Surface Properties of New York Talc as a Function of pH, Polymer Adsorption and Electrolyte Concentration

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DOCTOR OF PHILOSOPHY

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Publications

The work performed during the course of this thesis resulted in the following peer reviewed publications:

Burdukova, E., J. S. Laskowski and D. J. Bradshaw (2006). "Rheological behaviour of talc suspensions as a function of pH and polymer dosage". Proc. 23rd Int. Minerals Processing Congress, Istanbul, Promed Advertising Agency.

Burdukova, E., D. J. Bradshaw and J. S. Laskowski (2006). "Effect of CMC and pH on the rheology of suspensions of isotropic and anisotropic minerals". Interfacial Phenomena in Fine Particle Technology - Proc. 6th UBC-McGill-UA Int. Symp., Montreal, Canada, MetSoc.

Burdukova, E., D. J. Bradshaw and J. S. Laskowski (2007). "Effect of CMC and pH on the rheology of suspensions of isotropic and anisotropic minerals." Canadian Metallurgical Quarterly **46**(3): 1 - 6.

Burdukova, E., M. Becker, D. J. Bradshaw and J. S. Laskowski (2007). "The presence of a negative charge on the basal planes of New York talc." Journal of Colloid and Interface Science **Submitted for Review**.

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SYNOPSIS

Talc is a common siliceous gangue mineral found in ore bodies beneficiated by flotation. Talc is a layered anisotropic mineral, with a mineral structure comprising of basal planes and edges. The basal planes of talc are considered completely neutral, while the edges of talc are thought to undergo a change from positive to negative at a highly acidic pH.

Talc is highly floatable, requiring polymeric depressants to be added to flotation pulps in order to prevent it from entering the concentrate and reducing its grade. Various polymers such as non-ionic guar gums and anionic Carboxymethyl cellulose (CMC) depressants are employed for this purpose. However, the industrial use of these reagents is still inefficient. One of the factors affecting the performance of these polymers as depressants is the water quality of the flotation medium, specifically the concentration and type of electrolyte present.

The objective of this thesis was to investigate of the surface properties and structure talc, and its effect on the adsorption mechanisms of different types of polymeric depressants in the presence of varying types of metal cations in solution in the context of mineral flotation.

The surface potential of talc was investigated using rheological, titration and electron microprobe analyses. It was found that the rheological behaviour of talc is inconsistent with the premise that the talc basal planes carry no electrical charge. Furthermore, potentiometric titration measurements showed that the point of zero charge of talc does not correspond to the electrophoretic isoelectric point of talc. The discrepancy was attributed to the unsuitability of zeta potential measurements for evaluation of anisotropic plate-like minerals.

An alternative surface charge distribution of talc was proposed, whereby the basal planes of talc carry a negative charge as a result of substitution of silicon ions in the tetrahedral layers of talc with aluminium ions of a lesser charge. This was supported by both ToF - SIMS and electron microprobe analyses. It was also proposed that the edges of talc undergo a change from positive to negative in an alkaline pH range.

The effect of talc surface charge distribution on the adsorption characteristics of polymeric depressants was investigated using rheological measurements. The effect of the presence of calcium and potassium cations on the surface charge distribution of talc and hence polymer adsorption was studied using surface specific ToF-SIMS measurements.

The adsorption of guar gum onto talc was found to take place by means of hydrogen/hydrophobic bonding and was independent of the surface charge of the mineral particles. The adsorption of guar gum was found to take place primarily on the basal planes of talc.

The adsorption of CMC onto talc was found to take place by means of electrostatic attraction to the positively charged talc edges. The adsorption onto the basal planes of talc was found to take place by means of electrostatic attraction as well as acid/base interaction with metal hydroxide species present on the talc surface.

The effect of calcium and potassium ions on the adsorption of CMC as a result of solution interaction between polymer molecules and ions was studied by examining the using ToF - SIMS measurements. It was found that the adsorption of CMC molecules onto talc is further promoted by the chemical interaction between the polymer and Ca^{+2} ions in the solution medium, which causes an increased amount of polymer coiling, thus promoting denser adsorption.

Table of Contents

List of Figures

List of Tables

Glossary

LIST OF TERMS

Anisotropic	– A mineral that contains multiple plains with varying surface charge distributions.
Apparent isoelectric point	– The isoelectric point obtained by means of an electrophoretic mobility measurement which does not directly correspond to the point of zero charge of the mineral.
Intrinsic viscosity	– The relative viscosity of a Newtonian solution at the concentration of solute approaching zero.
Isoelectric point	– The pH value at which the electrophoretic mobility of a mineral is zero
Isotropic	– A mineral that has a homogenous surface charge distribution
Point of zero charge	– The pH value at which the overall surface charge of a mineral is zero
Phyllosilicate	– Layered sheet silicate mineral
Rheology	– The study of flow and deformation of matter

LIST OF SYMBOLS

C – Molar Concentration (M)
e – Charge on an electron (F)
F – Faraday constant
κ – Reciprocal Debye length (m^{-1})
N – Avogadro's number
r_i – Ionic radius (m)
V_A – Attractive energy (kJ/mol)
V_E – Repulsive energy (kJ/mol)
z_i – Ion valency
τ – Shear Stress (Pa)
γ – Shear Rate (s^{-1})
η_C – Casson viscosity (Pa s)
τ_C – Casson yield stress (Pa)
ΔG_{ads} – Gibbs free energy (kJ/mol)
Γ_δ – Adsorption density (mol/m^2)
Ψ_δ – Stern Potential (mV)
ε_0 – Electric permittivity of space
ε_{bulk} – Dielectric constant of water
ε_{solid} – Dielectric constant of the solid
ϕ – Volumetric fraction
η – Intrinsic viscosity (cm^3/g)
η_0 – Viscosity of the medium (Pas)
η_{red} – Reduced viscosity (cm^3/g)
η_{rel} – Relative viscosity
k – Huggins coefficient
ζ – Electrokinetic potential (zeta potential)
τ – Average equilibrium retention time
τ_i – Average equilibrium retention time in the presence of an ion

ΔE	– Hydration Energy (kJ/mol)
R	– Ideal gas constant (kJ/mol K)
T	– Temperature (K)

LIST OF ABBREVIATIONS

AA	– Atomic Adsorption
BET	– Burnauer, Emmet, Teller
CMC	– Carboxymethyl Cellulose
DEP 267	– Depramin 267
DLVO	– Derjaguin, Landau, Verwey, Overbeek
i.e.p	– Isoelectric point
IS	– Ionic Strength
p.z.c	– Point of zero charge
SEM	– Scanning Electron Microscope
ToF - SIMS	– Time of Flight Secondary Ion Mass Spectroscopy
XRF	– X-ray Fluorescence

List of Electronic Appendicies

Appendix A - Microprobe Analysis of New York Talc

A1	Detailed Microprobe analysis of New York talc	D:\Appendix A\ Microprobe Analysis.xls
A2	Calculation procedure for the formula of New York talc	D:\Appendix A\ Calculation Procedure.pdf
A3	MATLAB code for the statistical analysis of the microprobe data	D:\Appendix A\Error Analysis.pdf

Appendix B - ToF – SIMS Analysis of New York Talc

B1	List of sample codes with corresponding conditions for the ToF - SIMS data	D:\Appendix B\Sample Codes.pdf
B2	ToF SIMS Images of talc particles with Low Resolution SEM Images	D:\Appendix B\Images**.png
B3	Raw ToF - SIMS analysis data	D:\Appendix B\ ToF - SIMS Analysis data.xls
B4	ToF - SIMS Ca – CMC Intensities Correlation Data	D:\Appendix B\ Ca-CMC Corrleation.xls
B5	ToF - SIMS CaOH – CMC Intensities Correlation Data	D:\Appendix B\ CaOH-CMC Corrleation.xls
B6	ToF - SIMS K – CMC Intensities Correlation Data	D:\Appendix B\ K-CMC Corrleation.xls

Appendix C - Rheological Data for suspensions of New York Talc

C1	Sample codes with corresponding conditions for rheological data	D:\Appendix C\Sample Codes.pdf
C2	Raw rheological data	D:\Appendix C\Raw Data*.xls
C3	Processed rheological data	D:\Appendix C\Processed Data*.png
C4	Error Analysis	D: \Appendix C\Error Analysis.xls

Appendix D - Analysis of Polymers

D1	Intrinsic viscosity analysis of guar gum	D:\Appendix D\CZD519 data.xls
D2	Intrinsic viscosity analysis of CMC	D:\Appendix D\DEP267 data.xls
D3	Summary of molecular weight distributions of CZD 519 and DEP 267	D:\Appendix D\Molecular Weight Distributions.pdf
D4	Size exclusion chromatography data for CZD 519	D:\AppendixD\CZD519 MW Data*.xls
D5	Size exclusion chromatography data for DEP 267	D:\AppendixD\DEP 267 MW Data*.xls

Appendix E - Miscellaneous Raw Experimental Data

E1	Potentiometric Titration Data	D:\Appendix E\Titration.xls
E2	Zeta Potential Measurement Data	D:\Appendix E\Zeta Potential.xls

1 Introduction

For over one hundred years, flotation has been an important process for recovering valuable minerals from ores. Flotation is a complex process that is dependent on both the mineral constituents of the feed material as well as the physical and chemical environment in which it takes place. The main challenge of flotation is to recover the maximum amount of valuable material out of ore, which occurs in small quantities (from a few percent to a few parts per million), whilst recovering the minimum amount of gangue which constitutes the remainder of the ore deposit.

