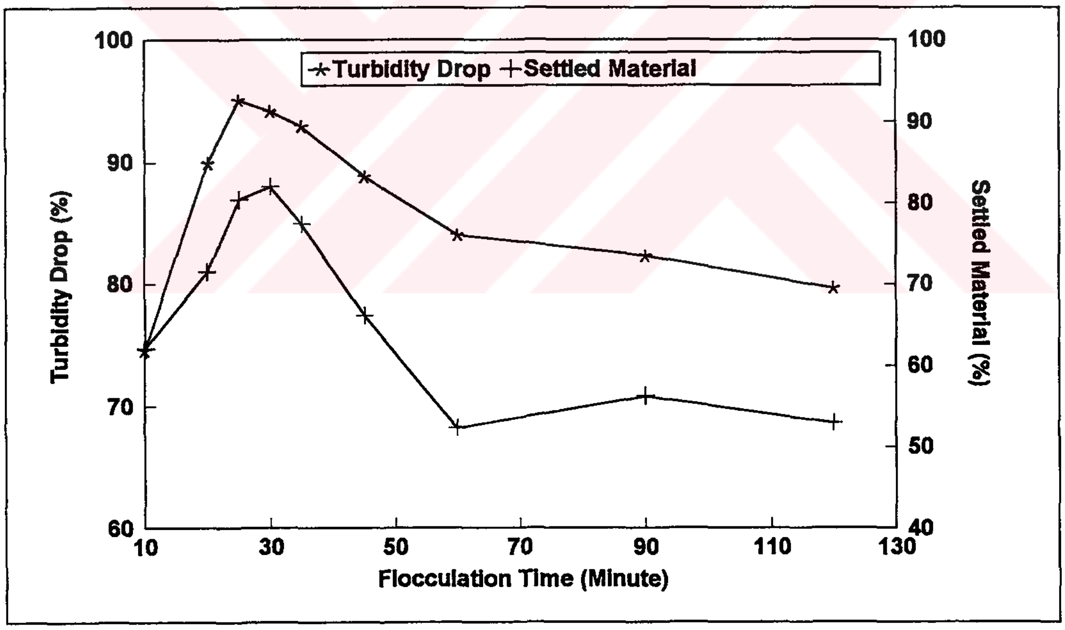

Figure 5.19. Effect of Flocculation Time on Shear Flocculation of Chromite with Dodecyl Amine Acetate (pH: 9.0; Collector: 20 mg/l; Stirrer Speed: 630 rpm)

5.3.1.5. Effect of Stirrer Speed on Shear Flocculation of Chromite

The turbidity drop and the amount of settled material resulting from the shear flocculation of chromite particles by sodium oleate and dodecyl amine acetate at various stirrer speeds, given in Table 4.28 and 4.29, are shown in Figures 5.20 and 5.21.

It is interesting that aggregation is possible at a wide stirrer speed range from 0 rpm to 870 rpm but optimum results were obtained at intermediate stirrer speeds of 490, 580 and 630 rpm, as indicated by high amount of settled material and high turbidity changes. The amount of settled material and the turbidity drop started to decrease at 870 rpm and almost no aggregation was recorded at 1200 rpm. The amounts of settled material obtained at 1200 rpm were 23% and 28% for the shear flocculation with sodium oleate and dodecyl amine acetate, respectively. They are very low compared to 78% and 82% obtained at 630 rpm. This suggests that chromite particles can not aggregate at very high speeds since energy of impact exceeds the energy of hydrophobic association, leading to particle re-dispersion.

The results show the necessity of stirring. However, partial flocculation with no stirring is interesting. This is probably due to the repelling action of water to force the hydrophobic particles to aggregate together (Lu and Li, 1984). The other reason may be the hydrophobic association between two

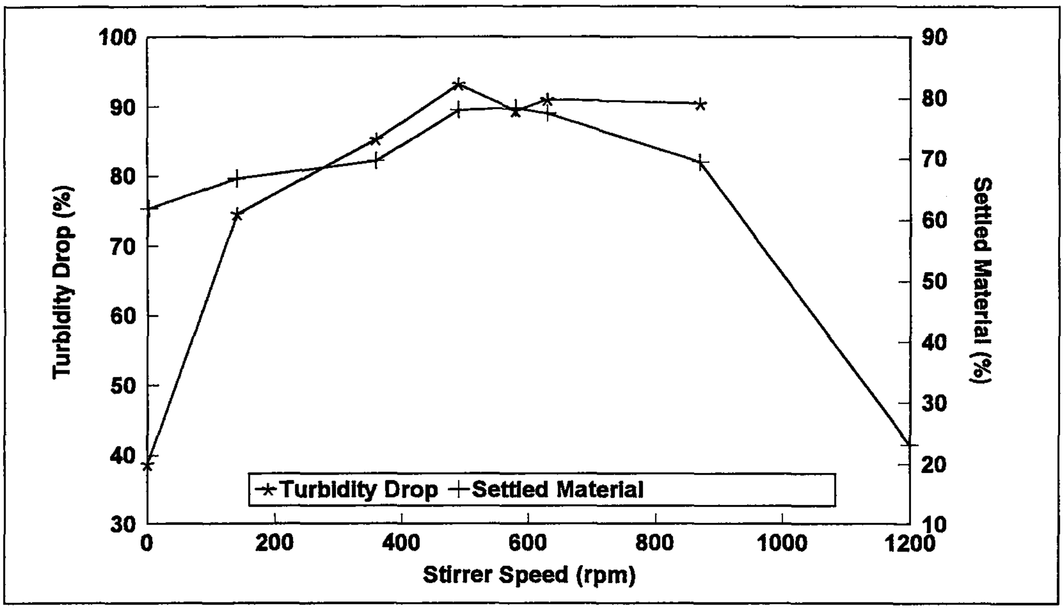

Figure 5.20. Effect of Stirrer Speed on Shear Flocculation of Chromite with Sodium Oleate (pH: 3.0; Collector: 30 mg/l; Flocc Time: 30 min.)

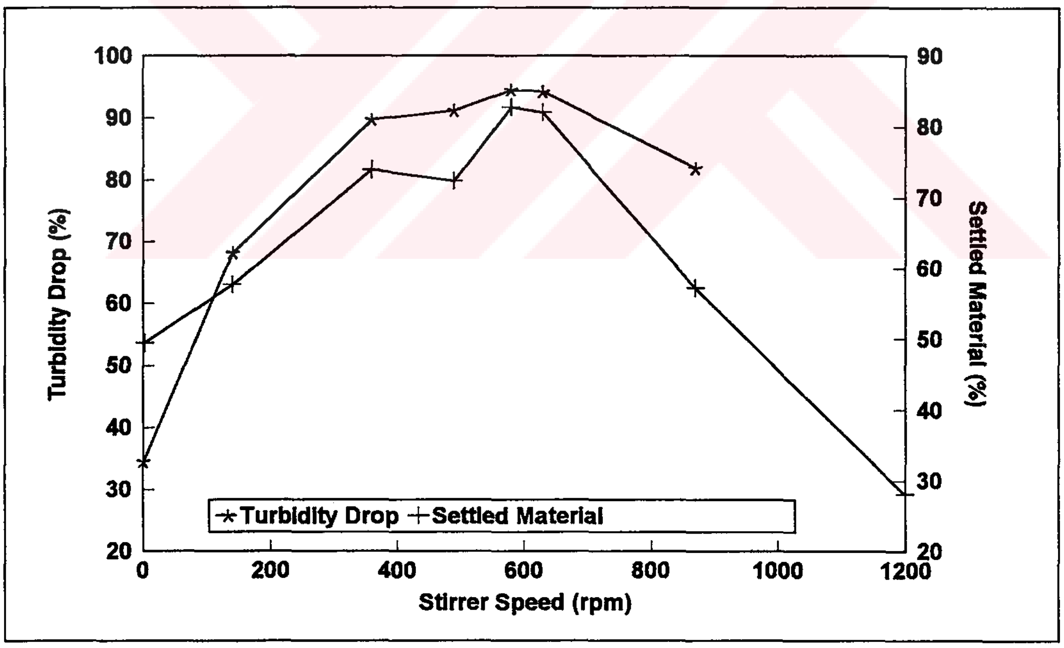

Figure 5.21. Effect of Stirrer Speed on Shear Flocculation of Chromite with Dodecyl Amine Acetate (pH:9.0; Collector:20 mg/l; Flocc Time:30 min.)

particles. The hydrophobization of particle surface is often accompanied by a distinct flocculation (Lu and Song, 1991).

5.3.1.6. Effect of Suspension Concentration on Shear Flocculation of Chromite

The results of experiments carried out to investigate the effect of solid concentration on the shear flocculation of chromite with sodium oleate and dodecyl amine acetate, given in Tables 4.30 and 4.31 are drawn in Figure 5.22 and Figure 5.23, respectively.

The general trend is that the extent of aggregation increases with increasing particle concentration. This increase is more significant when the solid concentration increases from 0.35 g/l to 1.4-2.1 g/l. For additions above this there is almost no change in the flocculation. The effect is best seen by the increase of settling rate from 43.90% to 74.47% upon increasing the solid concentration from 0.35 to 0.53 g/l, with sodium oleate flocculation.

Warren's (1975) experiments indicated that a ten-fold increase in the suspension concentration increased the initial rate of aggregation about 50 times. However, our experiments indicated that the effect of suspension concentration is not of this order. The amount of settled material increased from 43.90 % to 87.40 %, a two-fold increase, by increasing the solid concentration from 0.35 g/l to 3.5 g/l,

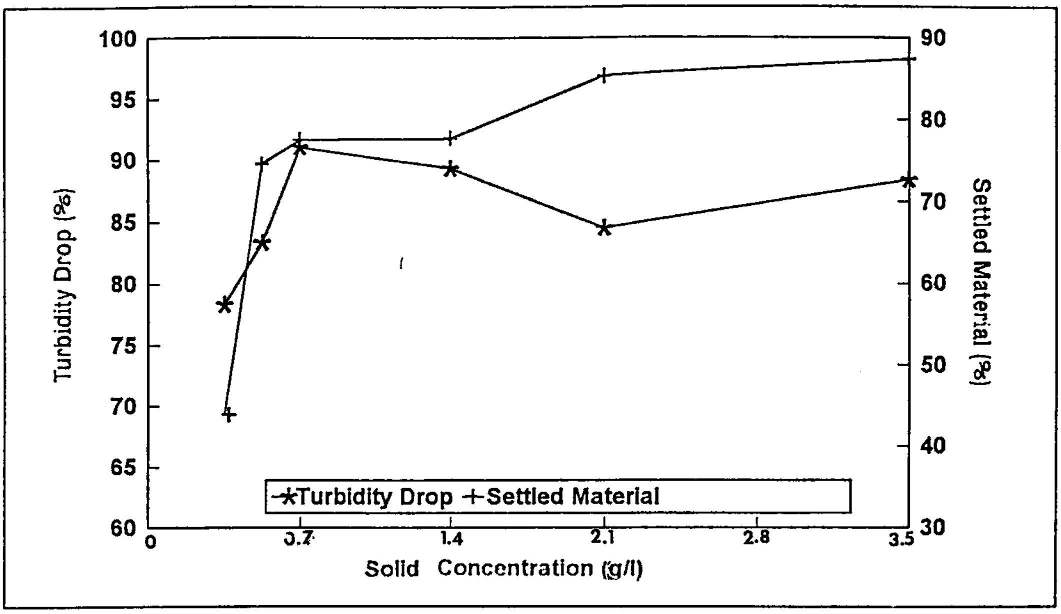

Figure 5.22. Effect of Suspension Concentration on Shear Flocculation of Chromite with Sodium Oleate (pH: 3.0; Cóllector: 30 mg/l; Stirrer Speed: 630 rpm; Flocculation Time: 30 min.)

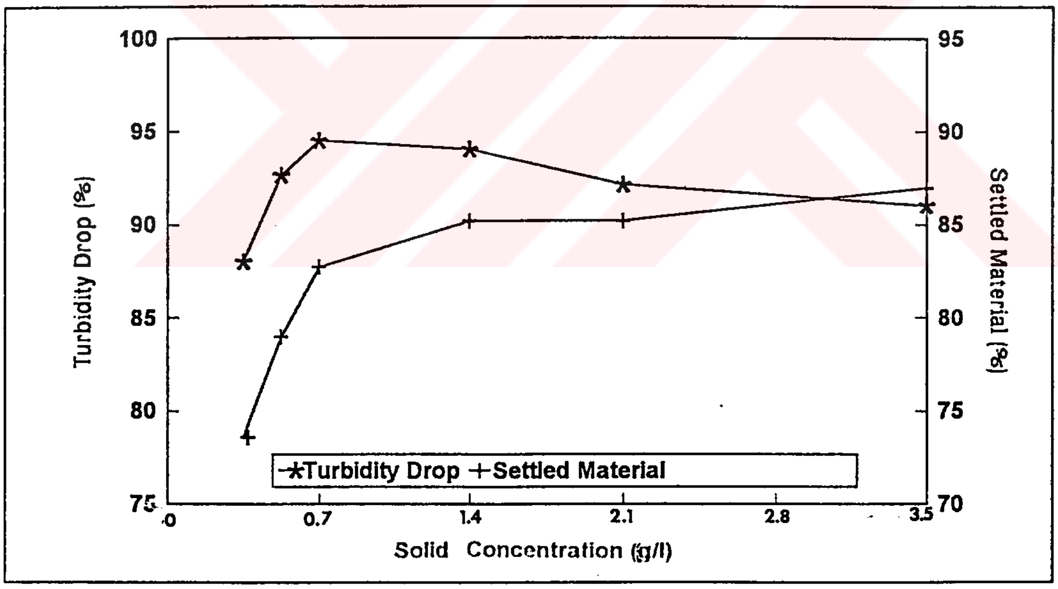

Figure 5.23. Effect of Suspension Concentration on Shear Flocculation of Chromite with Dodecyl Amine Acetate (pH: 9.0; Collector: 20 mg/l; Stirrer Speed: 580 rpm; Flocculation Time: 30 min.)

in oleate flocculation. The effect is less for the aggregation with dodecyl amine acetate; settled amount increasing from 73.58% to 86.92%.

5.3.2. Shear Flocculation of Serpentine

The effect of various factors on the shear flocculation of serpentine was discussed in this section. These factors include pH, collector concentration, flocculation time, stirrer speed and suspension concentration. The importance of surface hydrophobization on the stability of suspensions was also discussed by comparing the settling rate and turbidity drops of bare and hydrophobic suspensions.

5.3.2.1. Role of Collector on Aggregation of Fine Serpentine Suspensions

The coagulation behaviour of serpentine particles at different pH values, given in Table 4.32, were plotted in Figure 5.24. It is seen that maximum aggregation of the particles without a collector is in the pH range of 9-11 where the particles have low zeta potential. The optimum results are obtained at pH 10 where the amount of settled material and turbidity drop are 33.33% and 18.88%, respectively. On the other hand, the settling rate and the turbidity drop in neutral and acidic pH values are about 10% and 0%. These results show that there is a significant coagulation of serpentine fines in the absence of collector in contrast to chromite particles. This is in good aggreement with study of Bolandakhtari (1993) who found that maximum coagulation occurs in the pH range 9-11.