Talc is a magnesium rich phyllosilicate mineral that occurs as a gangue component of many base metal sulfide ore deposits around the world, such as the Bushvelt Complex in South Africa and Birchtree ore body in Canada (Shcousstra and Kinloch 2000; Muinonien 2006) among others. These ores are generally beneficiated by means of the flotation process. Due to its natural floatability, talc readily enters the flotation concentrate, reducing the grade.

Furthermore, the geological formation of talc within the ore body is often such that it forms by means of mineral alteration of other siliceous gangue minerals such as pyroxene. This alteration process causes the formation of extensive talc rims around the non floatable gangue components, which renders them floatable by association (Becker et al. 2006).

In order to render talc and other associated gangue minerals non-floatable, polymeric depressants such as guar gum and carboxymethyl cellulose (CMC) are commonly utilised, particularly in the flotation of platinum group metals. Various studies have shown that the structural and chemical differences between guars and CMCs play significant roles in their effectiveness as depressants under different conditions. However, despite these differences, these polymers are often used interchangeably in industrial situations. A number of studies have been dedicated to the investigation of the mechanism of adsorption of these polymers onto talc (as well as other minerals), in order to increase the efficiency of their use in the flotation process.

Previous research has shown that one of the key factors in determining the adsorption characteristics of polymers onto minerals is the chemical composition of the water which forms the basis of flotation pulps. The quality of processed water is becoming a major issue for minerals processing operations around the world.

Water scarcity in arid and semi arid regions such as South Africa and Australia has forced mining operations to drastically cut down on the amount of fresh water consumed in their processes (Marr and Petrie 2002), which naturally leads to an increase in the recycle rate of process water. Regions with abundance of water are forced with stricter environmental constraints regarding their tailings discharge, and are similarly forced to reduce their water usage. As a result of both of these effects, the water used in the flotation processes contains a much higher concentration of inorganic metal salts, such as calcium, sodium and potassium.

The presence of these ions in flotation systems has been shown to have a strong effect on both the surface properties of minerals in flotation systems (such as hydrophbocity) and the interactions between minerals and flotation reagents (such as polymeric depressants). This thesis addresses the interactions between minerals such as talc, polymeric depressants and metal cations in solution, which is schematically represented in Figure 1.1.

1.1 OVERALL OBJECTIVE

To investigate the surface properties and structure of talc, and its effect on the adsorption mechanisms of different types of polymeric depressants in the presence of selected metal cations in solution in the context of mineral flotation.

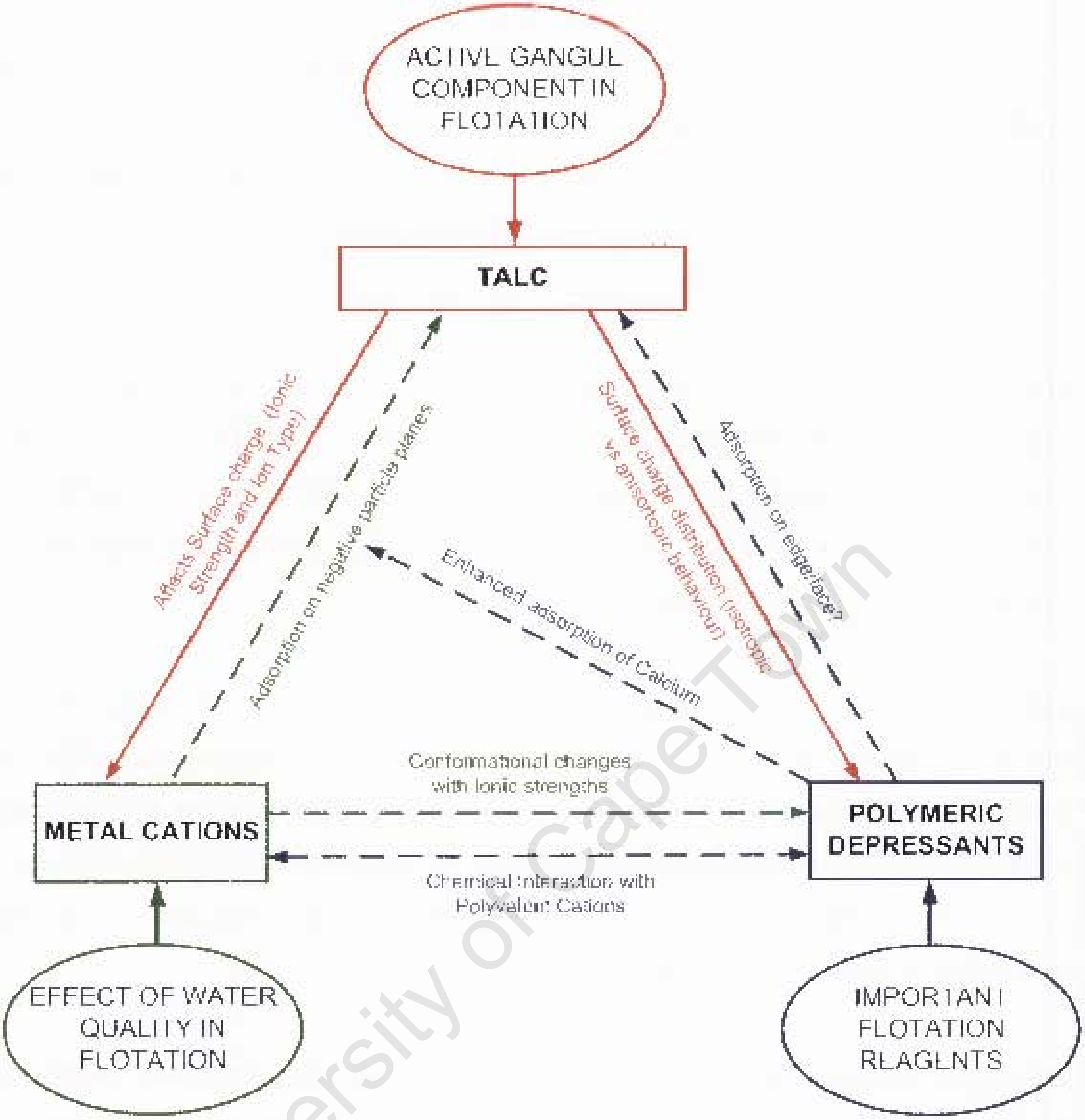

Figure 1.1 - Schematic representation of the thesis

1.2 SCOPE AND BOUNDARIES

The study focuses on the behaviour of New York talc, which was selected for its very low degree of impurities and well defined sheet-like morphology. This well defined morphology allows the study of both the basal planes and edges of talc particles. Other talc minerals with less well defined morphology such as South African Scotia talc have not been included.

Two types of polymeric depressants have been selected for this study, non-ionic guar gum and anionic carboxymethyl cellulose (CMC). Both of these polymers are commonly used in industrial situations to depress talc out of the flotation concentrate. Other depressant types, such as synthetic or inorganic depressants, were not included in the study. The effect of polymer degree of substitution and molecular weight were not investigated

Divalent calcium ions and monovalent potassium ions were chosen to study the effect of ions on both the surface properties of talc as well as mechanisms of polymer adsorption. Calcium ions are commonly abundant in industrial recycled water (Xu and Wilson 2000). The effect of other ion types as well as the effect of organic constituents of recycled water were not considered.

Various techniques were employed to obtain information as to the nature of the interaction between the three abovementioned factors, both surface and bulk solution. Titration and zeta potential measurements (noting their constraints) are used to estimate the distribution of surface potential of New York talc under various solution conditions. Electron microprobe analysis is used to estimate the chemical composition of the talc samples, allowing one to determine its crystalline structure.

Rheological measurements are used to study the inter-particle interactions within talc suspensions. These measurements, in conjunction with titration and electrophoretic measurements are then used to extract information regarding the surface potential of talc particles. Rheological measurements are also used to examine the effect of polymeric depressants on talc inter-particle forces in order to determine the interactions between talc particles and the polymer molecules.

ToF-SIMS analysis is used to measure the adsorption of inorganic ions as well as anionic polymers directly on the surface of talc, as a function of talc particle morphology (i.e. basal planes vs. edges).

1.3 STRUCTURE OF THE THESIS

The following chapter (Chapter 2) contains the summary of the relevant literature available on the subject matter. The available information is critically discussed and the main hypotheses which this thesis sets out to test are outlined. Chapter 3 contains the descriptions of the materials and methods used in this work.

The results of the study are presented and discussed in three separate chapters. The first results chapter (Chapter 4) deals with the surface characteristics and surface charge distribution of New York talc in the absence of both polymers and variation in the concentration and type of metal cations. The surface properties of talc are inferred using titration, rheological and electron microprobe techniques.

The second results chapter (Chapter 5) builds onto the information gained in the first chapter regarding the surface charge distribution of talc minerals in order to evaluate the effect that this distribution has on the adsorption characteristics of both non-ionic and anionic polymeric depressants. This is done by means of analysing the rheological behaviour of talc suspensions in the presence of polymers as well as rheological measurements of the polymer behaviour in solution.

The third results chapter (Chapter 6) combines the information obtained in the previous two chapters in order to study the effect that metal cations have on the surface charge distribution of New York talc and the consequent effect on the adsorption characteristics of anionic CMC. It then examines the solution interactions between the anionic polymer and metal cations. This is achieved by means of surface specific ToF-SIMS analysis.

Finally the summarised discussion of all the results is presented in Chapter 7, where the final conclusions and recommendations of this thesis are also presented.

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2 Literature Review

The aim of this chapter is to present a summary of the relevant literature available on the subject matter of this thesis, as well as to place the work done in an appropriate context.

The fundamentals of the rheology of mineral suspensions are presented and discussed in relation to the surface properties of various minerals, both isotropic and anisotropic, with specific reference to mineral flotation. The structure and surface properties of anisotropic talc are also discussed, with specific reference to its surface charge distribution. The adsorption characteristics of metal cations onto minerals such as talc and quartz are discussed, as well as their effect on the surface properties of these minerals. The different adsorption mechanisms of polymeric depressants, both anionic and non-ionic are presented and discussed, with specific reference to their behaviour as a function of the presence of metal cations both in solution and on the mineral surfaces.

Finally, a critical review of the relevant literature is presented. The appropriate hypotheses are then put forward on the basis of the literature review.

2.1 RHEOLOGY OF MINERAL SUSPENSIONS

Rheological measurements are rapidly finding applications in the mineral processing industry. Rheological properties of slurries affect a host of different mineral processing operations (Boger 1999). Milling efficiency in certain mill types is largely controlled by the throughput of slurry through the mill, which strongly depends on the rheological properties of the slurry (Shi et al. 1999). Dewatering operations depend on both the settling rate of particles as well as the compressibility of the concentrated slurry. These are necessary in order to ensure fast slurry settling times as well as adequate water recovery from industrial processes such as flotation.

Rheology of suspensions is strongly affected by a large number of factors, such as particle size and properties as well as the chemistry of the suspension medium. For many disperse systems rheological research methods offer a unique possibility of studying the surface properties of the suspended solid particles.

2.1.1 Rheology fundamentals

Rheology is a study of flow and deformation of matter. The rheological properties of fluids are normally represented in the form of flow curves or rheograms, where the fluid shear stress is plotted vs. the shearing rate as shown Figure 2.1. Some of the more common fluid properties that can be used to describe suspension behaviour are its viscosity and yield stress.

Viscosity is defined as the resistance to deformation by a fluid, and is generally given as the ratio between the shear stress and shear rate, at constant temperature. In the case of a Newtonian fluid, the viscosity is constant throughout the entire shear rate range. However, as can be seen from Figure 2.1, in case of non-Newtonian fluids (pseudo plastic, dilatant) this value changes as a function of shear rate. Therefore the viscosity of a non-Newtonian fluid at any point is referred to as "apparent viscosity".

The yield stress of a suspension is the minimum force required for deformation to take place and is a characteristic property of pseudo-plastic fluids. Most mineral suspensions exhibit pseudo-plastic behaviour (Boger 1999). Yield stress is a difficult property to measure directly, as it requires the measurement of the shear stress of the fluid at shear rates approaching zero. A direct measurement method has been developed by Nguyen and Boger (Nguyen and Boger 1983; Nguyen and Boger 1985), which makes use of a vane rotating within a fluid at a constant shear rate $<< 1\ s^{-1}$.

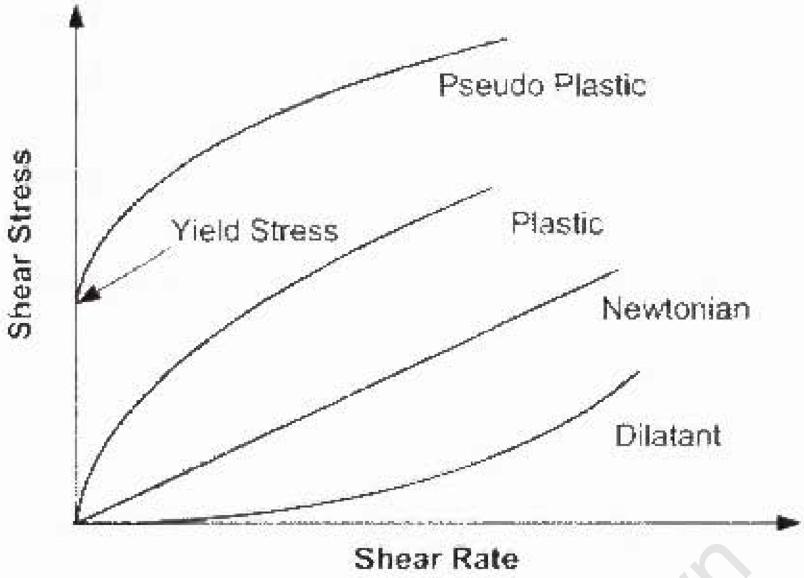


Figure 2.1 – Rheograms of various types of fluids

This method has been successfully applied to concentrated mineral suspensions of ultra fine particles. However, when dealing with particle suspensions of a size range common in flotation systems, this method becomes less appropriate due to the lack of sensitivity in most laboratory instruments to detect shear stresses at such low shear rates. In such cases, a rheological model is applied to the fluid rheograms, and the yield stress value mathematically extrapolated.

The rheological behaviour of pseudo plastic suspensions of single phase mineral particles is highly dependent on the surface charge of the suspended particles. Solid particles in aqueous environments are usually electrically charged. According to classic DLVO theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948), the degree of coagulation of a suspension depends on the relative magnitudes of the repulsive electrostatic forces and the attractive van de Waals forces (in the absence of other attractive forces such as the hydrophobic force).

At high levels of surface potential, the repulsive forces are much stronger than the attractive forces, so the energy barrier between particles forces the suspension into a dispersed state. As the surface potential of the particles decreases, the reduced electrostatic repulsive forces can no longer counteract the attractive forces and the system starts coagulating. When the overall surface charge of the particles is zero, electrostatic repulsion is absent and fast coagulation prevails. At this point, a continuous network of particles is formed throughout the suspension, which is manifested by high yield stress values. This phenomenon is graphically illustrated in Figure 2.2.

The force balance between the attractive and repulsive particle forces is shown in Equation (2.1).

$$V_{Total} = V_E + V_A \qquad (2.1)$$

V_E – Repulsive energy V_A – Attractive energy

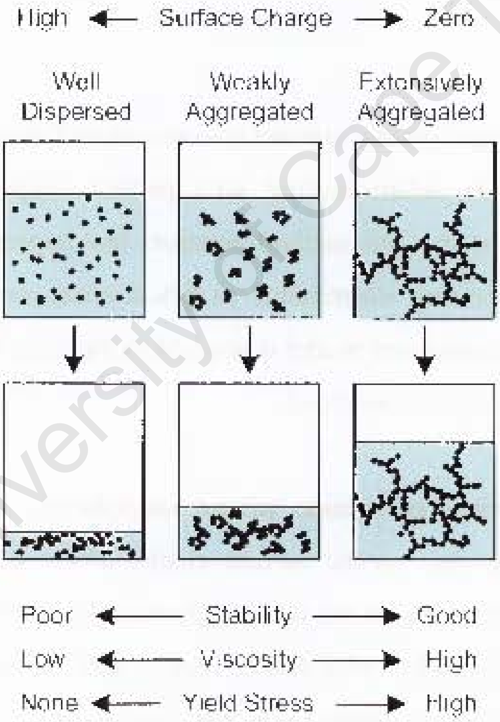


Figure 2.2 – Schematic representation of the rheological behaviour of isotropic minerals as a function of surface charge (Atlas et al. 1985)

2.1.2 Isotropic minerals

As was discussed in the previous section, the surface charge of mineral particles plays an important role in the consequent rheological behaviour of particle suspensions. Isotropic particles are a good example of such behaviour. The defining property of isotropic minerals is that all surfaces of such particles are created by breaking the same bonds and the resulting mineral surfaces are homogenous and do not vary as a function of position on the surface of a particle. Examples of such minerals are zircon and quartz. Zircon consists of uniform, tetragonal zirconium silicate crystals with a homogenous surface charge distribution (Subbanna et al. 1998).

Figure 2.3 – Tetragonal structure of an isotropic zircon particle (Barlow 2002)

The surface charge of isotropic oxide minerals such as zircon changes as a function of the concentration of potential determining ions in solution. In most cases, the potential determining ions are H^+ and OH^- ions, therefore the surface charge changes as a function of pH. As the suspension pH shifts from one extreme to another, the surface charge of these minerals undergoes a change from positive to negative, with the point where the overall charge is equal to zero is known as the point-of-zero charge. The equivalent point when measured zeta potential plotted vs. pH is equal to zero, is referred to as the isoelectric point

As discussed in the previous section, the yield stress of suspensions increases with the decreasing electrostatic repulsion between particles. Therefore, the yield stresses of suspensions of isotropic particles are low at the pH values where the surface charge of the mineral particles is high and gradually increases as charge approaches zero. The yield stress reaches its maximum at the isoelectric point of the suspensions of isotropic minerals (Johnson et al. 1999).