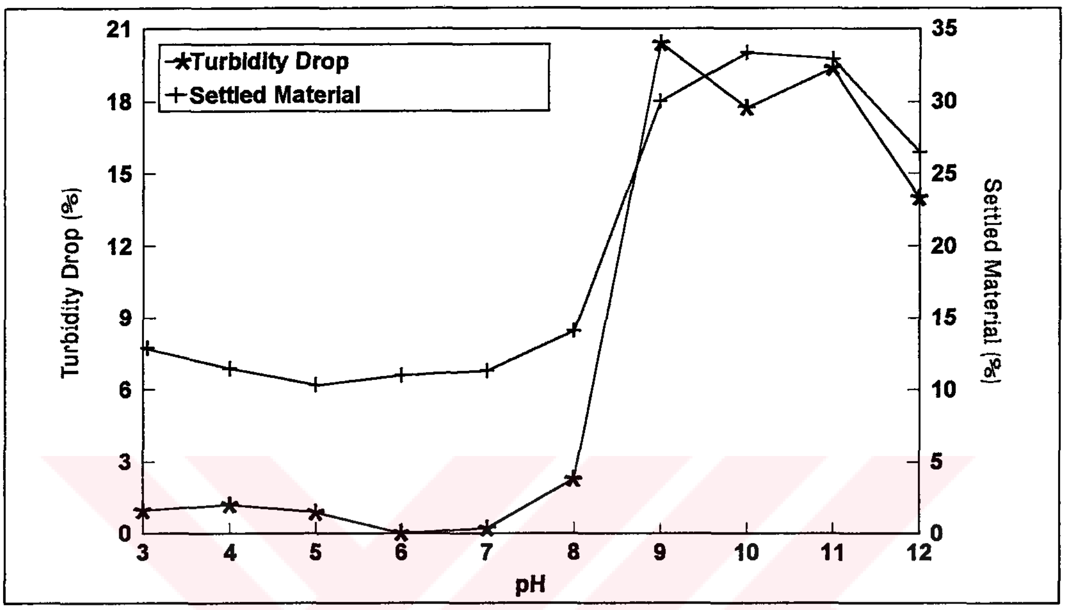

Figure 5.24. Coagulation of Serpentine Fines at Different pH Values (No Collector; Stirrer Speed: 360 rpm; Stirring Time: 30 min.)

The low zeta potential at these pH values is responsible for the unstability, reducing the effect of double layer repulsive force. This provides the particles to aggregate according to DLVO theory.

Higher aggregation rate of serpentine particles compared to chromite is probably due to higher degree of natural hydrophobicity of serpentine compared to chromite as indicated by greater contact angle of serpentine in double distilled water. This situation may provide an attractive force reducing the stability especially when particles carry low surface charge.

The results of experiments comparing the settling rates and turbidity drops of serpentine in the absence and presence of sodium oleate and dodecyl amine acetate are given in Table 5.2.

Table 5.2 Role of Collector on Aggregation of Serpentine Fines (Stirring Time: 20 min.)

pH	**Collector**	**Stirrer Speed (rpm)**	**Turbidity Drop (%)**	**Settled Material (%)**
6.0	No	360	0.00	10.96
6.0	30 mg/l Sodium Oleate	360	80.76	87.93
11.5	No	630	13.45	8.33
11.5	50 mg/l Dodecyl Amine Acetate	630	53.94	71.67

The marked effect of sodium oleate and dodecyl amine acetate on the aggregation of serpentine can clearly be seen from the above table. Collector is necessary to reduce the stability of fine serpentine suspensions, although the effect of coagulation can't be neglected as mentioned before.

5.3.2.2. Effect of pH on Shear Flocculation of Serpentine

Shear flocculation behaviour of serpentine fines at different pH values in the presence of sodium oleate and dodecyl amine acetate, given in Tables 4.33 and 4.34, is shown in Figures 5.25 and 5.26, respectively.

The figures show that serpentine particles can be flocculated at a wide pH range of 4-12 by sodium oleate where optimum results are obtained at pH 6. Shear flocculation with dodecyl amine acetate is possible at a narrower pH range of 10-12.5; the maximum settling rate and turbidity drop being obtained at pH 11.5.

Comparison of Figure 5.25 with Figure 5.7 and Figure 5.26 with Figure 5.8 points out that the pH values 6 and 11.5 are almost iso-electrical points of serpentine conditioned with sodium oleate and dodecyl amine acetate, respectively. This indicates that maximum aggregation occurs when zeta potential is minimum.

The possibility of aggregation even when the zeta potential is high, for example -37.95 mV at pH 11 by 30 mg/l sodium oleate, is probably due to the extensive hydrophobicity of particles indicated by high contact angle values of serpentine conditioned with sodium oleate. The energy of hydrophobic

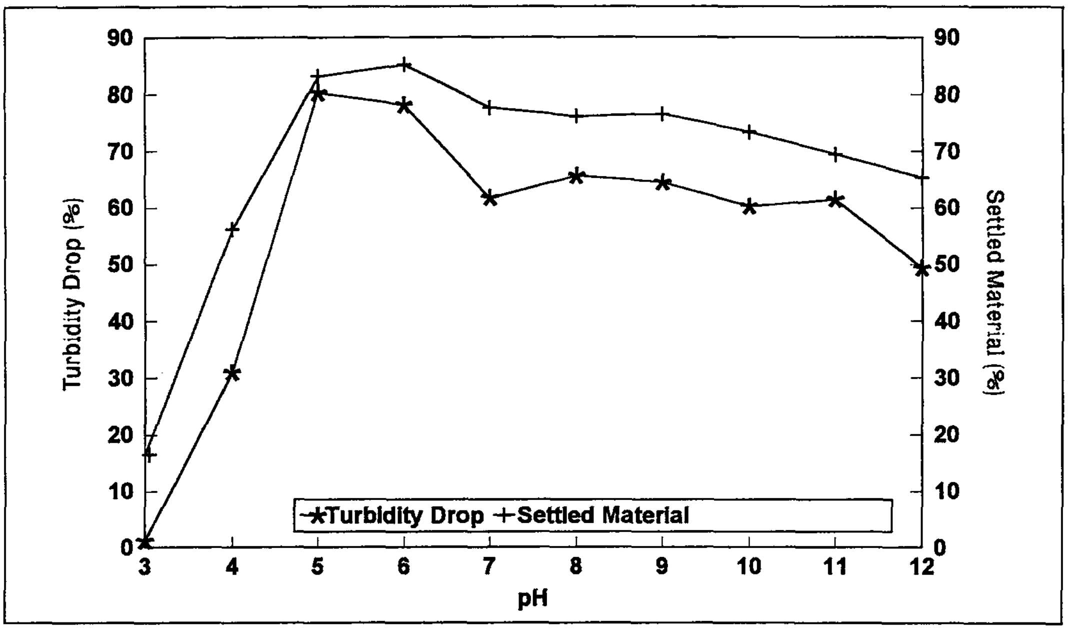

Figure 5.25. Effect of pH on Shear Flocculation of Serpentine with Sodium Oleate (Collector: 30 mg/l; Stirrer Speed: 630 rpm; Flocculation Time: 30 min.)

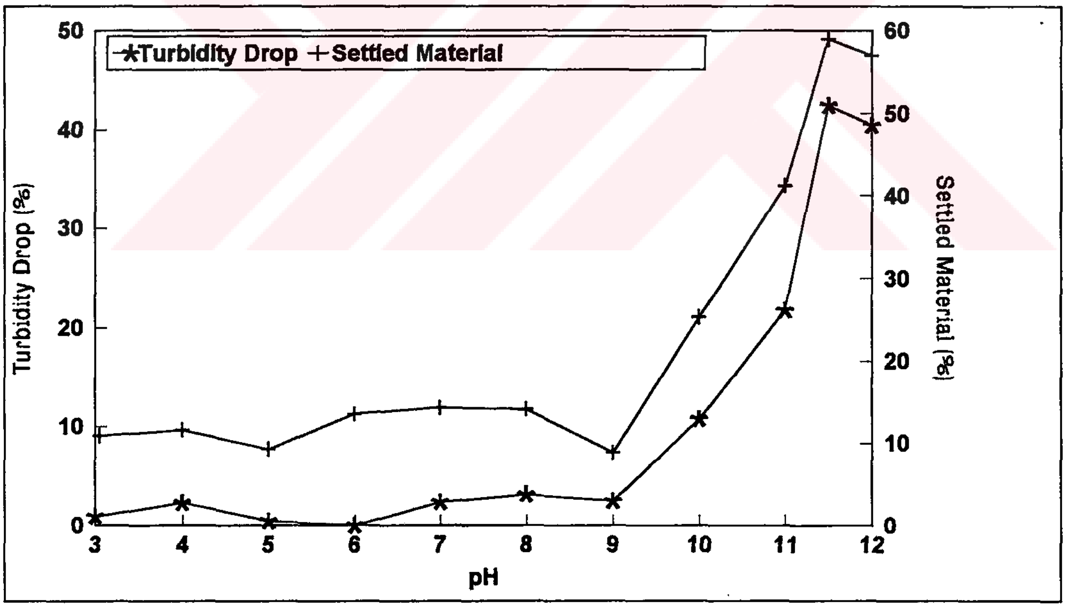

Figure 5.26. Effect of pH on Shear Flocculation of Serpentine with Dodecyl Amine Acetate (Collector: 30 mg/l; Stirrer Speed: 630 rpm; Flocculation Time: 30 min.)

association may be high enough to make particles aggregate even when electrical double layer repulsive force is large.

Comparison of Figures 5.25 and 5.26 with Figure 5.12 indicates that there is no correlation between contact angle and degree of shear flocculation of serpentine fines. The maximum contact angle points (pH 8 and 9) do not coincide with the pH values of optimum flocculation (pH 6 and 11.5) with sodium oleate and dodecyl amine acetate, respectively. However, the contact angles at pH 6 and 11.5 are still large.

It can be concluded from all discussions that surface hydrophobization by collector addition is necessary for the shear flocculation of serpentine. The most extensive aggregation is observed when the electrokinetic mobilities of the particles are minimum. The aggregation of highly charged serpentine particles is easier compared to that of chromite particles probably because of their less-wettable properties.

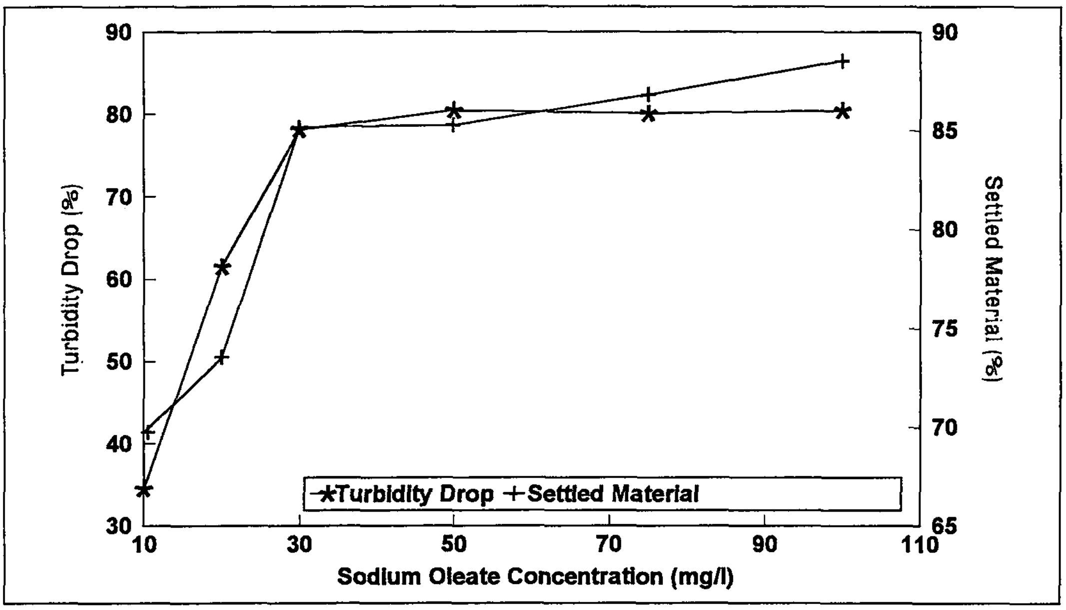

Figure 5.27. Effect of Sodium Oleate Concentration on Shear Flocculation of Serpentine (pH:6.0; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

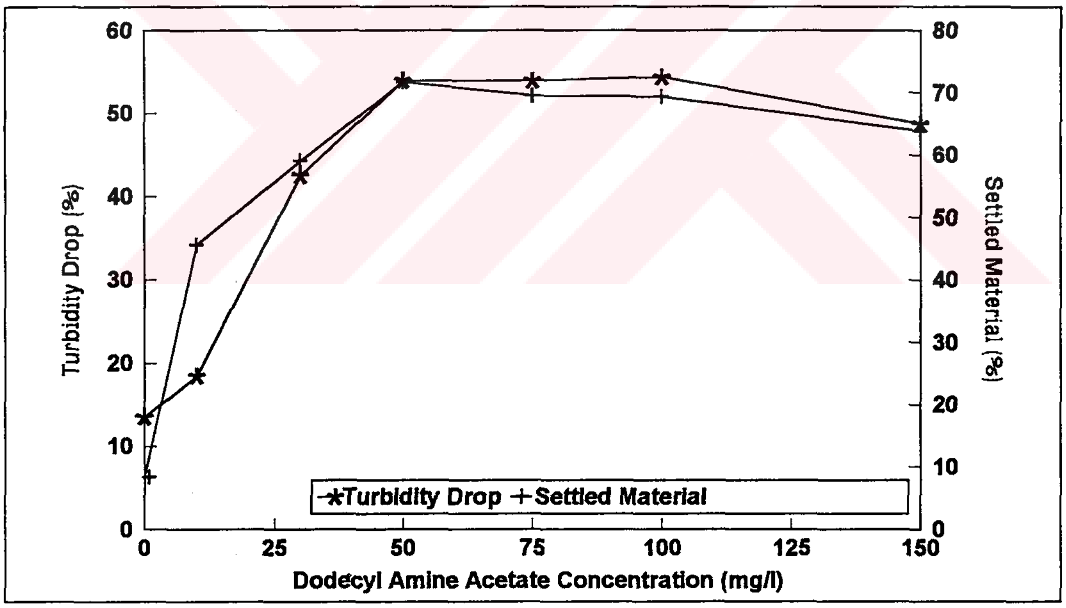

Figure 5.28. Effect of Dodecyl Amine Acetate Concentration on Shear Flocculation of Serpentine (pH:11.5; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

5.3.2.3. Effect of Collector Concentration on Shear Flocculation of Serpentine

Figures 5.27 shows the variaton of turbidity drop and settling rate of serpentine particles at different sodium oleate concentrations. Their flocculation behaviour in the presence of different concentrations of dodecyl amine acetate was plotted in Figure 5.28.

Increase in the sodium oleate and dodecyl amine acetate dosages increases the degree of flocculation up to certain levels and further additions do not effect the turbidities and the amount of settled material significantly. The addition of 30 mg/l sodium oleate was found to be sufficient for complete flocculation where turbidity drop and the amount of settled material are 78.08% and 85.14%, respectively. Optimum results with dodecyl amine acetate, on the other hand, were obtained at a higher concentration, 50 mg/l. The percentage of turbidity drop and the amount of settled material were 53.94% and 71.67%, respectively.

5.3.2.4. Effect of Flocculation Time on Shear Flocculation of Serpentine

The results of experiments carried out to investigate the effect of stirring time (flocculation time) on the shear flocculation of serpentine with sodium oleate and dodecyl amine acetate, tabulated in Tables 4.37 and 4.38, were plotted in Figure 5.29 and 5.30.

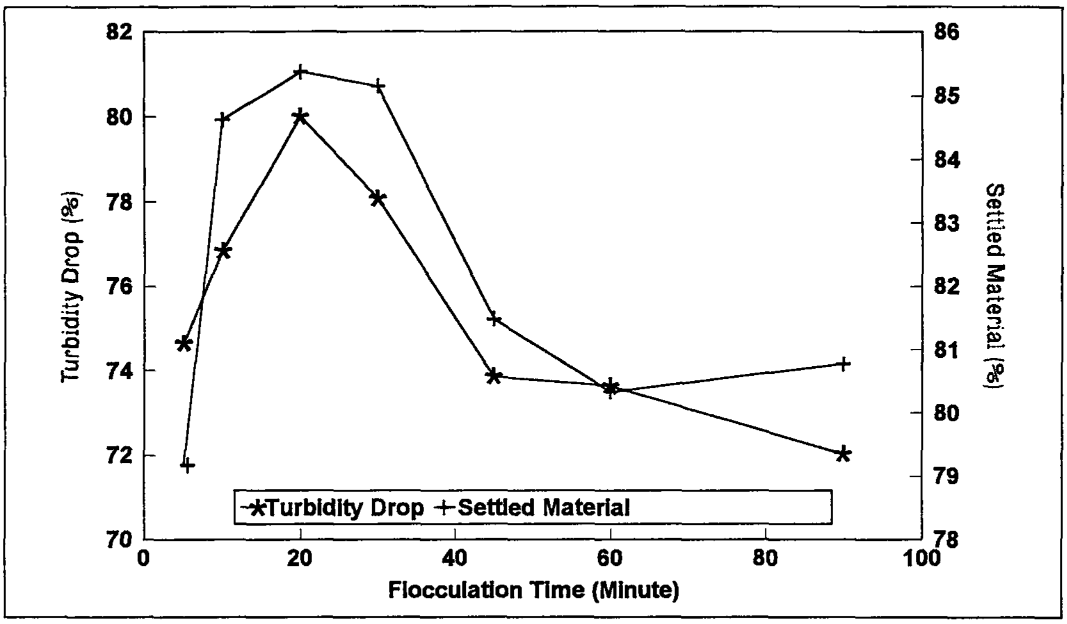

Figure 5.29. Effect of Flocculation Time on Shear Flocculation of Serpentine with Sodium Oleate (pH: 6.0; Collector: 30 mg/l; Stirrer Speed: 630 rpm)

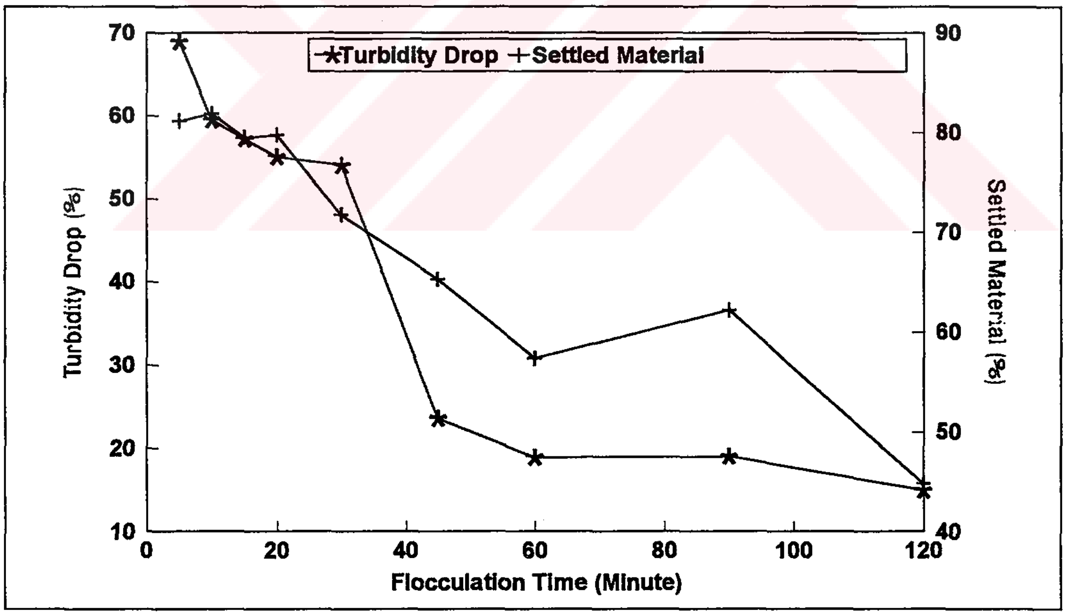

Figure 5.30. Effect of Flocculation Time on Shear Flocculation of Serpentine with Dodecyl Amine Acetate (pH: 11.5; Collector: 50 mg/l; Stirrer Speed: 630 rpm)

It is seen that the aggregation of serpentine fines with both sodium oleate and dodecyl amine acetate is a rapid process, starting immediately and reaching to maximum in 20 and 10 minutes for oleate and amine flocculation, respectively. Further stirring reduces the amount of settled material and percentage turbidity drop, especially when using dodecyl amine acetate. The amount of settled material decreases from 81.82% to 44.78% and turbidity drop reduces from 59.43% to 14.94% when the duration of stirring is increased from 10 minutes to 120 minutes. This effect is less with sodium oleate where turbidity and settling rate change hardly after 20 minutes.

The higher rate of aggregation of serpentine compared to chromite, which reached equilibrium in 30 minutes, is probably due to higher hydrophobic character of serpentine particles. The hydrophobic association between them may be stronger than that between chromite particles so easier aggregation is obtained.

5.3.2.5. Effect of Stirrer Speed on Shear Flocculation of Serpentine

The variation of turbidity drop and the settling rate of serpentine fines flocculated with sodium oleate and dodecyl amine acetate at different stirrer speeds are shown in Figures 5.31 and 5.32.

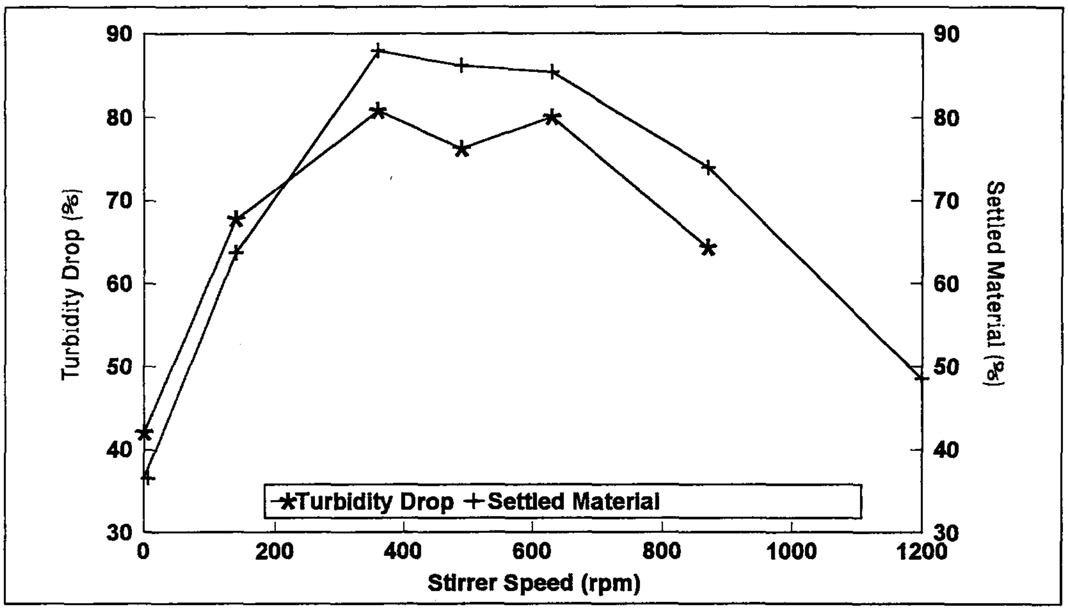

Figure 5.31. Effect of Stirrer Speed on Shear Flocculation of Serpentine with Sodium Oleate (pH: 6.0; Collector: 30 mg/l; Flocc. Time: 20 min.)

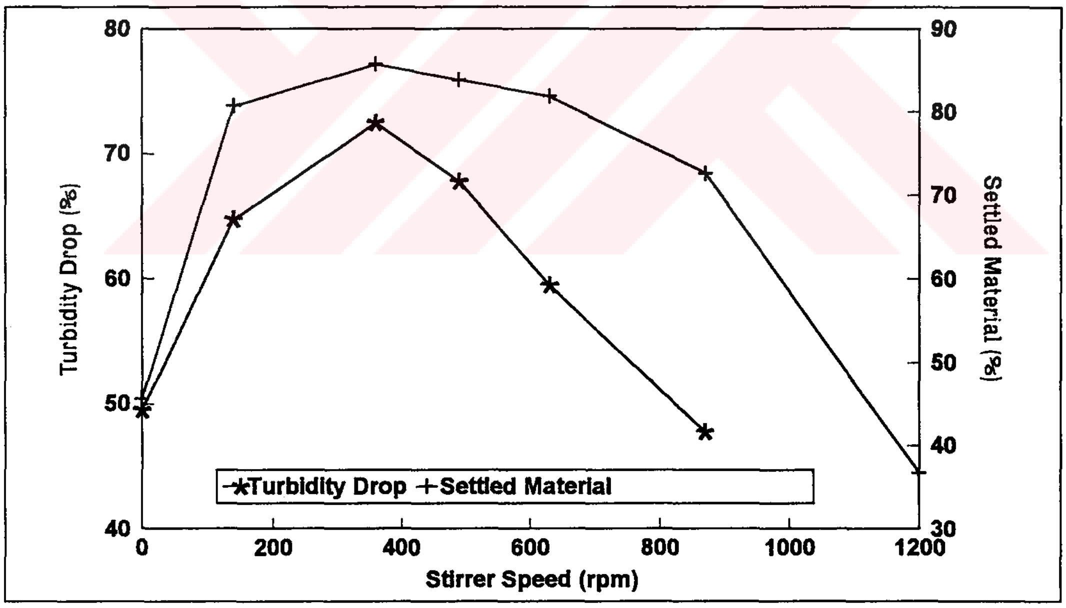

Figure 5.32. Effect of Stirrer Speed on Shear Flocculation of Serpentine with Dodecyl Amine Acetate (pH: 11.5; Collector: 50 mg/l; Flocc. Time: 10 min.)

The figures indicate that extensive flocculation of serpentine fines is possible at intermediate stirrer speeds, 360-630 rpm. Optimum results were obtained at 360 rpm, where turbidity drops were 80.76% and 72.43% and the amounts of settled material were 87.93% and 85.71% for oleate and amine flocculation, respectively. Considerable aggregation is also seen at a low (140 rpm) speed and at a high (870 rpm) speed but the amount of settled material and turbidity drop are smaller than those obtained at intermediate speeds.

The partial aggregation at 0 rpm can be explained by the potential energy of hydrophobic interaction between the hydrophobic surfaces which exceeds the energy resulting from double layer and van der Waals inteactions (Lu and Song, 1991).

The flocculation at 1200 rpm is only about half of that obtained at 360 rpm. This suggests that aggregation of serpentine is dificult at very high speeds because the energy of impact exceeds the energy of hydrophobic association.

The comparetively lower speed required for the shear flocculation of serpentine than that for chromite may be because of their more hydrophobic character which force the particles to come together by a lower kinetic energy.

5.3.2.6. Effect of Suspension Concentration on Shear Flocculation of Serpentine

Figures 5.33 and 5.34 show the variation of turbidity drop and settling rate of serpentine at different solid concentrations by sodium oleate and dodecyl amine acetate, respectively.

It can be concluded from the figures that the degree of shear flocculation increases with increasing solid concentration since the number of collisions between the particles increases. Optimum results were obtained when using 3.5 g/l serpentine, where the amount of settled material and turbidity drops were 92.06 % and 93.67 %, respectively by oleate flocculation. When using dodecly amine acetate as collector, the maximum settling rate and turbidity drop were 90.38 and 92.42 %, respectively, obtained with 2.1 g/l serpentine.

The significant effect of solid concentration on the flocculation can be seen more clearly by comparing the results of experiments carried out with 0.35 and 0.7 g/l material for oleate flocculation. Increasing solid concentration from 0.35 g/l to 0.7 g/l increases the amount of settled material from 48 % to 87 %.

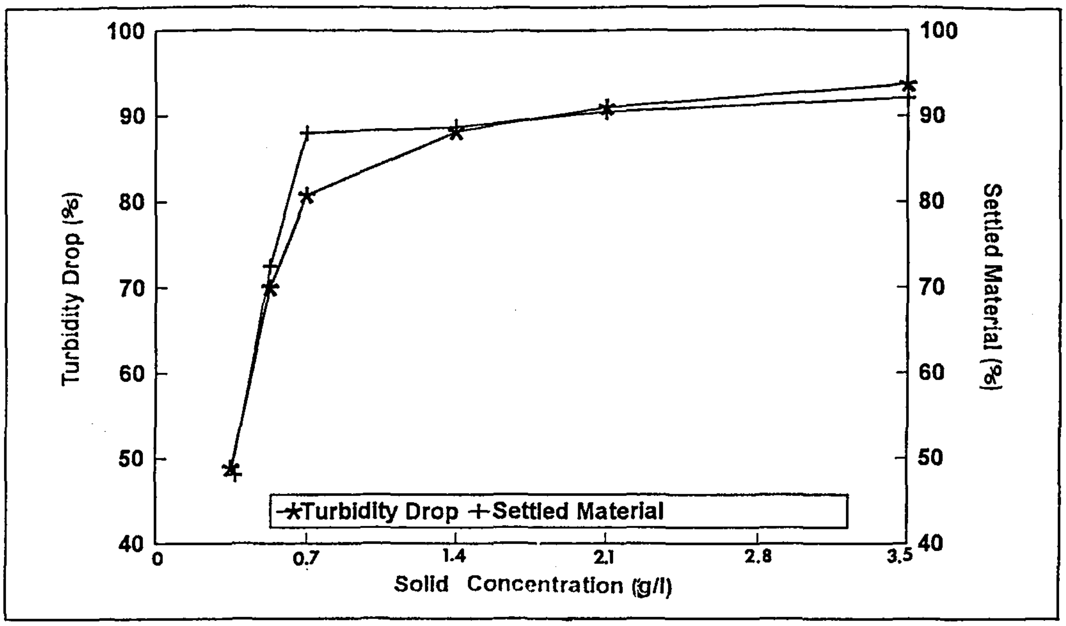

Figure 5.33. Effect of Suspension Concentration on Shear Flocculation of Serpentine with Sodium Oleate (pH: 6.0; Collector: 30 mg/l; Stirrer Speed: 360 rpm; Flocculation Time: 20 min.)

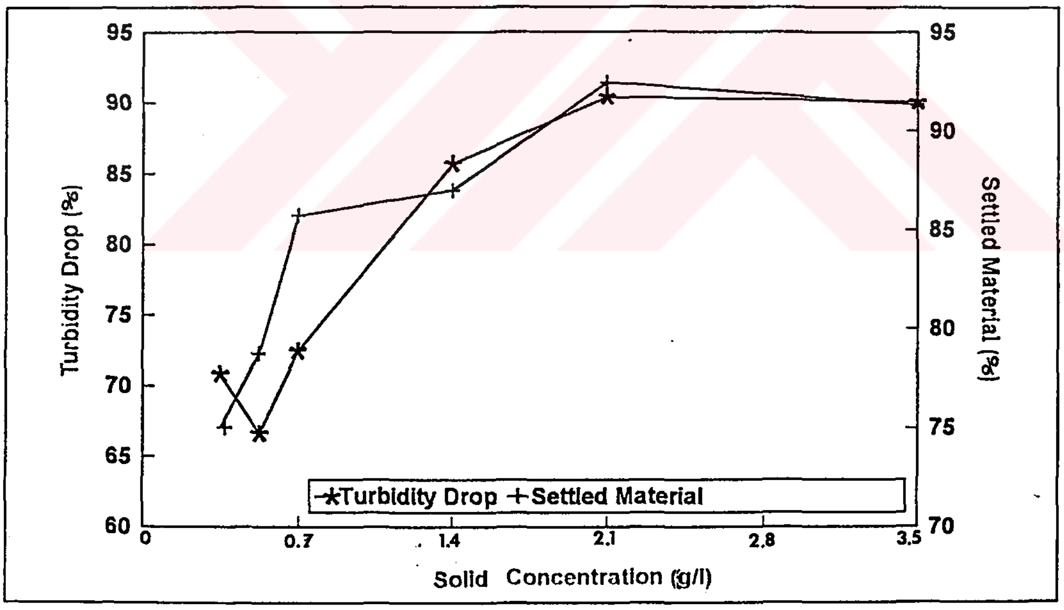

Figure 5.34. Effect of Suspension Concentration on Shear Flocculation of Serpentine with Dodecyl Amine Acetate (pH: 11.5; Collector: 50 mg/l; Stirrer Speed: 360 rpm; Flocculation Time: 10 min.)