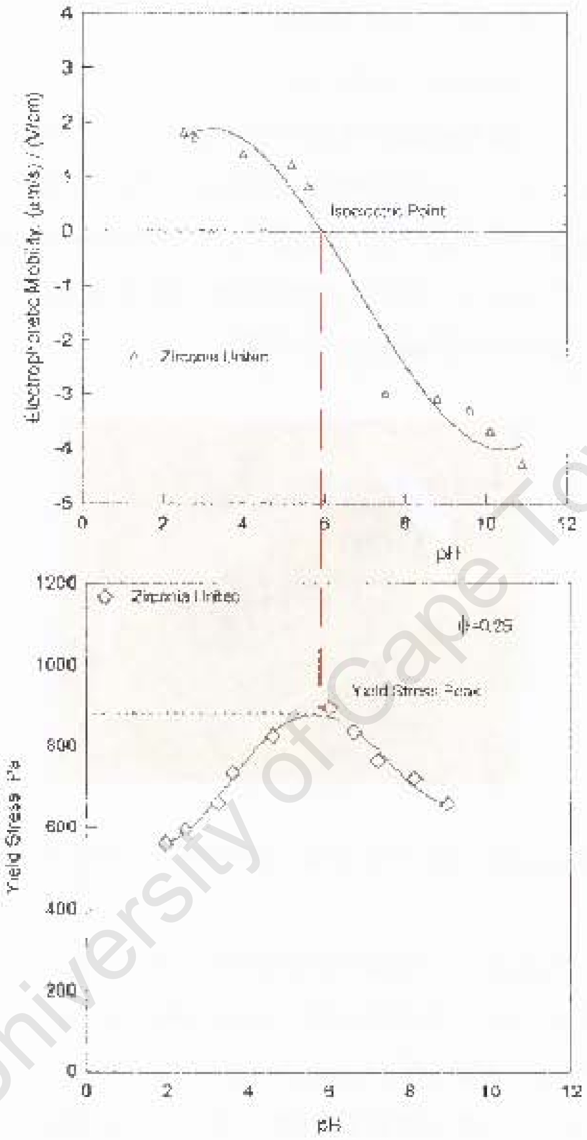


Figure 2.4 – Zeta potential of zircon suspensions showing the suspension isoelectric point along with the yield stress of zircon suspensions showing the point of maximum coagulation (Subbanna et al. 1998)

Figure 2.4 shows the yield stress measured for concentrated suspension of isotropic zirconia as a function of pH. The yield stress peak appears at pH ≈ 6, which corresponds to the isoelectric point of this mineral.

2.1.3 Anisotropic minerals

The process of aggregation of particles in a suspension becomes more complex when the surface charge of the particles is anisotropic. In the case of anisotropic particles the surface charge varies as a function of the position on the particle surface. An example of such a mineral is kaolinite. Kaolinite is a 1:1 layered silicate mineral, the structure of which is shown in Figure 2.5.

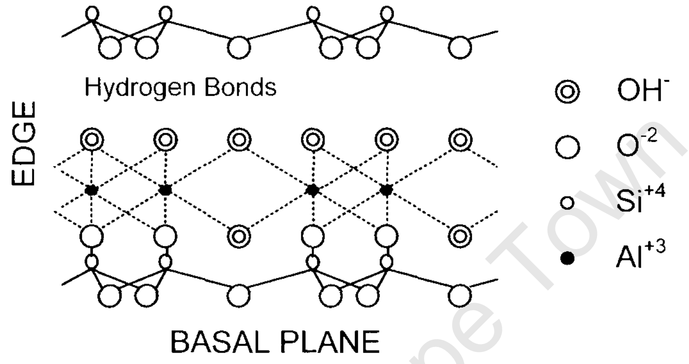


Figure 2.5 – Crystallochemical structure of kaolinite (Flegmann and George 1975)

Unlike symmetric 2:1 sheet minerals such as montmorillonite and talc, kaolinite has two types of basal planes, the tetrahedral Si – O layer and the octahedral Al – OH layer (Carty 1999). The tetrahedral basal plane of kaolinite was originally considered completely neutral, however was later shown to carry a permanent negative charge due to isomorphic substitution of Si^{+4} ions with Al^{+3} ions in the silicon-oxygen tetrahedra. The presence of Al^{+3} ions causes a proton deficiency and therefore results in an overall negative charge on the tetrahedral basal planes of kaolinite (Van Olphen 1951; Kitchener 1969; Swartzen-Allen and Matijevic 1974). The octahedral basal plane layer of kaolinite, as well as its edges carry a charge that depends on solution pH. The charge arises from the presence of amphotheric OH groups on the mineral surface, exposed to the aqueous medium and therefore amenable to H^+/OH^- transfer (Carty 1999; Tombacz and Szekeres 2006).

The surface charge distribution of kaolinite particles is shown in Figure 2.6. The figure shows that the surface charge on the edges of kaolinite particles shifts from negative to positive as the suspension medium becomes more acidic, while the charge on the tetrahedral particle faces remains negative throughout the pH range. At the point where the charge on the particle edges becomes positive, the electrostatic force between faces and edges of particles changes from repulsive to attractive.

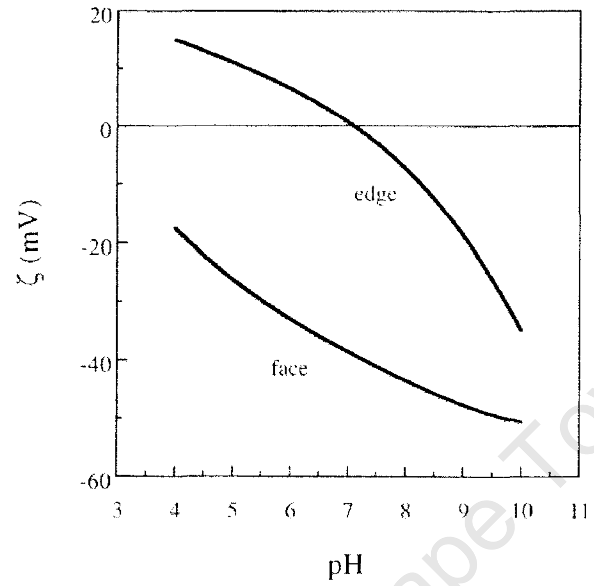


Figure 2.6 – ζ potential of kaolinite faces and edges as a function of pH (Johnson et al. 1998)

This implies that the point of maximum coagulation of suspensions of anisotropic particles occurs not at the apparent point of zero charge, but at the point where the attractive electrostatic force between oppositely charged particle planes and edges is at its maximum. This kind of coagulation process is referred to as "heterocoagulation".

The relationship between the zeta potential measurements of kaolinite and the yield stress of kaolinite suspensions is shown in Figure 2.7. The isoelectric point of kaolinite obtained by zeta potential measurement lies at a pH ≈ 3.5, while the point of maximum coagulation of kaolinite lies at pH ≈ 5.5 (Johnson *et al.* 1998).

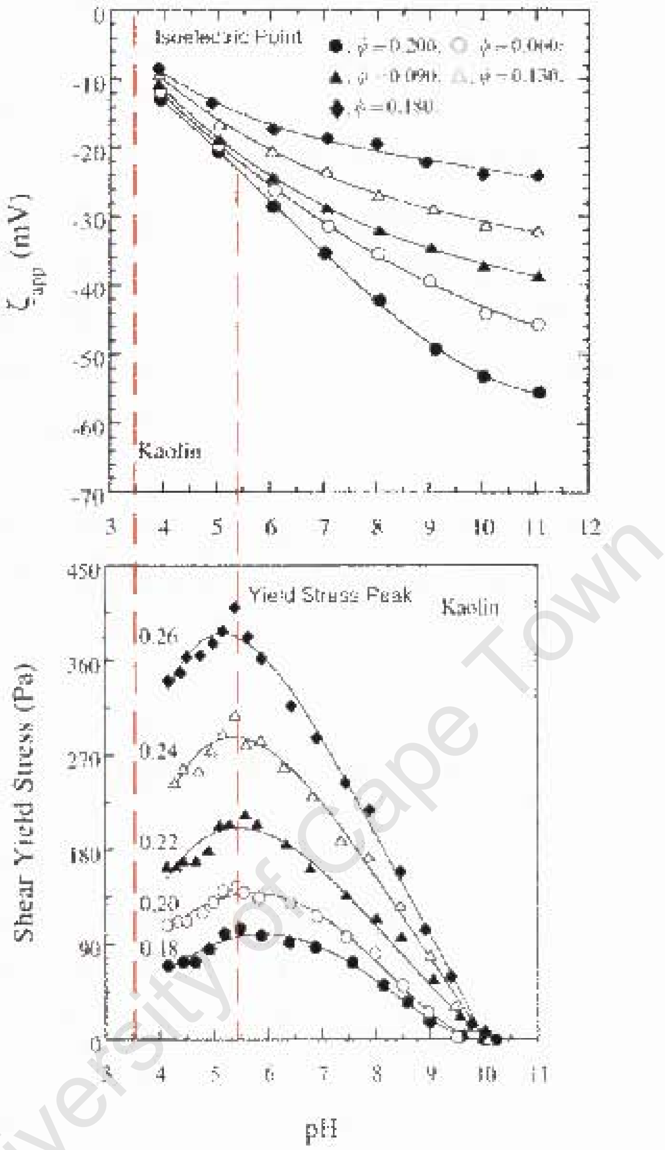


Figure 2.7– Zeta potential of kaolinite suspensions showing the suspension isoelectric point along with the yield stress of zircon suspensions showing the point of maximum coagulation, at different solids concentrations (Johnson et al. 1998)

The reason for the isoelectric point and the yield stress peak no longer converging on the same value is that the state of maximum aggregation of the suspension occurs not at the isoelectric point, but at the point where the attractive force between the positively charged edges and negatively charged faces is at its maximum, causing the suspension to heterocoagulate.

Another reason for the disparity between isoelectric point and the yield stress point of kaolinite lies in the use of electrophoretic measurements to study the charge distribution of anisotropic, non-spherical particles (e.g. kaolinite). Electrophoretic measurements make use of Smulochowki's equation (Dukhin and Derjaguin 1976) to convert electrophoretic mobility to zeta potential. However, Smulochowki's equation has been derived for spherical, or near-spherical, isotropic particles. There is currently no mathematical model that allows calculation of the zeta potential value from the measured electrophoretic mobility for the plate-like anisotropic minerals. This is due to both complex hydrodynamics and charge heterogeneity of such particles.