5.4. Selective Shear Flocculation of Chromite

5.4.1. Role of Sodium Oleate on Selective Shear Flocculation of Chromite

Table 5.3 presents the grades and recoveries of settled (concentrate) and dispersed (tailing) fractions of selective shear flocculations experiments. pH 3.5 was the optimum value for selectively flocculating chromite from serpentine.

Table 5.3 Role of Sodium Oleate Addition on Selective Shear Flocculation of Chromite

Sodium Oleate (mg/l)	Material	Grade (%Cr_2O_3)	Recovery (%)	Experimental Conditions
0	Concentrate	36.82	40.54	pH : 3.5 Stirrer Speed: 630 rpm Flocc. Time: 30 min. Settling Time: 5 min.
	Tailing	26.17	59.46	
30	Concentrate	42.56	68.99	
	Tailing	16.90	31.03	

The stirring of chromite serpentine mixture (1:1) in the absence of collector does not initiate aggregation. Flocculation is only possible when the surfaces are treated with sodium oleate. The increase in the grade of settled material from 36.82% Cr_2O_3 to 42.56% Cr_2O_3 indicates that the aggregation is selective, i.e the chromite particles are flocculated whereas most of serpentine particles are not affected by sodium oleate and remains dispersed.

5.4.2. Effect of pH on Selective Shear Flocculation of Chromite

The variation of grade and recovery of settled material and the selectivity indices at different pH values were plotted in Figure 5.35 and 5.36, respectively.

It can be seen from figures that optimum results are obtained at a very narrow pH range of 3-3.5. The high values of grades and selectivity indices at these points indicate that the separation is selective.

It is also seen that pH is very critical for selective separation. Increasing pH from 3.5 to 4 decreases the selectivity of chromite shear flocculation significantly and reduces the grade of settled material from 42.56 % Cr_2O_3 to 35.60 % Cr_2O_3. This is because of the low zeta potential of chromite at pH 3-3.5 and high zeta potential of serpentine particles. So, chromite particles are flocculated whereas the aggregation of serpentine particles will be difficult.

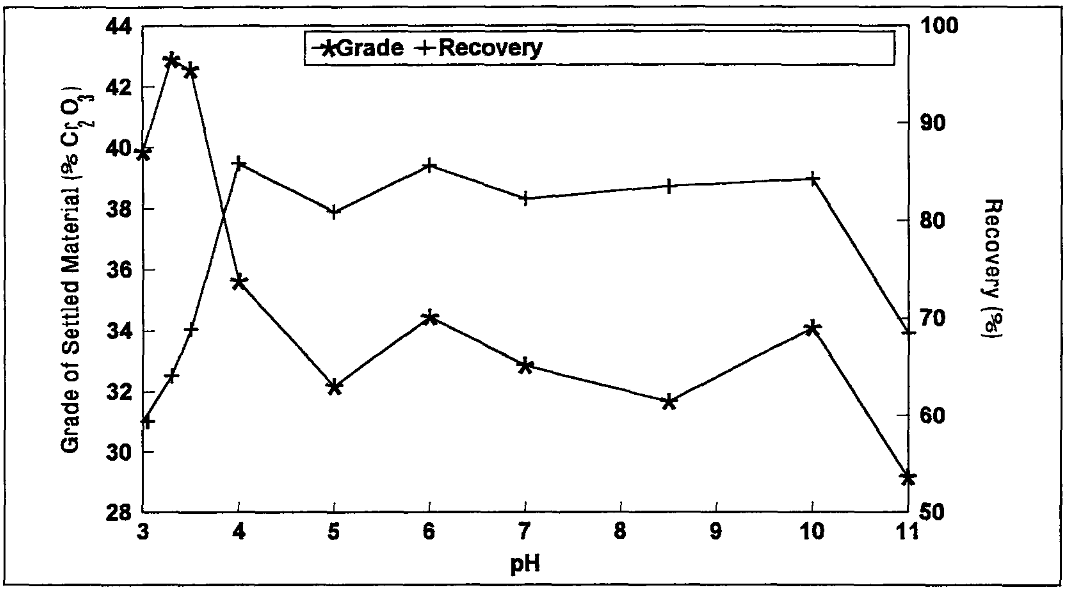

Figure 5.35. Effect of pH on Selective Shear Flocculation of Chromite (pH: 3.5; Stirrer Speed: 630 rpm; Flocc.Time: 30 min; Settling Time: 5 min.)

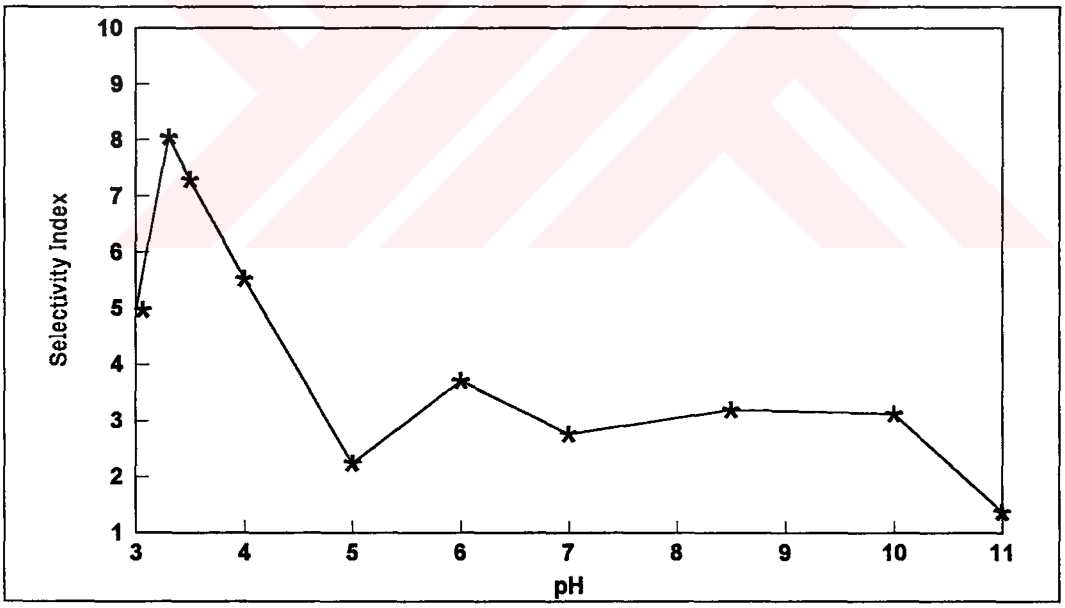

Figure 5.36. Selectivity Indices for Chromite-Serpentine Separation at Different pH Values

High recoveries and low grades at pH values higher than 4 indicate that both chromite and serpentine particles are flocculated to form hetero-flocs and settle together.

5.4.3. Effect of Sodium Oleate Concentration on Selective Shear Flocculation of Chromite

The results of selective shear flocculation experiments carried out with different concentrations of sodium oleate, given in Table 4.44, are shown in Figure 5.37 and 5.38.

The grades and selectivity indices increase first with increasing sodium oleate concentration and then decreases whereas the recovery always increases with increasing collector amount. The optimum results were obtained with 30 mg/l sodium oleate, where the grade, recovery and selectivity index were 42.56% Cr_2O_3, 68.99% and 7.28, respectively. Further additions reduced the selectivity by flocculating serpentine together with chromite. For example, increasing sodium oleate concentration from 30 mg/l to 50 mg/l decreased the grade of settled material from 42.56% Cr_2O_3 to 39.27% Cr_2O_3 although the recovery increased from 68.99% to 70.28%.

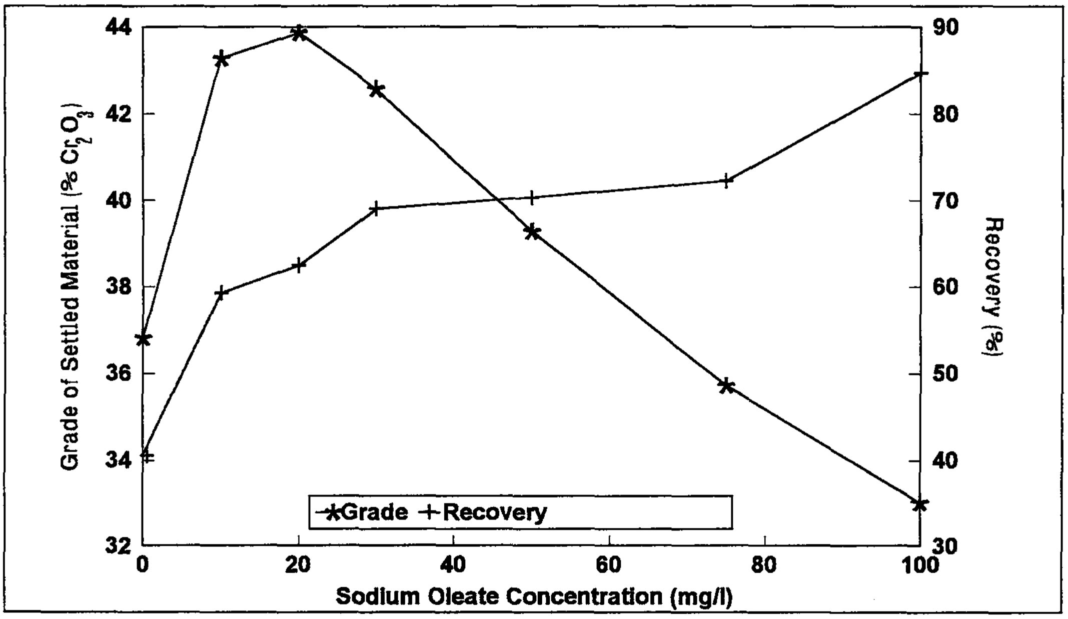

Figure 5.37. Effect of Sodium Oleate Concentration on Selective Shear Flocculation of Chromite (pH: 3.5; Stirrer Speed: 630 rpm; Flocculation Time: 30 min.; Settling Time: 5 min.)

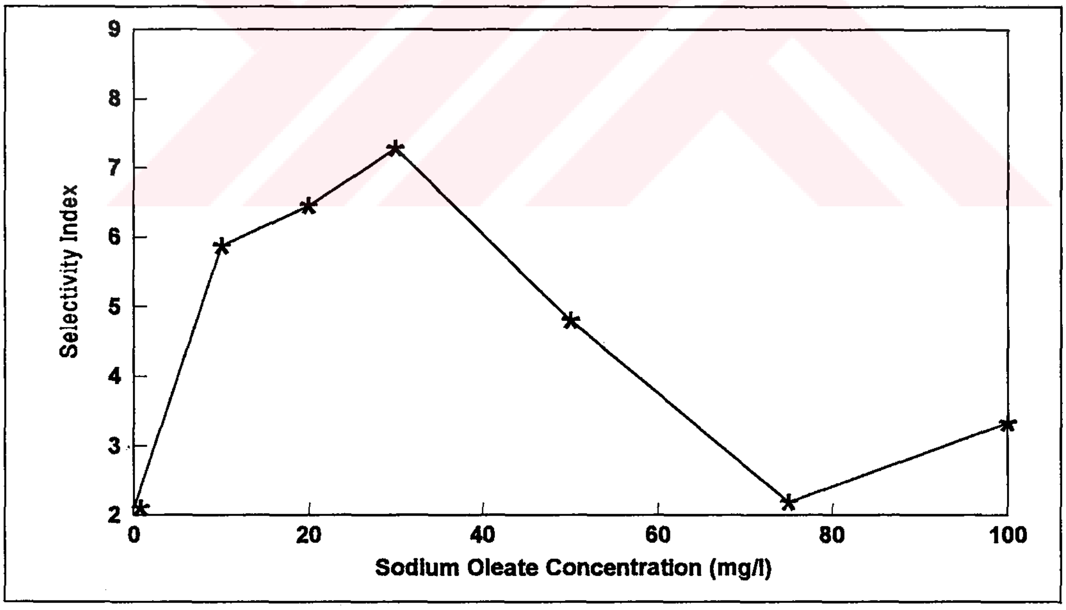

Figure 5.38. Selectivity Indices for Chromite-Serpentine Separations with Different Sodium Oleate Concentrations

5.4.4. Effect of Flocculation Time on Selective Shear Flocculation of Chromite

The grades and recoveries of settled materials (concentrates) obtained from selective flocculation of chromite at different flocculation times and corresponding selectivity indices were plotted in Figures 5.39 and 5.40, respectively.

Optimum results are obtained if the suspension is stirred for 60 minutes where the grade, recovery and selectivity index are 43.18% Cr_2O_3, 71.58% and 7.61, respectively. Further agitation decreases both grade and recovery.

The higher value of optimum flocculation time for selective shear flocculation compared to that of shear flocculation of chromite alone (30 min.) may be due to the reduction in the number of collisions between two chromite particles since serpentine fines are also present in the system.

5.4.5. Effect of Stirrer Speed on Selective Shear Flocculation of Chromite

The results of selective shear flocculation experiments stirred at different speeds, given in Table 4.46, are shown in Figures 5.41 and 5.42.

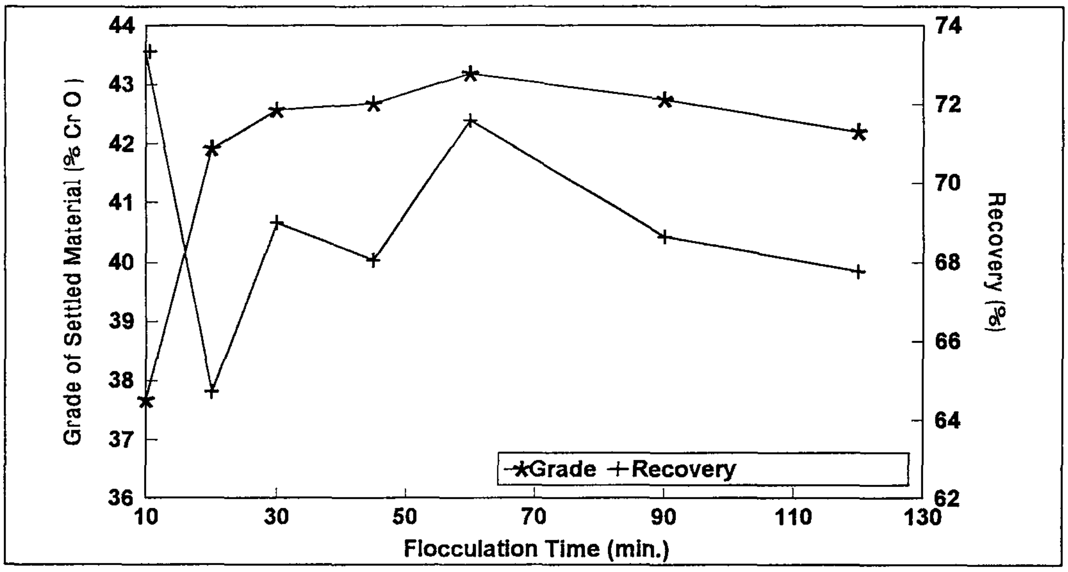

Figure 5. 39. Effect of Flocculation Time on Selective Shear Flocculation of Chromite (pH: 3.5; Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 630 rpm; Settling Time: 5 min.)