Since kaolinite particles are both plate-like and anisotropic, zeta potential measurements of kaolinite must be treated as apparent and comparative only (Lyklema 1995).

2.2 PROPERTIES OF ANISOTROPIC TALC

As mentioned in the introduction, talc occurs as a gangue mineral in the flotation of base metal sulfide ore deposits around the world (Sheousstra and Kinloch 2000; Muinonien 2006). Although talc forms only a minor part of the gangue components of these ores (less than 10%), it tends to have a disproportionately large effect on the efficiency of the flotation process (Steenberg and Harris 1984; Fuerstenau et al. 1988).

2.2.1 Crystallochemistry of talc

Talc is a layered silicate mineral that consists of octahedral magnesium hydroxide structures sandwiched between sheets of silicon-oxygen tetrahedra. The layered talc sheets are held together by weak van de Waals forces (Flegmann and George 1975). Talc is an anisotropic mineral and the particles exhibit distinct edges and basal planes. Figure 2.8 shows the layered structure of talc, pointing out the chemical structure of the basal planes and edges.

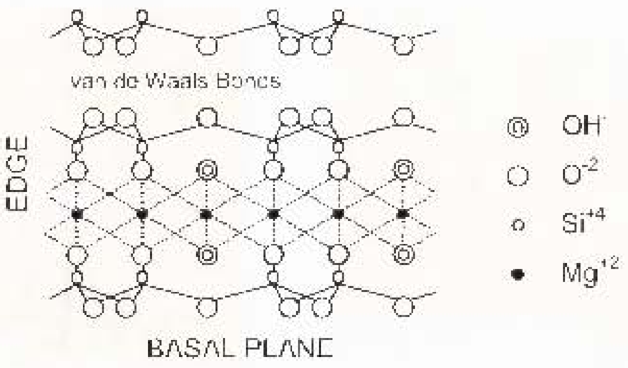
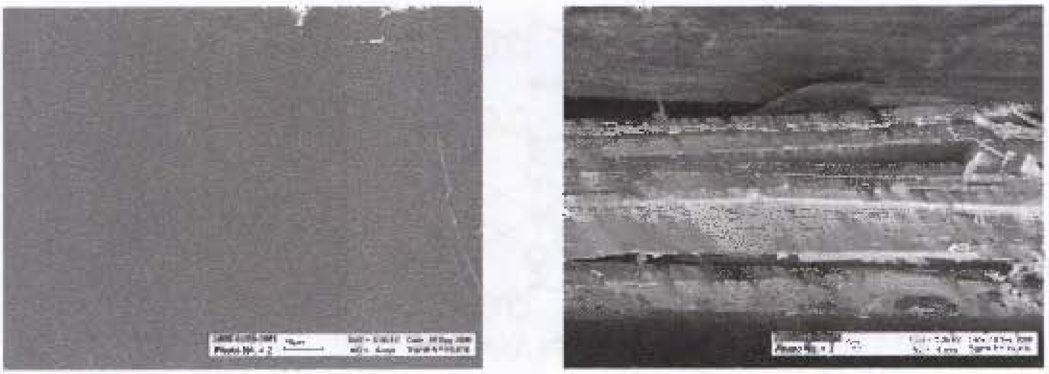


Figure 2.8 Crystal chemical structure of talc (Flegmann and George 1975)

Talc crystals can also be represented geometrically, showing the tetrahedral structure of the top-most silicon oxygen layer and the octahedral structure of the inner brucite layer as shown in Figure 2.9. In some cases, small amounts of titanium or aluminium can substitute for silicon in the tetrahedral layer, while calcium may substitute for magnesium in the octahedral brucite layer (Deer et al. 1997).

Figure 2.9 – Geometric representation of talc tetrahedral and octahedral layers

The layered nature of talc is further evident when observed under a scanning electron microscope (SEM), which shows the smooth basal planes of talc along the stratified edges. Such images are shown in Figure 2.10.



(A) (B)

Figure 2.10 – SEM images of (A) basal plane of a New York talc particle, (B) edge of a New York talc particle (photographs by Peter von Blokland, Akzo Nobel)

2.2.2 Surface charge distribution of talc

The basal planes of talc are hydrophobic, with a contact angle of $\theta \approx 60°$. Because of this talc particles exhibit a high degree of floatability. The edges of talc were found to have a low contact angle of $\theta \approx 10°$, however the non-zero contact angle was attributed to the impurities on the edge surface. (Fuerstenau and Huang 2003).

It is commonly stated in many publications (Steenberg and Harris 1984; Fuerstenau et al. 1988; Morris et al. 2002; Fuerstenau and Huang 2003) that the tetrahedral layers are fully charge compensated, thus rendering the basal planes of talc free of electrical charge. On the other hand, talc edges are considered to possess a negative charge as a result of the cleavage of ionic and co-valent bonds in the brucite layer.

Based on electrokinetic measurements, the isoelectric point of talc was estimated to be at pH ≈ 2.5. Table 2.1 shows the isoelectric points of talc which have been obtained by a number of different researchers based on various sources of talc, which illustrates the close agreement between the isoelectric points of talc across different sources.

Table 2.1 – Isoelectric points of talc from various sources

Researcher	Talc Source	I.e.p Value
Steenberg & Harris, 1984	Barberton, South Africa	≈ 2.5
Morris *et al.*, 2002	Poole, England	≈ 2
Fuerstenau & Huang, 2003	New York Talc	≈ 2.5
Wang & Somasundaran, 2005	Unspecified	≈ 2.5
Bremmel & Addai-Mensah, 2005	Australia	≈ 3

A typical zeta potential curve for talc is shown in Figure 2.11, which corresponds to New York talc, same talc as was used in this study. The figure illustrates the position of the apparent isoelectric point at a low pH value.

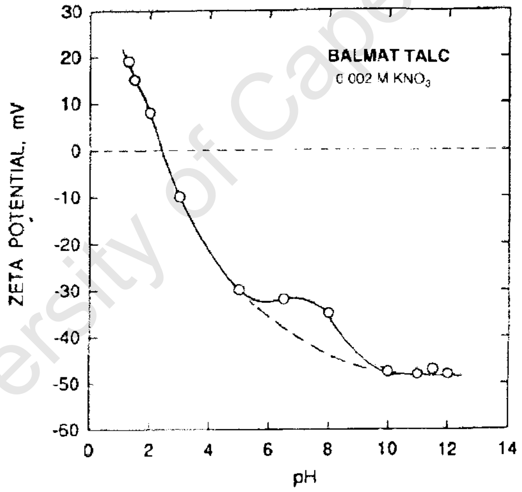


Figure 2.11 – Typical curve of zeta potential vs. pH for New York talc (Fuerstenau and Huang 2003)

Figure 2.11 also shows that the zeta potential – pH curves for talc are comparable to those of quartz (Brien and Kar 1968), where the electrical charge arises from highly charged silicon-oxygen tetrahedral structures. If it is assumed that the electrical charge of talc arises from the bond breakage in the brucite layer, it becomes impossible to explain the position of the isoelectric point of talc at pH ≈ 2.5.

This discrepancy can once again be explained by the inappropriate use of zeta potential measurements with regards to plate like minerals. For plate-like particles such as talc, the Smoluchowski's equation (which was derived for spherical or near-spherical particles) cannot be used to calculate the zeta potential values from the experimental electrophoretic mobility values. Therefore, in the case of talc and other plate like minerals such as kaolinite, zeta potential measurements should not be treated as absolute values, but rather as apparent ones with no specific physical meaning.

Nalaskowski *et al.* performed a study of talc surface charge distribution by measuring the zeta potential on the basal planes and edges respectively using streaming potential technique (Nalaskowski et al. 2006). The cell employed in this study comprises several parallel rectangular capillary channels formed by firmly pressing the test surface against a grooved spacer which forms the second side of the capillaries. The streaming potential phenomena in such asymmetric capillaries must pose all the theoretical problems similar to those in the movement of the anisotropic particle in a fluid within an electric field (electrophoresis).

The study showed that the zeta potential of both basal planes as well as edges of talc was similar to that obtained using conventional electrophoretic measurements, where the isoelectric point was detected at pH 3. However, the theoretical electrokinetic problems involved with the screaming potential cell when applied to anisotropic minerals are similar to those involved in zeta potential measurements. That, as well as the drawbacks of the sample preparation procedure employed puts the reliability of these results into question.

The surface charge distribution of talc was also estimated from the floatability of talc as a function of pH. The findings of theses studies vary. Some studies showed that the recovery of talc by flotation was completely independent of pH (Rath et al. 1997; Morris *et al.* 2002). However, Fuerstenau and Huang (2003) found that the floatability of talc decreased with increasing pH. However, none of the studies observed a floatability peak at the electrophoretic isoelectric point, which raises further questions regarding the validity of the electrophoretic measurements with regards to plate like minerals.

A study by Okuda *et al* (Okuda et al. 1969) examined the possibility that the basal planes of talc carry a negative charge. They employed a technique where the talc particles were contacted with a positively charged AgI colloid which could then be detected under an electron microscope. They found that the positively charged colloidal particles adhered to the basal planes of talc at both acidic and alkaline pH. It was therefore concluded that the basal planes of talc carry a negative charge in a wide pH range.

2.3 EFFECT OF METAL CATIONS ON TALC

The effect of ion type on the surfaces of various minerals has been widely studied (James and Healy 1972; James and Healy 1972; James 1981; Fuerstenau *et al.* 1988; Johnson *et al.* 1998; Johnson *et al.* 1999; Bremmell and Addai-Mensah 2005; Ma and Pawlik 2005). In order to examine the effect of ion types on the surface, the ions can be looked at in terms of their structure making / structure breaking properties.

The structure making/structure breaking attributes of ions affect the mobility of water molecules in solution. Water molecules are in a constant state of Brownian motion. The time that a water molecule spends in equilibrium position with respect to another molecule is defined as the average retention time (τ). If ions are present in solution, their interaction with water molecules is different from that between the water molecules themselves. This causes a shift in the equilibrium, resulting in a different retention time (τ_i) (Samoilov 1965; Laskowski 1994). The hydration energy (ΔE) of an ion in solution can be expressed as a function of the ratio of the two retention times (Samoilov 1965), as shown in Equation (2.2).

$$\frac{\tau_i}{\tau} = e^{\left(\frac{\Delta E}{RT}\right)} \qquad (2.2)$$

Ions with small ionic radii (such as Li^+ and Na^+) as well as polyvalent ions, exhibit structure making properties, where $\tau_i > \tau$. These ions are referred to as *kosmotropes*.

Large monovalent ions with low levels of hydration, (such as Cs^+) exhibit structure breaking properties, where $\tau_i < \tau$. These ions are known *chaotropes*.

2.3.1 Monovalent cations

Monovalent cations such as potassium and sodium do not form charged hydroxide complexes and are common constituents of indifferent electrolytes. The major adsorption mechanisms of monovalent metal cations onto mineral surfaces is by means of ionic bonding onto a negatively charged mineral surface (Aplan and Fuersteanau 1962). However, the adsorption of these ions is complicated by their water structure making/structure breaking properties.

Alkali metal cations are generally arranged in a sequence that lists these ions from least hydrated and hence structure breaking to most hydrated and hence structure making, called the Hoffmeister series, ($Cs^+ > K^+ > Na^+ > Li^+$). Potassium ions have a relatively large ionic radius 1.33 Angstrom (Aplan and Fuersteanau 1962). This places potassium into a structure breaking category.

The effect of structure making/structure breaking properties of alkali metal cations on the surface potential of quartz was studied by Ma and Pawlik (2004, 2006) using zeta potential measurements. It was found that at the same level of ionic strength, the surface potential of quartz was reduced to a much greater extent in the presence of structure breaking K^+ and Cs^+ ions than that in the presence of structure making Na^+ and Li^+ ions. This finding indicates that the structure breaking ions are able to adsorb more onto the surface of quartz, reducing its surface potential.

2.3.2 Polyvalent cations

Unlike monovalent ions, divalent ions such as calcium tend to be structure makers or *kosmotropes* (Samoilov 1965). Calcium ions have a relatively small ionic radius 197 pm and an even smaller hydration radius of 114 pm and have a high energy of hydration (Tissandier et al. 1998).

The effect of divalent ions (Ca^{+2} and Mg^{+2}) on guar gum adsorption onto quartz was studied by Ma and Pawlik (2006). The adsorption density of guar gum was measured both in distilled water as well as in the presence of both Ca^{+2} and Mg^{+2} ions. The experiments were performed at pH 5.2 to ensure that no metal hydroxy complexes were formed. It was found that the presence of divalent cations in solution had no effect on the adsorption density of guar gum onto quartz, indicating that these ions did not adsorb onto the mineral and therefore had no effect on its surface properties.

Unlike monovalent ions, polyvalent ions are able to hydrolyse when placed in aqueous solution. Polyvalent ions are therefore able to undergo specific chemical adsorption onto a mineral surface (Fuerstenau *et al.* 1988; Koopal 1992). The adsorption of hydrolysable polyvalent cations is highly dependent on pH as the adsorption of ions increases with the increasing amount of hydrolysed ion species (e.g. $CaOH^{+}$ species formed instead of Ca^{+2} species), (Ahmed and Van Cleave 1965; James and Healy 1972; James 1981).

In the case of divalent calcium ions, the adsorption takes place between pH 8 and pH 11, with the sharp rise in the adsorption values occurring at pH values above pH 10, where the majority of hydrolysed cations form, as shown in Figure 2.12.

The effect of hydrolysable polyvalent ions onto talc was studied by Fuerstenau *et al*, (1988), by means of zeta potential and batch flotation measurements. Metal cations were found to adsorb onto the mineral surface in the pH range where they formed hydroxyl complexes. It was also found that the adsorption of metal cations such as Fe^{+3} and Al^{+3} onto the surface of talc resulted in a significant increase in the zeta potential of talc surfaces, rendering them positive in the pH range significantly above the apparent isoelectric point of talc in the absence of metal cations in solution (pH ≈ 2.5). However, despite the evidence of cation adsorption, the floatability of talc was relatively unaffected. This fact was used to deduce that metal hydroxide species do not interact with the basal planes of talc, but rather with the edges of talc.

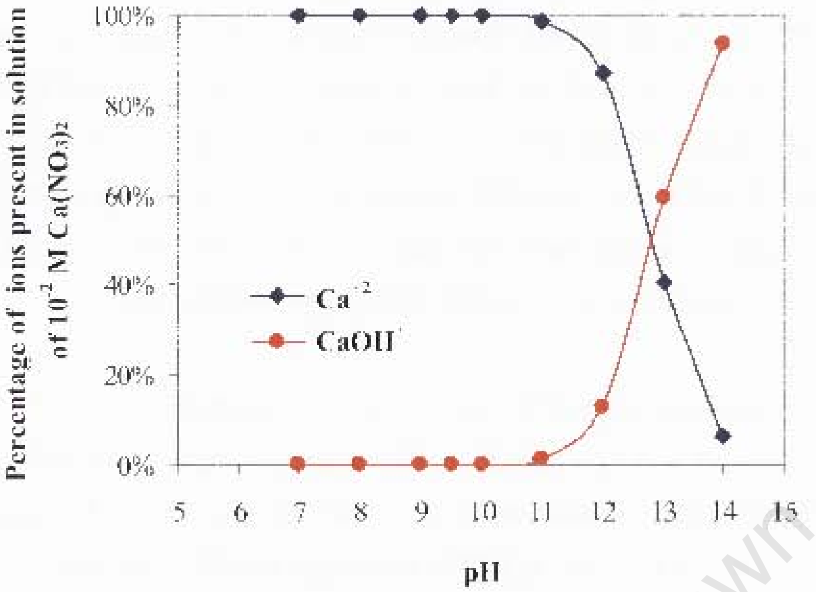


Figure 2.12 – Distribution diagram of $CaOH^+$ ions in solution (obtained from MINTEQA2 software)

2.4 POLYMERIC DEPRESSANTS

2.4.1 Types of polymers

Polysaccharide compounds are commonly utilized as polymeric depressants. The two polysaccharides commonly used in the mineral processing industry as depressants are Guar gum and Carboxymethyl Cellulose (CMC).

CMCs are anionic polysaccharides, with molecular weights ranging from 10^3 and 10^6 Dalton. Figure 2.13 shows the basic molecular structure of a typical CMC molecule.

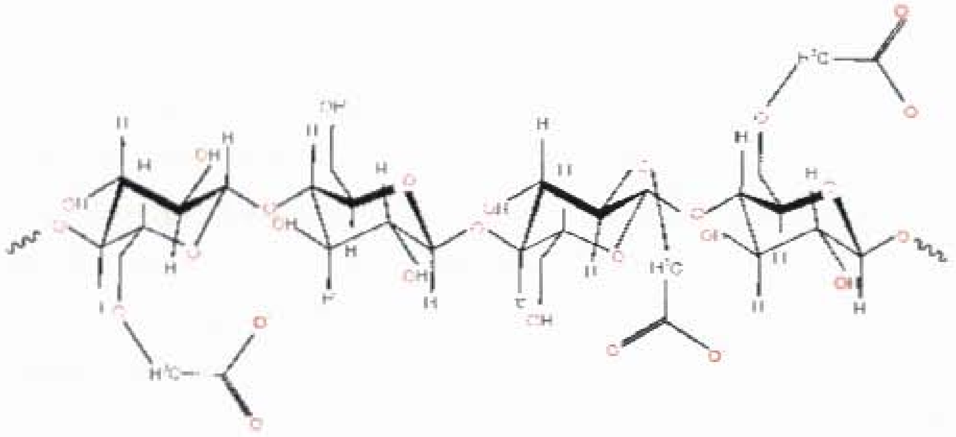


Figure 2.13 – Structure of a CMC molecule (Steenberg and Harris 1984)

On the other hand, guar gums are non-ionic macromolecules, derived from a naturally occurring guar bean, with similarly large molecular weights. Figure 2.14 shows the basic molecular structure of a typical guar gum macro molecule.