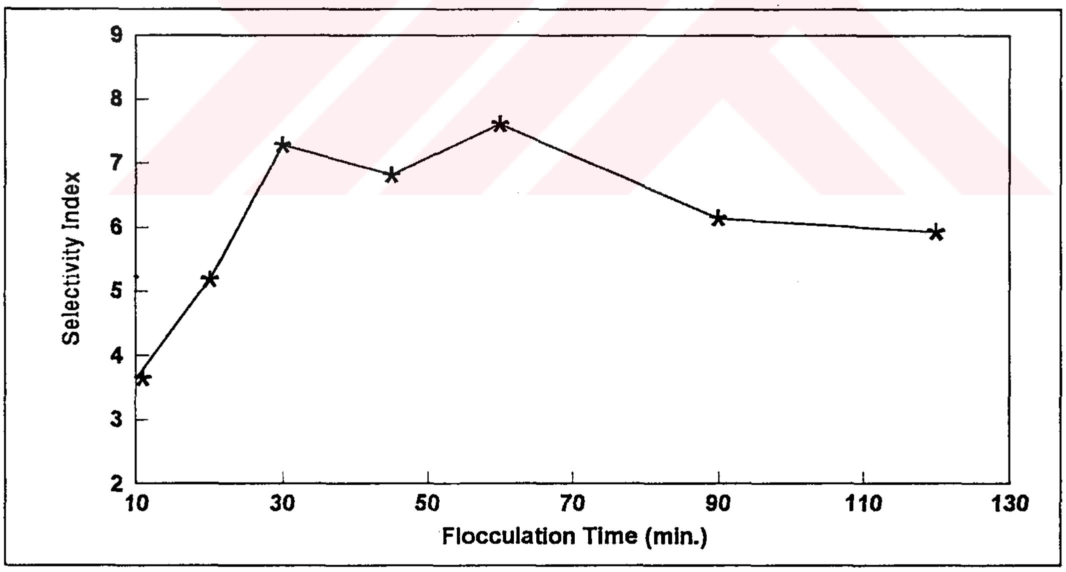

Figure 5.40. Selectivity Indices for Chromite-Serpentine Separations with Different Flocculation Times

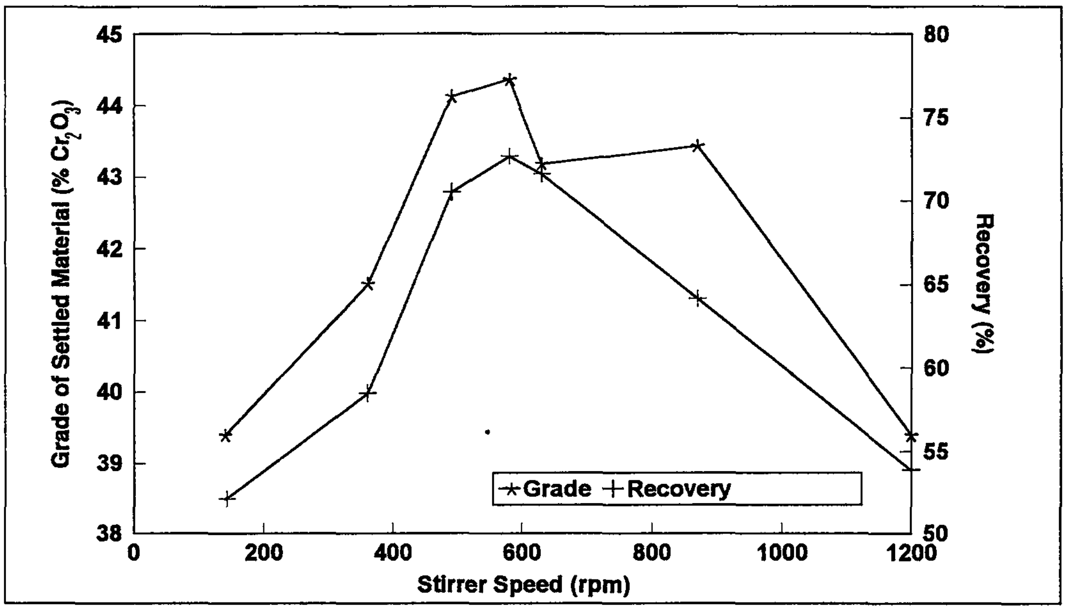

Figure 5.41. Effect of Stirrer Speed on Selective Shear Flocculation of Chromite (pH: 3.5; Collector: 30 mg/l Sodium Oleate; Flocculation Time: 60 min.; Settling Time: 5 min.)

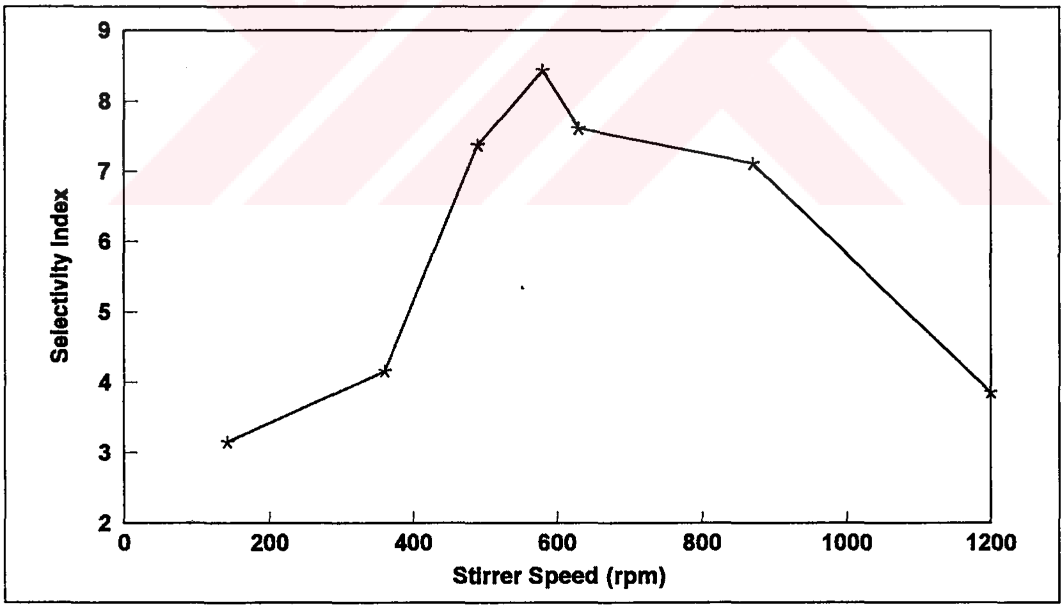

Figure 5.42. Selectivity Indices for Chromite-Serpentine Separations at Different Stirrer Speeds

Best results were obtained at intermediate stirrer speeds, 490 to 870 rpm; the maximum grade and recovery being obtained at 580 rpm. A settled portion containing 44.36% Cr_2O_3 were obtained with 72.65% recovery. The selectivity index for the separation at this speed was 8.44.

5.4.6. Effect of Settling Time on Selective Shear Flocculation of Chromite

The effect of settling time on the grades and recoveries of concentrates (settled material), shown in Table 4.50, were plotted in Figures 5.43. Figure 5.44 shows the variation of selectivity index.

An investigation of the figures indicates that the selectivity increases with increasing settling time up to 10 minutes, then the grade decreases. A 44.60% Cr_2O_3 concentrate was obtained with a recovery of 81.06% by allowing the suspension to settle for 10 minutes, where the selectivity index was 9.70.

5.4.7. Effect of NaF, Na_2SiF_6 and Na_2 SiO_3 on Selective Shear Flocculation of Chromite

Fluoride ion was shown to have good selective properties in the flotation of chromite that gualify it as a possible flotation reagent. Abido (1971)

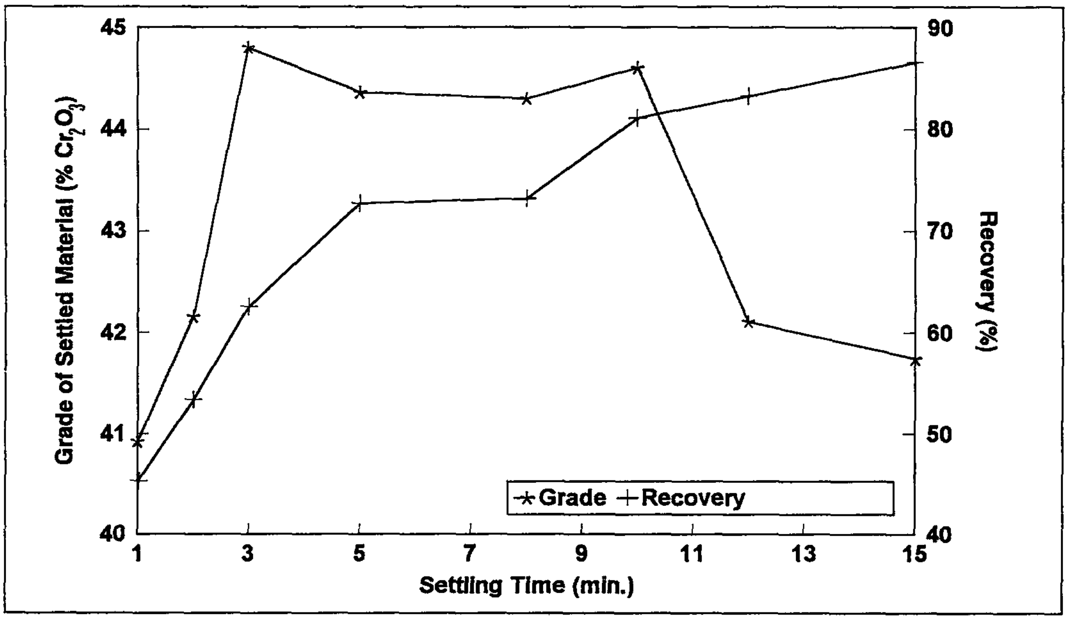

Figure 5.43. Effect of Settling Time on Selective Shear Flocculation of Chromite (pH: 3.5; Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 580 rpm; Flocculation Time: 60 min.)

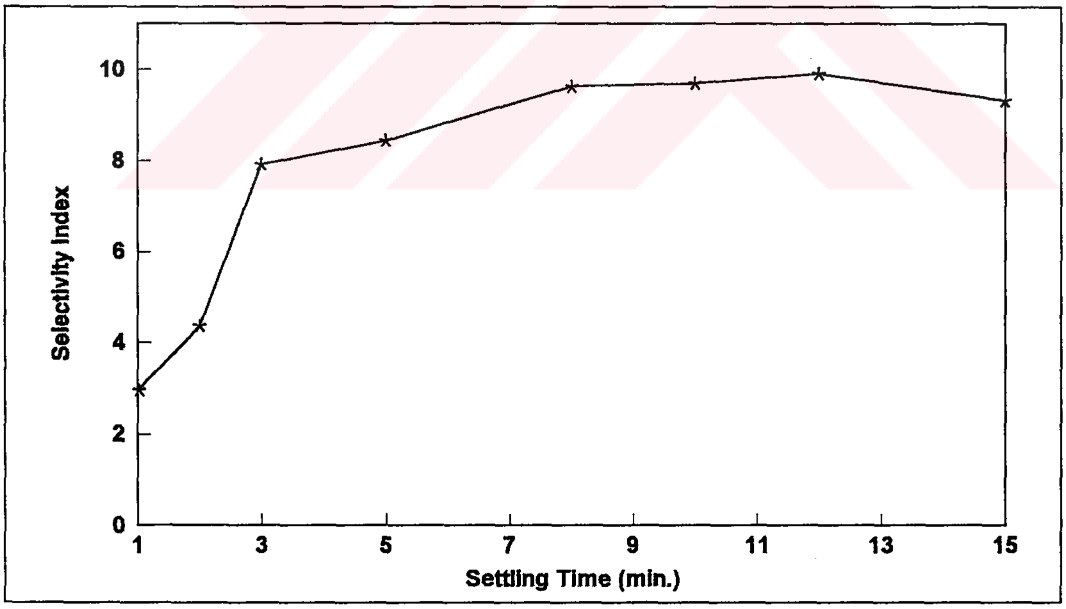

Figure 5.44. Selectivity Indices for Chromite-Serpentine Separations with Different Settling Times

studied the responses of chromite, olivine and serpentine to fluoride activation in soap and amine flotation. Hydrofluoric acid was shown to have good selective properties in amine flotation. In contrast, sodium fluosilicate has a detrimental effect on both soap and amine flotation. In another study, Na_2SiF_6 was found the most effective serpentine depressant (Kurochkin et al., 1968).

Figures 5.45 to 5.50 show the effects of NaF, Na_2SiF_6 and Na_2SiO_3 on selective shear flocculation of chromite, respectively.

No significant change on the grade of settled material was obtained by using various concentrations of NaF. The effect of Na_2SiF_6, is detrimental; the selectivity decreases with increasing Na_2SiF_6 concentration. The grade of the settled material decreased from about 43% Cr_2O_3 to 38-39% Cr_2O_3 after Na_2SiF_6 addition. The effect of Na_2SiO_3 is also similar to that of Na_2SiF_6 to a lesser extent, reducing the grade from 44.60 % Cr_2O_3 to as low 42.76 % Cr_2O_3 by using of 80 mg/l Na_2SiO_3.

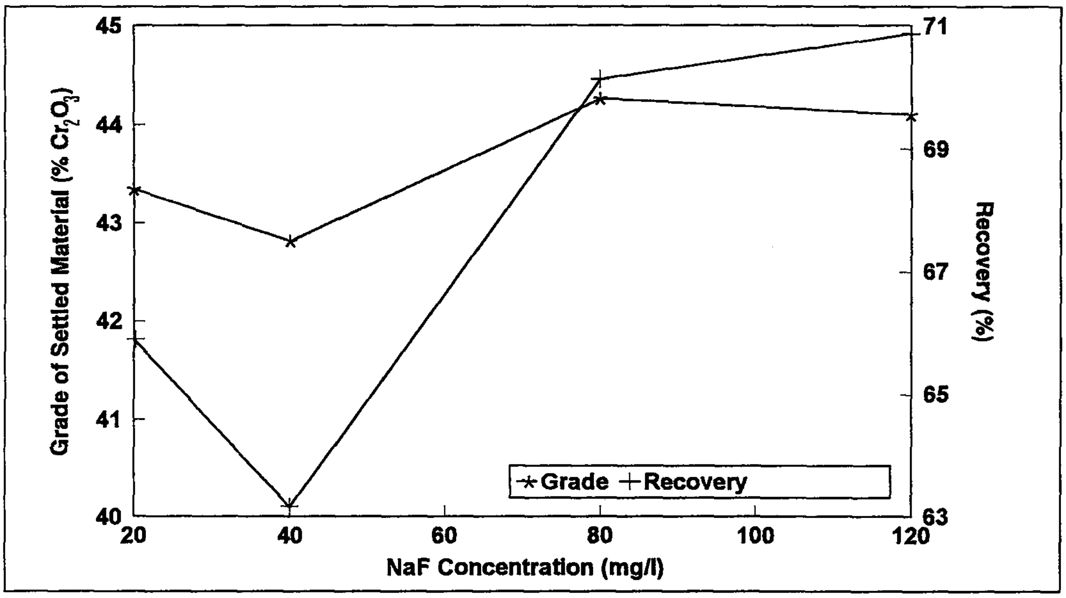

Figure 5.45. Effect of NaF Concentration on Selective Shear Flocculation of Chromite (pH: 3.0; Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 630 rpm; Flocculation Time: 60 min.; Settling Time: 5 min.)