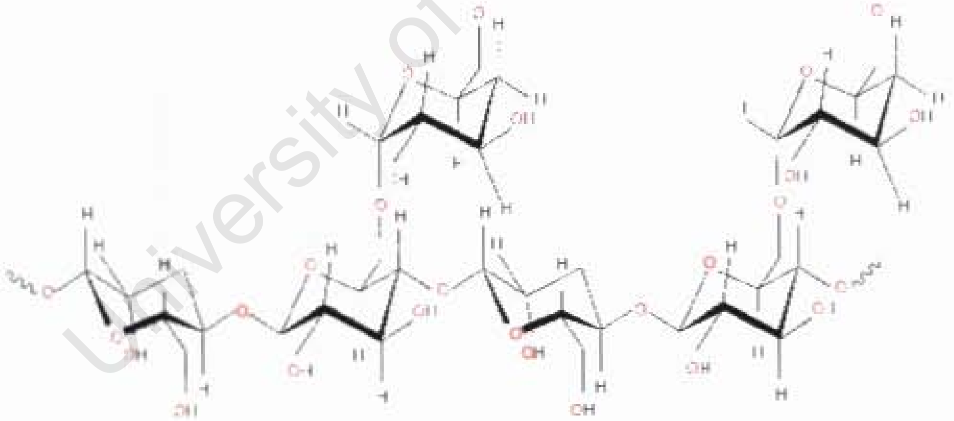


Figure 2.14 - Structure of a guar gum molecule (Steenberg and Harris 1984)

2.4.2 Solution behaviour

Macromolecules in a solvent may show different degrees of conformation, from fully extended to fully coiled. The conformation of anionic macromolecules has been found to be highly dependent on the ionic strength of the medium (Huggins 1942). In the absence of electrolyte such polymer macromolecules are fully extended. As the ionic strength of the solution increases, the polymer macromolecules begin to coil, at sufficiently high ionic strength, the behaviour of the macromolecules may resemble that of particles. The schematic representation of CMC conformation is shown in Figure 2.15.

The degree of coiling of polymers in solution can be inferred from viscosity measurements. When polymer macromolecules are fully extended, the viscosity of the solution is generally high, due to the frictional forces between the long stranded polymers. However, once the molecules begin to coil, they start to act more and more like particles in a suspension, thereby decreasing the amount of intermolecular friction and thus decreasing the solution viscosity.

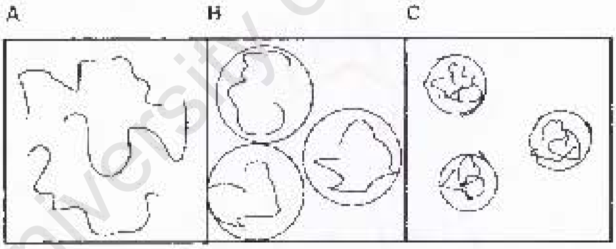


Figure 2.15 – Schematic representation of conformation of CMC molecules (A) Distilled water, (B) Dilute electrolyte, (C) Concentrated electrolyte (Liu and Laskowski 2006)

Intrinsic viscosity is a measure of solution viscosity that is independent of the concentration of polymer in solution (Huggins 1942), and therefore can be used to determine the degree of coiling of the polymer molecules in solution under varying conditions, such as change in ionic strength or pH of the medium.

Pawlik *et al.*(2003) studied the conformational changes of CMCs as a function of the ionic strength of supporting electrolyte in potash flotation systems. It was found that the intrinsic viscosity of CMC solutions decreased with increasing brine concentration, which is indicative of the increase in the degree of polymer coiling.

Parolis measured the degree of coiling of CMC molecules as a function of ionic strength as well as polymer type by measuring the intrinsic viscosity as well as the radius of gyration of these polymers (Parolis et al. 2006). It was found that the presence of calcium (a divalent cation) caused a greater degree of coiling of polymer molecules than that of potassium (a monovalent cation) for the same ionic strength, see Figure 2.16. Furthermore, the curve of viscosity vs. the inverse of the square root of ionic strength ($1/IS^{1/2}$) for K^+ was found to be linear, which is indicative of the interaction between polymer molecules and potassium ions to be purely electrostatic. However, the same curve in the presence of calcium ions was found to be non linear, which indicates a conformational change within the polymer (Fixman 1964).

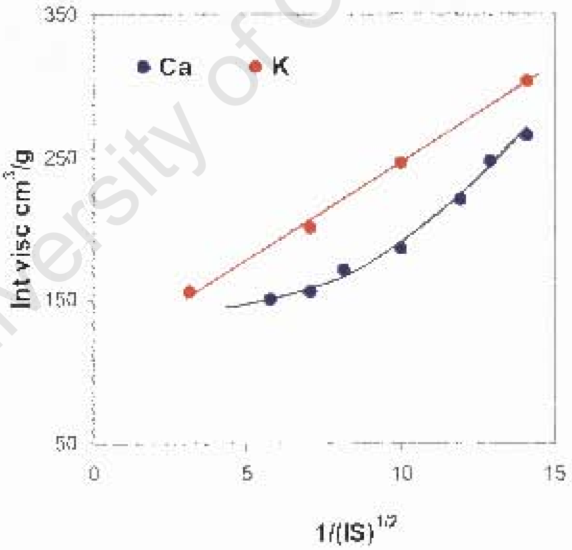


Figure 2.16 – Intrinsic viscosity of CMC solution as a function of ionic strength and cation type (Parolis et al. 2006).

2.4.3 Adsorption mechanisms onto talc

The mechanisms of adsorption of CMC's onto talc as well as other minerals has been widely studied with hydrophobic, hydrogen bonding considered to be the primary adsorption mechanisms (Steenberg and Harris 1984; Morris *et al.* 2002; Fuerstenau and Huang 2003; Wang and Somasundaran 2005; Wang and Somasundaran 2006) .

A mechanism was also proposed (Liu and Laskowski 1989; Liu and Laskowski 1999; Liu et al. 2000; Liu and Laskowski 2006), in which adsorption of polysaccharide macromolecules results from acid/base interactions between polysaccharide and mineral surface. The presence of basic metal hydroxide sites on the acidic surface (e.q. quartz) was shown to be essential for dextrin adsorption.

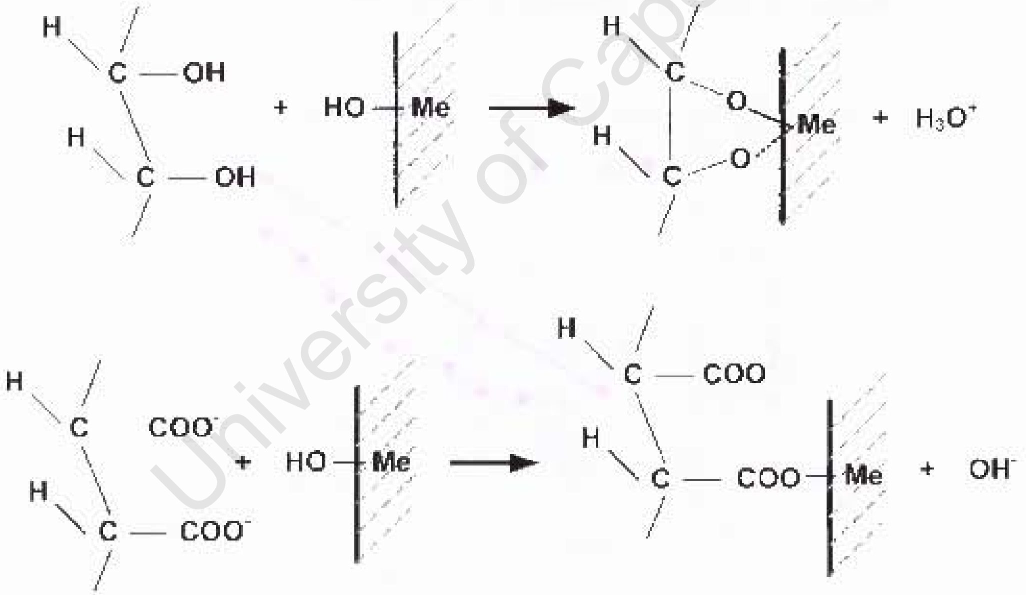


Figure 2.17- Schematic representation of an interaction between CMC molecules and metal hydroxide species on the mineral surface (Liu and Laskowski 1999)

Liu and Laskowski (1989) studied the adsorption of dextrin onto the surface of quartz. They found that in the absence of basic metal hydroxyl- species on the acidic surface of quartz (both natural hydrophilic quartz as well as quartz rendered hydrophobic by methylation), no adsorption of dextrin took place on the surface of quartz particles. However, when basic lead hydroxide (Pb-OH) species were present on the surface of quartz, dextrin acidic molecules began to adsorb on the quartz surface. The hydrophobicity of the quartz used in the tests played only secondary role, and this revealed that the hydrophobic bonding is not a dominant mechanism of dextrin adsorption onto quartz surfaces.

It has been shown that in some cases the interaction of anionic polymer with metal hydroxide sites acts in synergy with the hydrophobicity of the mineral surface. Rath *et al.*(1997) showed that the adsorption of dextrin onto talc (per unit surface area) increased with decreasing particle size. The increase in particle size is indicative of the increased basal plane/edge ratio of the talc particles. Since talc basal planes are hydrophobic, with a contact angle of ≈ 60° (Fuerstenau and Huang 2003), the increase in dextrin adsorption with increasing particle size is indicative of the role of hydrophobic surfaces in CMC adsorption. Similarly, such a synergy was also shown to exist for the adsorption of dextrin onto hydrophilic and methylated hydrophobic quartz (Liu and Laskowski 1989)

Researchers such as Fuerstenau & Huang (2003) and Wang *et al.* (2005, 2006). considered hydrogen bonding to be a dominant mechanism in polymer adsorption. Fuerstenau & Huang (2003) showed that the adsorption of dextrin onto the surface of talc took place in acidic pH as well as alkaline pH and attributed this to a weak hydrogen bonding between the polymer macromolecules and the talc surface. Wang *et al.* (2006) came to a similar conclusion by showing that the adsorption of CMC onto talc could be reduced by the addition of urea (a hydrogen bond breaker).