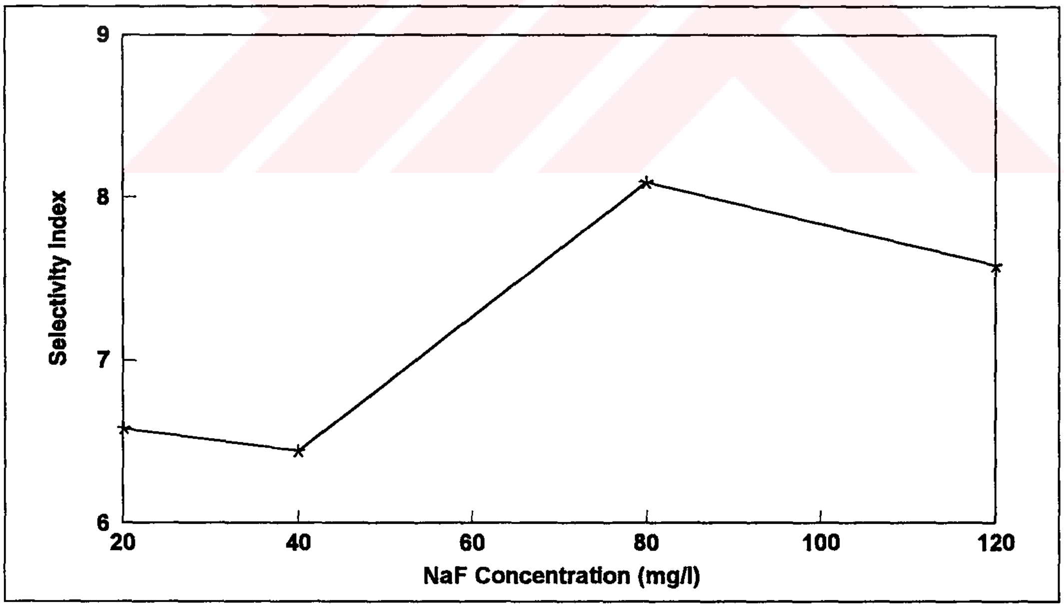

Figure 5.46. Variation of Selectivity Index with NaF Concentration

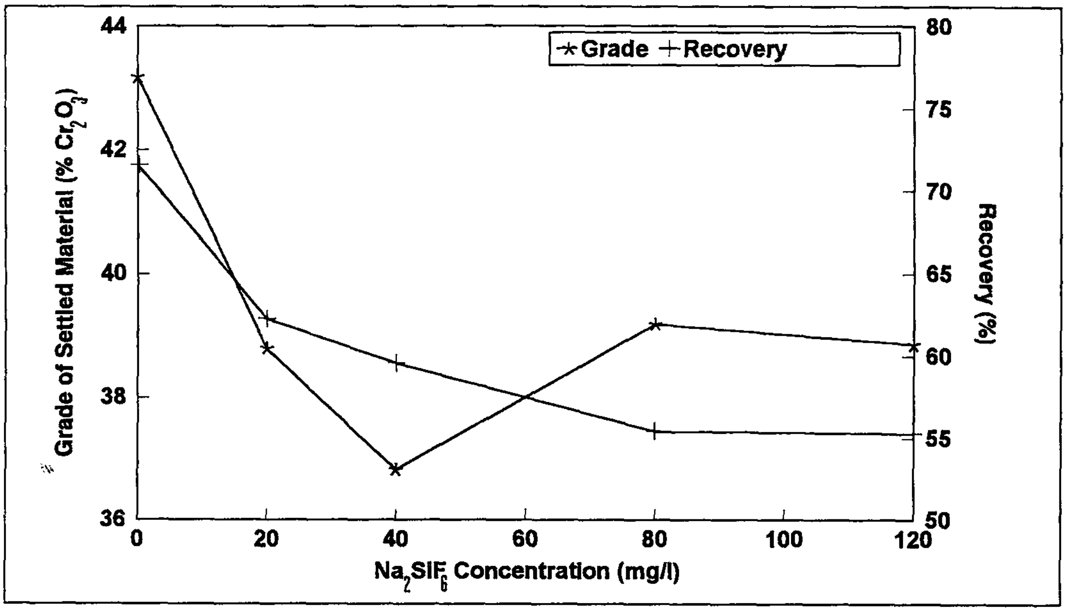

Figure 5.47. Effect of Na_2SiF_6 Concentration on Selective Shear Flocculation of Chromite (pH: 3.5; Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 630 rpm; Flocculation Time: 60 min.; Settling Time: 5 min.)

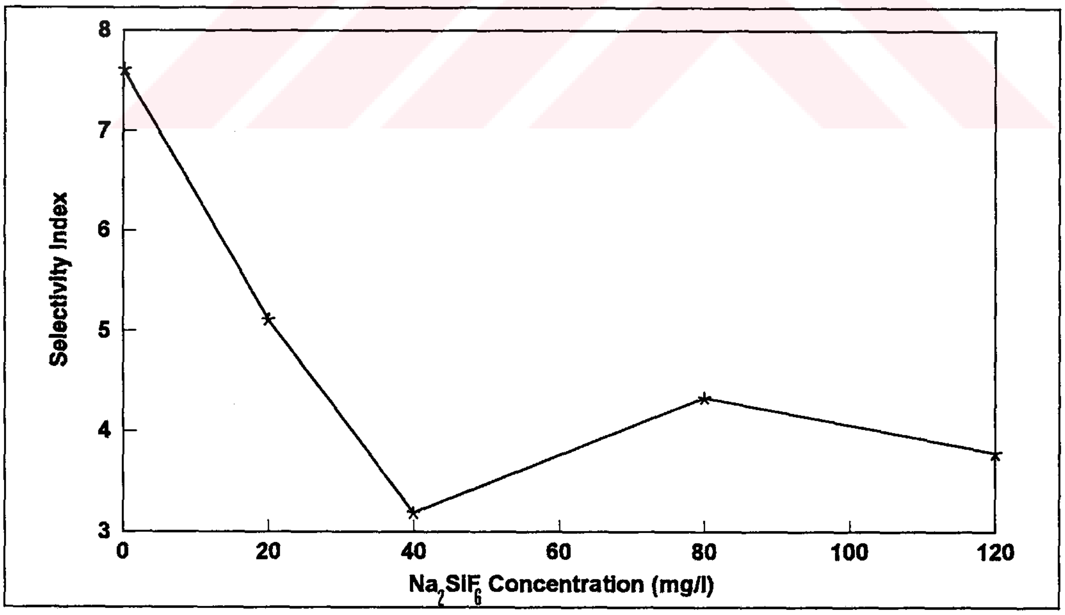

Figure 5.48. Variation of Selectivity Index with Na_2SiF_6 Concentration

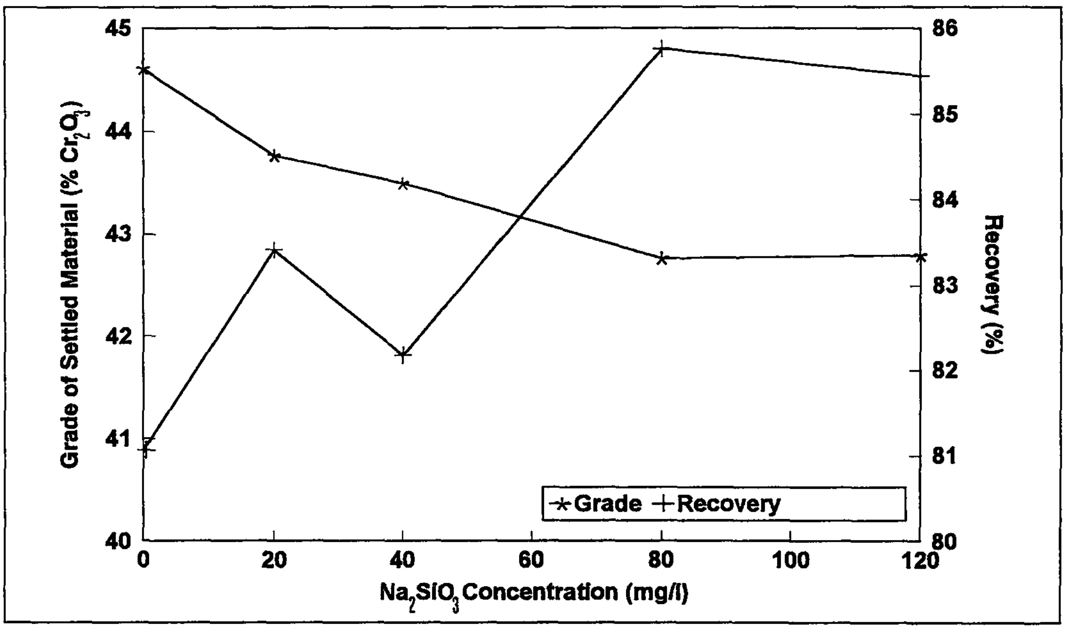

Figure 5.49. Effect of Na_2SiO_3 Concentration on Selective Shear Flocculation of Chromite (pH: 3.5; Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 580 rpm; Flocculation Time: 60 min.; Settling Time: 5 min.)

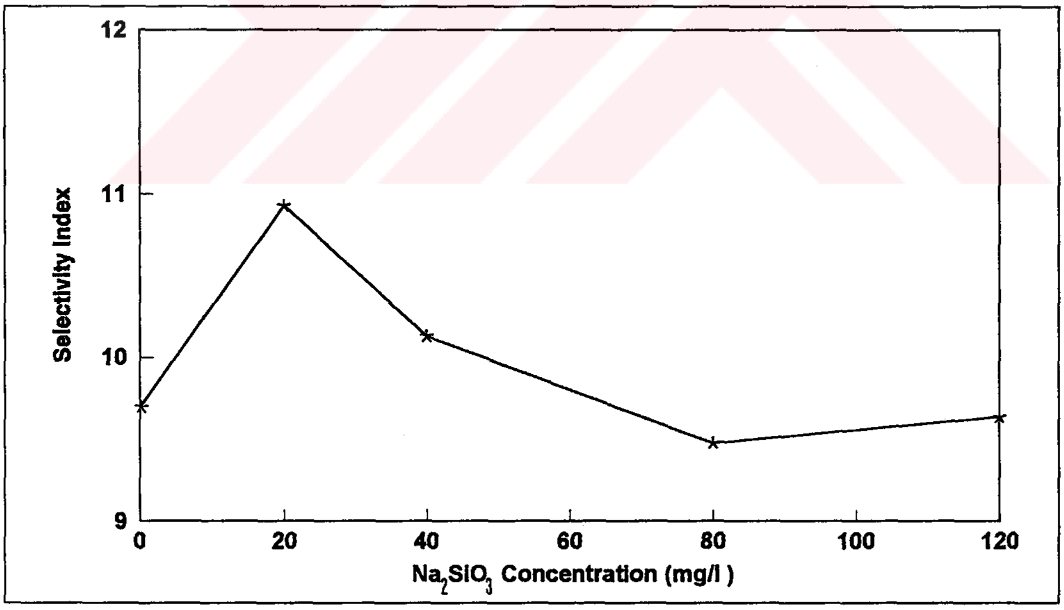

Figure 5.50. Variation of Selectivity Index with Na_2SiO_3 Concentration

5.4.8. Effect of Feed Grade on Selective Shear Flocculation of Chromite

The results of selective shear flocculation experiments carried out with mixtures of different chromite-serpentine ratios (i.e. different feed grades) are shown in Figure 5.51 and 5.52.

The results show that feed grade is very important for the success of flocculation selectivity.Almost no separation takes place with the material of 1/3 chromite / serpentine ratio. A 16.43% Cr_2O_3 concentrate can be obtained from a mixture assaying 14.42%. The very low selectivity index value of 1.46 indicates that there is almost no separation.

The results with a higher chromite / serpentine ratio (1/2) is better. A concentrate containing 27.81% Cr_2O_3 could be obtained from a 19.55% Cr_2O_3 mixture with a recovery of 67.82%. The selectivity index for this separation is 3.54.

The seperation efficiency with higher grade (29.47% and 37.19% Cr_2O_3) mixtures was higher than that obtained with 14.42% Cr_2O_3 and 19.55% Cr_2O_3 mixtures. The concentrates obtained from these materials assayed 44.60% Cr_2O_3 and 47.60% Cr_2O_3 with high recoveries of 81.06% and 85.86%, respectively. The selectivity index for the separation of 29.47% Cr_2O_3 material was 9.70 and that for the separation of 37.19% Cr_2O_3 material was 19.02.

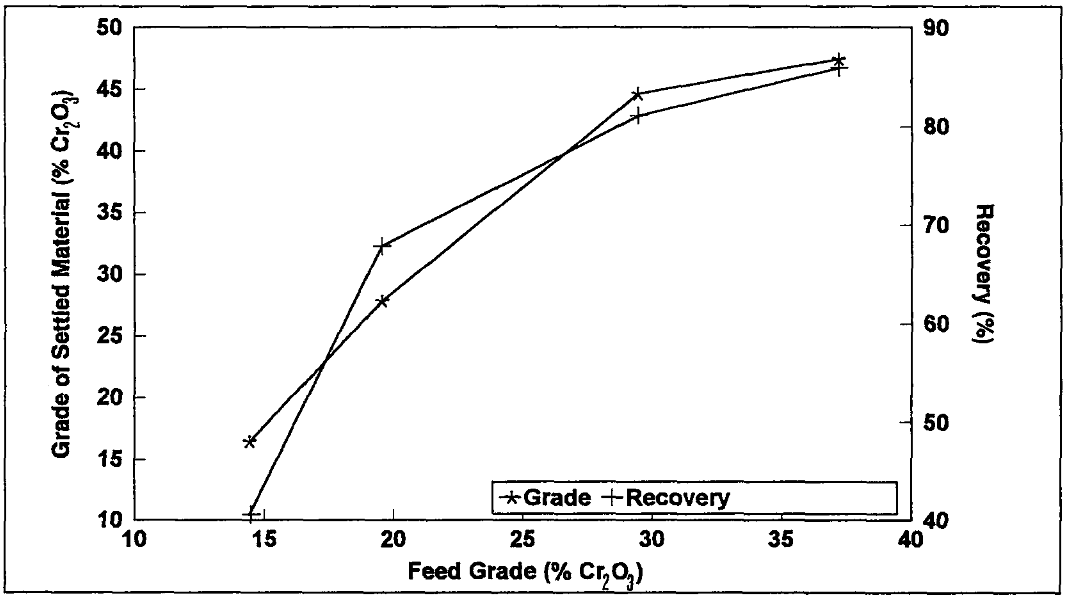

Figure 5.51. Effect of Feed Grade on Selective Shear Flocculation of Chromite (pH: 3.5; Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 580 rpm; Flocculation Time: 60 min; Settling Time: 10 min.)

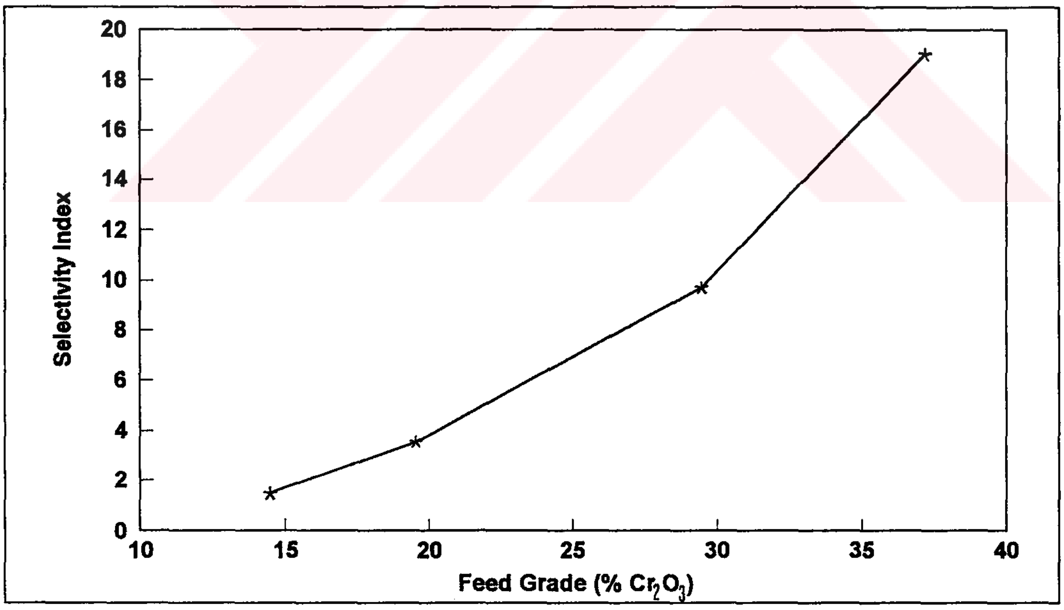

Figure 5.52. Selectivity Indices for Chromite-Serpentine Separations with Different Grade Feed Material

The results show that selective shear flocculation of chromite is sucessful only when the amount of chromite in the mixture is equal to or larger than the serpentine amount. It could be suggested that the reason is due to the optimizing of factors made at 1-1 chromite - serpentine ratio and also due to magnesium ions released from the serpentine. This release inhibits the collector adsorption on chromite surface. Decreasing number of chromite particles per unit volume reduces the number of collisions between two chromite particles. This is also probably why the selective flocculation is difficult with the mixtures containing low proportions of chromite.

CHAPTER VI

CONCLUSIONS

1. Chromite has i.e.p at pH 5.2. Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} ions shifted the i.e.p. in the direction of their corresponding oxides.

2. The adsorption of sodium oleate shifts the i.e.p of chromite to pH 3.1-3.8 depending on the collector concentration.

3. The i.e.p of chromite shifts to pH 9-9.5 in the presence of dodecyl amine acetate depending on collector concentration.

4. Serpentine has i.e.p at pH 8.7. Adsorption of Mg^{2+} ions shifted the i.e.p. to pH 11.5. Fe^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} additions did not change this point.

5. The adsorption of sodium oleate and dodecyl amine acetate shift the i.e.p of serpentine to pH 5.5-6.5 and 11.5-12, respectively depending on collector concentration.

6. Chromite has a contact angle 17.88° at pH 11.0 in double distilled water. Conditioning the sample in 30 mg/l sodium oleate at pH 9.0 increased the contact angle to 59.11^0. The maximum contact angle obtained with 20 mg/l dodecyl amine acetate is 69.49^0 at pH 10.0.

7. Serpentine has a contact angle 67.69^0 at pH 9.0 in double distilled water. Conditioning the sample in 30 mg/l sodium oleate at pH 8.0 increased the contact angle to 86.77^0. The maximum contact angle obtained with 50 mg/l dodecyl amine acetate at pH 9.0 is 81.83^0.

8. Collector adsorption is necessary for shear flocculation of chromite. Zeta potential is the most important parameter affecting the extent of shear flocculation. The most extensive aggregation takes place at pH values where the chromite has lowest zeta potential.

9. Collector concentration, stirrer speed, flocculation time and suspension concentration are the other factors affecting the degree of shear flocculation of chromite.

10. The optimum conditions for shear flocculation of chromite with sodium oleate were found as follows: pH: 3.0, collector amount : 30 mg/l, stirrer speed: 630 rpm, flocculation time: 30 minutes. The stirring of the suspension under these

conditions increased the amount of settled material from 11.3% to 87.40% and turbidity drop was 88.40%.

11. The optimum conditions for shear flocculation of chromite with dodecyl amine acetate are as follows: pH: 9.0, collector concentration: 20 mg/l, stirrer speed: 580 rpm, flocculation time: 30 minutes. The experiments carried out under these conditions increased the amount of settled material from 11.3% to 86.92% and turbidity drop was 90.99%.

12. Hydrophobization of serpentine particles by collector adsorption is the key for their shear flocculation. Most apparent aggregation is obtained when electrokinetic mobilities of particles are minimum although shear flocculation is possible over a wider pH range compared to chromite.

13. Collector concentration, stirrer speed, flocculation time and solid concentration also affected the extent of shear flocculation of serpentine.

14. The optimum conditions for shear flocculation of serpentine with sodium oleate were found as follows: pH: 6.0, collector concentration: 30 mg/l, stirrer speed: 360 rpm, flocculation time: 20 minutes. Under these conditions, the amount of settled material increased from 8.63% to 92.06% and the turbidity drop was 93.67%.

15. The optimum conditions for shear flocculation of serpentine with dodecyl amine acetate are as follows: pH: 11.5, collector concentration: 50 mg/l, stirrer speed: 360 rpm, flocculation time: 10 minutes. The amount of settled material and turbidity drop were 91.30% and 90.03%, respectively.

16. The separation of chromite from serpentine by selective shear flocculation yielded a concentrate assaying 44.60% Cr_2O_3 with 81.06% recovery from a chromite-serpentine mixture containing 29.47% Cr_2O_3. Selectivity index of this separation was 9.70.

17. Further research in this field could be subjected to shear flocculation of coarser size materials, effect of shear flocculation on the flotation rate of particles and improving selectivity between chromite and serpentine when the amount of chromite in the mixture is lower than that of serpentine.

REFERENCES

Abido, A.M., 1971. "Fluoride Activation in the Flotation of Chromite", J. Applied Chem. Biotech., 21, pp.19-21.

Adamson, A.W., 1967. Physical Chemistry of Surfaces, John Wiley and Sons Inc., pp.210-262.

Allen, T., 1974. Particle Size Measurement, Chapman and Hall, London.

Atalay, M.Ü., 1986. " Surface Properties of Chromite and Concentration of Chromite Gravity Tailings", Ph. D. Thesis, METU Mining Eng. Dept., Ankara, Turkey.

Bartell, F.E., and Osterhoff, H.J., 1928. "Colloid Symposium Monograph", The Chemistry Cataloque Co., New York, p. 113.

Bilgen, S., 1992. "Shear Flocculation of Fine Cassiterite", Ph. D. Thesis, Cornwall School of Mines, England.

Bolandakhtari, F., 1993. "Selective Flocculation of Chromite", M. Sc. Thesis, METU Mining Eng. Dept., Ankara, Turkey.

Buckton, G., 1990. "Contact Angle, Adsorption and Wettability-A Review with respect to Powders", Powder Technology, 61, pp. 237-249.

Bulatovic, S.M. and Salter, R.S., 1989, "High Intensity Conditioning-A New Approach to Improving Flotation of Mineral Slimes", Proceedings of Int. Symp. on Processing of Complex Ores, ed. Dobby, G.S., and Rao, S.R., pp.169-181.

Butler, J.N., 1964. Ionic Equilibrium, Addition Wesley Pub.Co., p.287.

Claessen, P.M., Blom, C.E., Herder, P.C., and Ninham, W.N., 1986. "Interactions Between Water-Stable Hydrophobic Langmuir-Blodgett Monolayers on Mica", Journal of Colloid and Interface Science, Vol.114, No 1, pp.234-242.

Clesceri, L.S., Greenberg,, A.E. and Trussell, R.R., 1989. Standart Methods for the Examination of Water and Wastewater, 17th edition, American Public Health Association, pp.2.11-2.16.

Cornelius, S.H., 1959. Dana's Manual of Mineralogy, John Wiley and Sons Inc., London, pp.310-311.

Crowl, V.T., and Wooldridge, W.D.S., 1967. Wetting, SCI Monograph, No.25, p.200.

De Bruyn, P.L., and Agar, G.E., 1962. "Surface Chemistry and Flotation, Froth Flotation-50th Anniversary Volume, AIME, New York, pp. 91-138.

Dippenaar, A-, 1985. "Shear Flocculation of Fines for Improved Flotation", MINTEK Report No. M230, South Africa.

Eitel, W., 1954. Physical Chemistry of Silicates, University of Chicago Press, Chicago, p. 379.

Fuerstenau, D.W., Chander, S., and Abouzeid, A.M., 1978. "The Recovery of Fine Particles by Physical Separation Methods", Beneficiation of Mineral Fines: Problems and Research Needs, ed. Somasundaran, P., and Arbiter, N., Nat. Sci. Foundation Workshop Report, pp. 3-59.

Gaudin, A.M., and Sun, S.C., 1946. "Correlation Between Mineral Behaviour in Cataphoresis and in Flotation", AIME Trans., Vol. 169, pp. 91-138.

Gaudin, A.M., 1930. "Selectivity Index; A Yardstick of the Segregation Accomplished by Concentration Operations", Trans. AIME, 87, pp. 483-487.

Glembotskii, V.A., Klassen, V.I., and Plaksin, I.N., 1972. Flotation, Primary Sources, New York, pp. 27-31.

Goldberger, W.M., 1973. "An Analysis of Technology for Improved Beneficiation of Ulrafine Mineral Particle Systems", Proceedings of Annual General Meeting of Can. Inst. Mining, Vancouver.

Grahame, D.C., 1947. "The Electrical Double Layer and the Theory of Electrocapillarity", Chem Reviews, 41, pp. 441-501.

Hunt, D.T.E., and Wilson, A.L., 1986. The Chemical Analysis of Water, 2nd edition, Royal Society of Chemistry, pp. 500-502.

Israelachvili, J., 1987. "Solvation Forces and Liquid Structure as Probed by Direct Force Measurements", Acc. Chem. Res., 20, pp. 415-421.

Iwasaki, I., Cooke, S.R.B., and Colombo, A.F., 1960. "Flotation Characteristics of Goethite", US Bureau of Mines, RI 5593.

Jarrett, R.G., and Warren, L.J., 1977. "Shear Flocculation in Mixtures of Scheelite and Garnet", Proc. Australas. Inst. Min. Metall., No. 262, pp. 57-65.

Koh, P.T.L., and Warren, L.J., 1980. "A Pilot Plant Test of the Shear Flocculation of Ultrafine Scheelite", Proceedings of 8th Australian Chemical Eng. Conference, Melbourne, pp. 90-94.

Koh, P.T.L., Andrews, J.R.T., and Uhlherr, P.H.T., 1986. "Floc-Size Distribution of Scheelite Treated by Shear Flocculation", Int. J. of Mineral Processing, 17, pp. 45-65.

Kolthoff, I.M., and Sandell, E.B., 1952. "Textbook of Quantitative Inorganic Analysis", The Macmillan Company, London, pp. 649-652.

Kolthoff, I.M., Sandell, E.B., Meehan, E.J., and Bruckenstein, S., 1971. "Quantitative Chemical Analysis", 4th Edition, The Macmillan Company, London, pp. 992-994.

Kurochkin, M.G., Potapenko, V.E., and Kvaskov, A.P., 1968. "Flotation Properties of Chromite and Serpentine", Izv. Vyssh. Ucheb. Zaved., Gorn. Zh., 11(7), pp. 165-167.

Latimer, V.M., 1952. Oxidation Potentials, Prentice Hall Inc., New York.

Lauer, O., 1966. Grain Size Measurements on Commercial Powders, Alpine A.G.

Leja, L., 1982. Surface Chemistry of Froth Flotation, Plenum Press, pp. 437-479.

Levich, V.G., 1962. Physicochemical Hydrodynamics, Prentice-Hall, Englewood Cliffs, N.J. p. 213.

Li, C., and Fuerstenau, D.W., 1987. "The Effects of the Adsorption of Sodium Dodecyl Sulphate on the Stability of Stirred Suspensions of Hematite Fines", Process Techn. Poc., 4 (Flocculation Biotechnol. Sep. Syst) pp. 695-706.

Lu, S., Li, G., 1984. J. Wuhan Iron and Stell Univ. pp. 1-8.

Lu, S., and Dai, Z., 1988. "Separation of Ultrafine Mineral Particles by Hydrophobic Aggregation Methods", Production and Processing of Fine Particles, ed. Plumpton, pp. 317-327.

Lu, S., Song, S., and Dai, Z. 1988. "The Hydrophobic and Magnetic Combined Aggregation of Paramagnetic Minerals- A New Way of Fine Particles

Separation", Proceedings of XVI. Int. Min. Process. Congress, ed. Forssberg; E., pp. 999-1009.

Lu, S., and Song, S.,, 1991. "Hydrophobic Interaction in Flocculation and Flotation. I. Hydrophobic Flocculation of Fine Mineral Particles in Aqueous Solutions", Colloids and Surfaces, 57(1-2), pp. 49-60.

Nemethy, G., and Scherage, H.A., 1962. J. of Phys. Chem., 66, 1773.

Özbayoğlu, G., 1977. "Determination of Flotation Characteristics of Several Turkish Bituminous Coal Seams in Zonguldak Basin", Ph.D. Thesis, METU Mining Eng. Dept., Ankara, Turkey.

Palmer, B.R., Fuerstenau, M.C., and Aplan, F.F., 1975. "Mechanism Involded in the Flotation of Oxides and Silicates with Anionic Collectors", Trans. AIME, 258, pp. 261-263.

Parks, A.G., 1965. "The Isoelectric Points of Solid Oxides,, Solid Hydroxides and Aqueous Hydroxo-Complex Systems", Chemical Review, pp. 177-198.

Pashley, R.M., and Israelachvili, J.N., 1981. "A Comparison of Surface Forces and Interfacial Properties of Mica in Purified Surfactant Solutions", Colloids and Surfaces, 2, p. 169.

Raju, G.B., Subrahmanyam, T.V., Sun, Z., and Forsling, W., 1991. "Shear Flocculation of Quartz", Int. J. of Min. Process., 32, pp. 283-294.

Raghavan, P., Chandrasekhar, S., Sivam, C., Lalithambika, M., and Damodaran, A.D., 1992. "Removal of Ulrafiine Graphite Impurities from China Clay by Floc-Flotation", Int. J. of Min. Process., 36, pp. 51-61.

Rodier, J., 1957. Analysis of Water, John Wiley and Sons, Inc., New York, pp. 53-63.

Samygin, V.D., Barskii, A.A., and Angelova, S.M., 1968. "Mechanism of Mutual Flocculation of Particles Differing in Size", Colloid J., 30, pp. 435-439.

Sastry, K.V.S., 1978. "Flotation of Mineral Fines", Beneficiation of Mineral Fines: Problems and Research Needs, Nat. Sci. Found Workshop Report, ed. Somasundaran, P., and Arbiter, N., pp. 283-290.

Sennett, P., and Young, R.H., 1978. "Current Problems in Beneficiation of Kaolin Clay", Beneficiation of Mineral Fines: Problems and Research Needs, Nat. Sci. Found. Workshop Report, ed. Somasundaran, P., and Arbiter, N., pp. 115-133.

Shaw, D.J., 1970. Introduction to Colloid and Surface Chemistry, 2nd edition, Butterworths, pp. 133-166.

Sivamohan, R., 1988. “Influence of Common Variables on the Shear Flocculation of, and Oleate Adsorption-Abstraction by Very Fine Fluorite and Scheelite”, Production and Processing of Fine Particles, ed. Plumpton, pp. 337-351.

Sivamohan, R., and Cases, J.M.,1990. “Dependence of Shear Flocculation on Surface Coverege and Zeta Potential”, Int. J. of Min. Process, 28, pp. 161-172.

Skoog, D.A., and West, D.M., 1971. Principles of Instrumental Analysis, Holt, Rinehart and Winston, Inc., pp. 242-247.

Skvarla, J., and Kmet, S., 1991. “Influence of Wettability on the Aggregation of Fine Minerals”, Int. J. of Min. Process., 32, pp. 111-131.

Somasundaran, P., 1976. “Fine Particles Treatment”, Research Needs in Mineral Processing, Nat. Sci. Found. Workshop Report, ed. Somasundaran, P., and Fuerstenau, D.W.

Somasundaran, P., 1978. "Principles of Selective Aggregation", Beneficiation of Mineral Fines: Problems and Research Needs, Nat. Sci. Found. Workshop Report, ed. Somasundaran, P., and Arbiter N., pp. 183-196.

Song, S., and Lu, S., 1990. "The Hydrophobic Aggregation Flotation of Rutile Particles", Advances in Fine Particles Processing, ed. Hanna, J., and Attia, A., pp. 279-283.

Stern, O., 1924. "The Theory of the Electrical Double Layer", Z. Electrochem., 30, pp. 508-516.

Stratton-Crawley, R., 1978. "Oil Flotation: Two Liquid Flotation Techniques", Beneficiation of Mineral Fines: Problems and Research Needs, Nat. Sci. Found. Workshop Report, ed. Somasundaran, P., and Arbiter, N., pp. 115-133.

Subrahmanyam, T.V., Sun, Z., Forssberg, K.S.E., and Forsling, W., 1990a; "Shear Flocculation of Galena and Synthetic PbS", Advances in Fine Particles Processing, ed. Hanna, J. and Attia, A., pp. 279-283.

Subrahmanyam, T.V., Sun Z., Forssberg, K.S.E., and Forsling, W., 1990b, "Variables in the Shear Flocculation of Galena", Sulphide Deposits, ed. Gray, P.M.J., Inst. of. Min. and Metallurgy, London, pp. 223-231.

Subrahmanyam, T.V., and Forsberg, K.S.E., 1990. "Fine Particles Processing : Shear Flocculation and Carrier Flotation-A Review", Int. J. of Min. Process., 30, pp. 265-288.

Tarjan, G., 1986. Mineral Processing, Akademiai Kiado, Budapest, Vol. 2, p. 199.

Tyler, P.M., and Waggman, W.H., 1953. "Report on Possible Utilization of Phosphate Rock Slimes", National Academy of Science, MMAB Report, 45-C.

Wang, Q., and Heiskanen, K., 1992. "Selective Hydrophobic Flocculation in Apatite-Hematite System by Sodium Oleate", Minerals Engineering, 5(3-5), pp. 493-501.

Warren, L.J., 1975a. "Shear Flocculation of Ultrafine Scheelite in Sodium Oleate Solutions", J. of Coll. and Interface Science, 50, pp. 307-318.

Warren, L.J., 1975b. "Slime Coating and Shear Flocculation in the Scheelite-Sodium Oleate System", Trans of Ins. of Min. and Metallurgy, 84, Section C, pp. 99-104.

Warren, L.J., 1981. "Shear Flocculation", Chemtech, March, pp. 180-185.

Warren, L.J., 1982. "Flocculation of Stirred Suspensions of Cassiterite and Tourmaline", Colloids and Surfaces, 5, pp. 301-319.

Wiese, G.R., and Healy, T.W., 1975. "Adsorption of Al^{3+} at the TiO_2-H_2O Interface", J. of Colloid and Interface Science, 51, No.3, pp. 434-442.

Wills, B.A., 1980. Mineral Processing Technology, 2nd Edition, Pergamon Press, Oxford, pp. 401-402.

Yang, C.D., 1978. "Flotation in Systems with Controlled Dispersion- Carrier Flotation etc.", Beneficiation of Mineral Fines: Problems and Research Needs, Nat. Sci. Found Workshop Report, pp. 259-308.

Yarui, S., and Daxin, S. 1986. "Study on the Shear Flocculation Flotation of Ultrafine Wolframite", Nonferrous Met. Chin. Soc. Met., 38, pp. 40-45.

Yongping, H., and Mulong, Y., 1988. "Controlled Dispersion-Shear Flocculation of Ultrafine Apatite from Rhodochrosite", Production and Processing of Fine Particles, ed. Plumpton, pp. 352-362.

Zettlemayer, A.C., 1969. Hydrophobic Surfaces, Academic Press, New York.

APPENDIX

APPENDIX A

TURBIDITY DATA FOR SHEAR FLOCCULATION OF CHROMITE AND SERPENTINE

Table Al. Turbidity Data for Coagulation of Chromite at Various pH Values (No Collector; Stirrer Speed: 630 rpm; Stirring Time: 30 min.)

pH	T_i (NTU)	T_f (NTU)	pH	T_i (NTU)	T_f (NTU)
2.0	2168	2158	7.0	2098	1816
3.0	2116	2072	9.0	2082	1810
5.0	2100	1782	11.0	2130	2128
6.0	2164	1788			

APPENDIX A

Table A2. Turbidity Data for Shear Flocculation of Chromite Fines at Different pH Values (Collector: 30 mg/l Sodium Oleate; Stirrer Speed: 630 rpm; Flocc. Time: 60 min.)

pH	T_i (NTU)	T_f (NTU)	pH	T_i (NTU)	T_f (NTU)
2.3	2118	961	5.0	2088	1780
3.0	2094	170	6.0	2068	1910
3.5	2132	181.1	7.0	2120	2060
4.0	2102	1086	9.0	2174	2174
4.5	2100	1612	11.0	2172	2284

APPENDIX A

Table A3. Turbidity Data for Flocculation Behaviour of Chromite Fines at Different pH Values (Collector: 20 mg/l Dodecyl Amine Acetate; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

pH	T_i (NTU)	T_f (NTU)	pH	T_i (NTU)	T_f (NTU)
3.0	2156	1582	8.5	2106	247.4
4.0	2166	831	9.0	2125	124.3
5.0	2126	662	10.0	2120	984
6.0	2180	671	11.0	2162	1168
7.0	2160	609	12.0	2110	2058
8.0	2158	363.9			

Table A4. Turbidity Data for Shear Flocculation of Chromite in Various Sodium Oleate Concentrations (pH: 3.0; Stirrer Speed: 630 rpm; Flocc. Time: 60 min.)

Sodium Oleate Conc. (mg/l)	T_i(NTU)	T_f (NTU)	Sodium Oleate Conc. (mg/l)	T_i (NTU)	T_f (NTU)
0	2122	1894	65	2094	132
10	2102	644	90	2096	243.2
30	2168	176	105	2100	98.4
55	2152	89.1			

Table A5. Turbidity Data for Shear Flocculation of Chromite in Various Dodecyl Amine Acetate Concentrations (pH: 9.0; Stirrer Speed: 630 rpm; Floc. Time: 30 min.)

D. Amine Acetate Conc. (mg/l)	T_i(NTU)	T_f(NTU)	D.Amine Acetate Conc. (mg/l)	T_i(NTU)	T_f(NTU)
0	2082	1810	50	2160	91
10	2146	342.9	75	2176	96.9
20	2125	124.3	100	2138	95.6
30	2110	164.6			

APPENDIX A

Table A6: Turbidity Data for Shear Flocculation of Chromite Fines as a Function of Flocculation Time with Sodium Oleate (pH: 3.0; Collector : 30 mg/l; Stirrer Speed: 630 rpm)

Flocc. Time (min.)	T_i (NTU)	T_f (NTU)	Flocc. Time (min.)	T_i (NTU)	T_f (NTU)
10	2162	463.8	60	2168	176
20	2098	378.8	90	2172	127.4
30	2124	191.1	120	2100	182.8
45	2002	178.2			

Tablo A7: Turbidity Data for Shear Flocculation of Chromite Fines as a Function of Flocculation Time with Dodecyl Amine Acetate (pH:9.0 ; Collector: 20 mg/l ; Stirrer Speed: 630 rpm)

Flocc. Time (min.)	T_i (NTU)	T_f (NTU)	Flocc. Time (min.)	T_i (NTU)	T_f (NTU)
10	2128	542	45	2142	239.7
20	2064	207.9	60	2072	331.8
25	2122	104.4	90	2102	372.9
30	2125	124.3	120	2076	423
35	2976	147			

APPENDIX A

Table A8: Turbidity Data for Shear Flocculation of Chromite Fines as a Function of Stirrer Speed with Sodium Oleate (pH:3.0; Collector 30 mg/l; Flocculation Time:30 min.)

Stirrer Speed (rpm)	T_i (NTU)	T_f (NTU)	Stirrer Speed (rpm)	T_i (NTU)	T_f (NTU)
0	2100	1288	580	2138	226.9
140	2140	544	630	2124	191.1
360	2092	308.5	870	2134	204.9
490	2126	144.6	1200	-	-

Table A9. Turbidity Data for Shear Flocculation of Chromite Fines as a Function of Flocculation Time with Dodecyl Amine Acetate (pH: 9.0; Collector: 20 mg/l ; Flocc. Time: 30 min.)

Stirrer Speed (rpm)	T_i (NTU)	T_f (NTU)	Stirrer Speed (rpm)	T_i (NTU)	T_f (NTU)
0	2112	1384	580	2122	117.5
140	2142	683	630	2125	124.3
360	2058	213	870	2120	385.2
490	2110	187.1	1200	-	-

APPENDIX A

Table A10: Turbidity Data for Effect of Suspension Concentration on Shear Flocculation of Chromite with Sodium Oleate (pH: 3.0; Collector: 30 mg/l ; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

Solid Conc. (g/l)	T_i (NTU)	T_f (NTU)	Solid Conc. (g/l)	T_i (NTU)	T_f (NTU)
0.35	1175	255.3	1.4	3910	421
0.53	1774	296	2.1	6112	951
0.7	2124	191.1	3.5	9618	1116

Table A11: Turbidity Data for Effect of Suspension Concentration on Shear Flocculation of Chromite with Dodecyl Amine Acetate (pH: 9.0; Collector: 20 mg/l; Stirrer Speed: 630 rpm; Flocc. Time:30 min.)

Solid Conc. (g/l)	T_i (NTU)	T_f (NTU)	Solid Conc. (g/l)	T_i (NTU)	T_f (NTU)
0.35	1075	129.2	1.4	4128	248
0.53	1572	116.5	2.1	6100	483.9
0.7	2122	117.5	3.5	10500	946

APPENDIX A

Table A12. Turbidity Data for Coagulation of Serpentine at Different pH Values (No collector; Stirrer Speed: 360 rpm; Stirring Time: 20 min.)

pH	T_i (NTU)	T_f (NTU)	pH	T_i (NTU)	T_f (NTU)
3.0	741.5	734.5	8.0	750.5	733.5
4.0	760.5	751.5	9.0	760.5	605.5
5.0	750.0	743.5	10.0	711.0	585.0
6.0	739.5	743.0	11.0	721.0	581.5
7.0	747.5	745.5	12.0	737.0	634.0

Table A13. Turbidity Data for Shear Flocculation of Serpentine Fines at Different pH Values with Sodium Oleate (Collector: 30 mg/l; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

pH	T_i (NTU)	T_f (NTU)	pH	T_i (NTU)	T_f (NTU)
3.0	789.5	780.5	8.0	769.0	264.3
4.0	781.5	539.5	9.0	772.5	274.5
5.0	764.5	151.2	10.0	793.0	315.6
6.0	765.0	167.7	11.0	769.5	296.5
7.0	775.5	297.0	12.0	778.0	394.5

APPENDIX A

Table A14. Turbidity Data for Shear Flocculation of Serpentine Fines at Different pH Values with Dodecyl Amine Acetate (Collector: 30 mg/l; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

pH	T_i (NTU)	T_f (NTU)	pH	T_i (NTU)	T_f (NTU)
3.0	772.5	765.5	9.0	784.0	764.5
4.0	798.0	779.5	10.0	789.0	704.0
5.0	793.0	789.5	11.0	760.0	594.5
6.0	758.0	758.5	11.5	770.5	443.5
7.0	772.5	754.0	12.0	775.5	462.0
8.0	772.5	748.0	12.4	787.5	478.0

Table A15. Turbidity Data for Shear Flocculation of Serpentine in Various Sodium Oleate Concentrations (pH: 6.0; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

Sodium-Oleate Conc. (mg/l)	T_i (NTU)	T_f (NTU)	Sodium-Oleate Conc. (mg/l)	T_i (NTU)	T_f (NTU)
10	776.5	509.5	50	778.0	152.7
20	785.5	303.5	75	786.5	157.2
30	765.0	167.7	100	767.0	150.3

APPENDIX A

Table 16. Turbidity Data for Shear Flocculation of Serpentine in Various Dodecyl Amine Acetate Concentrations (pH: 11.5; Stirrer Speed: 630 rpm; Flocc. Time: 30 min.)

Sodium-Oleate Conc. (mg/l)	T_i (NTU)	T_f(NTU)	Sodium-Oleate Conc. (mg/l)	T_i (NTU)	T_f(NTU)
0	773.5	669.5	75	768.0	354.0
10	763.0	622.5	100	782.0	357.0
30	770.5	443.5	150	775.5	398.0
50	775.0	357.0			

Table A17. Turbidity Data for Effect of Flocculation Time on Shear Flocculation of Serpentine with Sodium Oleate (pH: 6.0; Collector:30 mg/l; Stirrer Speed: 630 rpm)

Floc.Time (min.)	T_i (NTU)	T_f(NTU)	Floc. Time (min.)	T_i (NTU)	T_f(NTU)
5	772.5	195.6	45	777.0	203.1
10	768.0	177.9	60	786.2	207.3
20	790.5	158.1	90	788.0	220.5
30	765.0	167.7			

Table A18. Turbidity Data for Effect of FlocculationTime on Shear Flocculation of Serpentine with Dodecyl Amine Acetate (pH: 11.5; Collector:50 mg/l; Stirrer Speed: 630 rpm)

Floc.Time (min.)	T_i (NTU)	T_f(NTU)	Floc. Time (min.)	T_i (NTU)	T_f(NTU)
5	767.5	238.8	45	759.5	580.5
10	772.0	313.2	60	764.5	620.0
15	782.0	335.0	90	775.5	628.0
20	775.5	349.0	120	763.0	649.0
30	775.0	357.0	-	-	-

Table19. Turbidity Data for Shear Flocculation of Serpentine Fines Stirred at Different Speeds with Sodium Oleate (pH: 6.0; Collector: 30 mg/l; Flocc. Time: 20 min.)

Floc.Time (min.)	T_i (NTU)	T_f(NTU)	Floc. Time (min.)	T_i (NTU)	T_f(NTU)
0	780.0	452.0	630	790.5	158.1
140	780.0	252.0	870	787.0	281.0
360	777.0	149.6	1200	-	-
490	775.5	184.4	-	-	-

APPENDIX A

Table A20. Turbidity Data for Shear Flocculation of Serpentine Fines Stirred at Different Speeds with Dodecyl Amine Acetate (pH: 11.5; Collector: 50 mg/l; Flocc. Time: 10 min.)

Stirrer Speed (rpm)	T_i (NTU)	T_f(NTU)	Stirrer Speed (rpm)	T_i (NTU)	T_f(NTU)
0	773.0	390.5	490	767.5	247.8
140	775.5	273.9	630	772.0	313.2
360	790.0	217.8	870	780.5	408.0

Table A21. Turbidity Data for Effect of Suspension Concentration on Shear Floccculation of Serpentine with Sodium Oleate (pH: 6.0; Collector: 30 mg/l; Stirrer Speed: 360 rpm; Flocc. Time: 30 min.)

Solid Conc. (g/l)	T_i (NTU)	T_f(NTU)	Solid Conc. (g/l)	T_i (NTU)	T_f(NTU)
0.35	357.5	183.5	1.4	1514.0	180.3
0.53	532.0	159.6	2.1	2214.0	201.6
0.7	777.5	149.6	3.5	2890.0	182.9

Table A22. Turbidity Data for Effect of Suspension Concentration on Shear Floccculation of Serpentine with Dodecyl Amine Acetate (pH: 11.5; Collector: 50 mg/l; Stirrer Speed: 360 rpm; Flocc. Time: 10 min.)

Solid Conc. (g/l)	T_i (NTU)	T_f(NTU)	Solid Conc. (g/l)	T_i (NTU)	T_f(NTU)
0.35	365.5	106.7	1.4	1572.0	225.3
0.53	536.5	179.3	2.1	2156.0	207.3
0.7	790.0	217.8	3.5	3062.0	305.2

CURRICULUM VITAE

Ünal Akdemir was born in Kayseri, Turkey in 1965. He completed primary and secondary school education in Kayseri and high school education in Ankara. He graduated from Mining Engineering Department of Middle East Technical University with the degree of B.Sc. in 1987. He was awarded the M.Sc. degree by the same department in 1990.

He worked as a research assistant in Mining Engineering Department of Middle East Technical University from 1988 to 1993. He has been working as a research assistant in Mining Engineering Department of Sivas Cumhuriyet University since 1993.