However, hydrogen bonding itself can be treated as an acid base interaction (Fowkes 1989). Most polymer macromolecules placed in solution possess acidic properties. Mineral surfaces in solution show either prevailing basic or acidic properties (for instance, while quartz is acidic, alumina is basic) Therefore, an interaction between an acidic polymer and a basic mineral would be strong enough to be considered a chemical bond. An interaction between a weakly acidic polymer and a weakly basic mineral would take form of a weak interaction, commonly labelled as hydrogen bonding (Liu *et al.* 2000; Liu and Laskowski 2006).

CMC is an anionic polymer; the possibility of the existence of electrostatic bonding mechanisms onto the talc surface is also likely, and has therefore been widely investigated. Several studies (Steenberg and Harris 1984; Morris *et al.* 2002) ruled out this possibility on the basis that the adsorption of CMC onto talc failed to shift the electrophoretic isoelectric point of talc particles. However, a recent study (Wang and Somasundaran 2005) showed a change in the apparent isoelectric point of talc suspensions as a function of CMC dosage and suggested a stronger presence of electrostatic forces in the mechanism of CMC adsorption.

The adsorption of charged polymers has also been found to depend on the conformational changes of polymer molecules in solution. A study by Morris (2002) showed that the floatability of talc in the presence of CMC was constant in a pH range from pH 5 - 9, and underwent a sharp decrease at pH 3, indicating an increase in CMC adsorption. Similarly, the adsorption isotherms of CMC onto talc showed much higher adsorption at pH 3.5 than at pH 9. A study by Parolis (2006) showed that the adsorption density of CMC onto talc gradually increased with decreasing pH. In both of these studies, this effect was attributed to the increased degree of coiling of CMC macromolecules with decreasing pH. The increased amount of coiling is thought to decrease the effective molecular radius of anionic macromolecules and therefore allows for denser spatial adsorption.

Many studies have demonstrated the CMC adsorption density onto talc to be strongly dependent on the ionic strength of the solution (Morris *et al.* 2002; Pawlik et al. 2003; Khraisheh et al. 2005; Parolis *et al.* 2006; Pawlik and Laskowski 2006). This phenomenon is chiefly attributed to two factors: the thinning of electrical double layers around both the mineral surface and the CMC macromolecules, thus reducing the electrostatic repulsion, as well as the increased degree of coiling of a CMC macromolecule in the presence of a high concentration of electrolyte.

The dependence of CMC adsorption on the type of ions present in solution was also tested by Shortridge (2000). He has shown that the CMC's adsorbs more densely onto the surface of talc in the presence of hydrolysable Ca^{+2} ions than K^{+} ions, for the same solution ionic strength at a constant pH of 9. These findings were later confirmed by Parolis (2004) who found similar trends, shown in Figure 2.18.

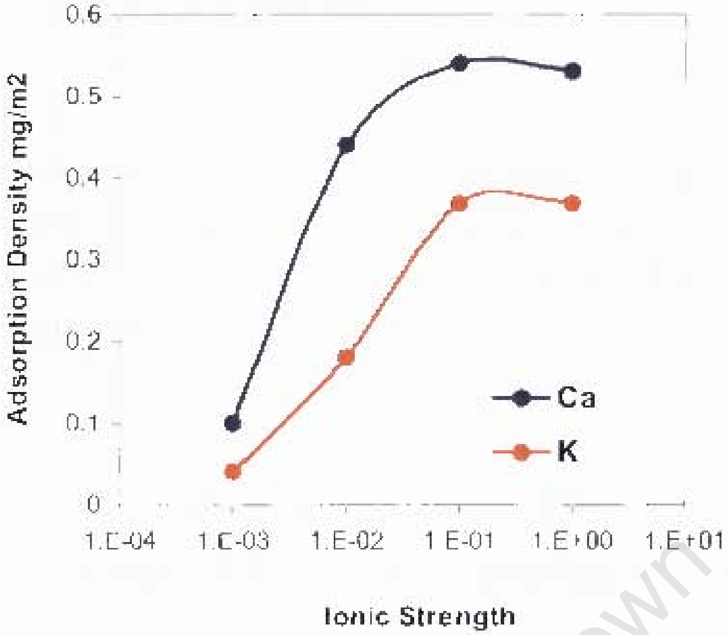


Figure 2.18 – Adsorption density of CMC onto talc as a function of ionic strength and ion type (Parolis et al. 2004)

Guar gum is a non-ionic polymer. Numerous studies have been performed to determine the mechanism of adsorption of this polymer onto talc. The general consensus is that the adsorption occurs by means of hydrogen and hydrophobic bonding, primarily onto the faces of talc (Steenberg and Harris 1984). The adsorption of guar gum onto talc was found to be largely independent of both pH and ionic strength of the suspension medium (Rath *et al.* 1997; Wang et al. 2005).

The effect of the presence of different electrolytes on the adsorption of guar gum onto quartz was studied by Ma and Pawlik (2005, 2006). It was found that the adsorption density of guar gum onto quartz was strongly affected by the presence of some monovalent cations such as K^+ and Cs^+, while being less affected by other monovalent ions such as Na^+ and Li^+, as well as divalent ions such as Ca^{+2} and Mg^{+2}. This was attributed to the water structure making/structure breaking characteristics of these ions, whereby the presence of structure breaking ions such as potassium on the mineral surface was conducive to guar gum adsorption. The adsorption of guar gum onto quartz in the presence of hydrolysable cations (calcium and magnesium) was found to increase over an alkaline pH range, were these ions began to form hydroxide complexes, which suggests that guar gum molecules may also interact with metallic sites on mineral surfaces in a manner similar to that of dextrin.

However, it is important to note that the above study was carried out on quartz, a highly acidic mineral that interacts weakly with a polymer such as guar gum. It is unclear whether a similar effect of structure making/structure breaking ions on the adsorption of guar gum plays a role in the adsorption on more basic mineral surfaces (Laskowski et al. 2006).

2.5 CRITICAL REVIEW OF THE LITERATURE

2.5.1 Surface charge distribution of talc

There are still many questions regarding the distribution of the electrical surface charge on the surface of talc. The main source of information is zeta potential measurements, and as already discussed, there is no a model that can describe electrokinetic phenomena for plate like anisotropic particles. Therefore, all the existing zeta potential measurements for talc must be treated as only a very rough estimation.

The vast structural similarity of talc to kaolinite raises questions regarding the perceived lack of electrical charge on the basal planes of talc. The Si^{4+} ions in the tetrahedral layers of talc are as amenable to isomorphic substitution with Al^{3+} ions as those on the surface of kaolinite. Such substitutions have previously been shown to take place inside the talc crystal lattice (Deer *et al.* 1997).

The study that does proposed the presence of a negative charge on the basal planes of talc (Okuda *et al.* 1969), attribute the presence of this negative charge to ionic substitutions in the tetrahedral layers of talc, similar to those that take place on the surface of Kaolinite.

This leads to a hypothesis that such substitutions indeed take place, causing the proton deficiency on the basal planes of talc, resulting in them carrying a negative charge.

Similarly, the edges of talc might undergo a change from positive to negative at a pH substantially higher than 2.5.

On the basis of the available published data on the subject of talc surface charge, the following general hypothesis has been put forward:
The basal planes of talc carry a negative charge resulting from natural substitution of silicon ion with ions of a lesser valency on the talc basal planes, while the charge on the edges of talc changes as a function of pH. As a result the surface charge distribution of talc cannot be studied using electrophoretic measurements.

2.5.2 Effect of talc surface charge on polymer adsorption

The adsorption mechanisms of anionic polymeric depressants have been widely studied. However, the derivation of these mechanisms largely rely on the assumption that the basal planes of talc carry no negative charge. As has been shown in Section 2.5.1, this assumption may not be valid. Therefore, the adsorption characteristics of polymeric depressants need to be re-evaluated with regards to the possibility of the presence of negative charge on the basal planes of talc. Furthermore, the effect of pH on the adsorption characteristics of anionic polymers is still questionable, as the evidence relating to it is contradictory, and requires further investigation.

The majority of studies of polymer adsorption onto the surface of talc and other minerals have been performed using bulk adsorption techniques. While these techniques provide valuable information regarding the adsorption characteristics of polymers onto the mineral surfaces, they cannot be used to evaluate the changes in surface charge of mineral as a result of polymer adsorption. Such information can however be obtained using rheological measurements since these measurements strongly reflect mineral surface properties. From the available information, the following general hypothesis can be put forward:

Rheological measurements of talc suspensions in the presence of polymeric depressants provide important information regarding the adsorption mechanism of these depressants. Rheological behaviour of talc suspensions in the presence of guar gum *will be consistent with the adsorption of guar gum onto the basal planes of talc. Rheological behaviour of talc suspensions in the presence of CMC will be consistent with electrostatic attraction being a major adsorption mechanism of CMC onto talc, with the adsorption taking place primarily on talc edges.*

2.5.3 Effect of metal cations on the surface charge of talc and polymer adsorption

The presence of metal cations in the water used in flotation processes has been found to have a strong effect on the performance of industrial flotation systems. The presence of metal cations in the aqueous phase of flotation pulps has been shown to have a strong effect on the surface charge of mineral species (Fuerstenau *et al.* 1988), adsorption characteristics of reagents (Morris *et al.* 2002; Parolis *et al.* 2004; Ma and Pawlik 2005; Ma and Pawlik 2006; Parolis *et al.* 2006) as well as an effect on the conformational structure of polymeric depressants (Pawlik *et al.* 2003; Parolis *et al.* 2006; Pawlik and Laskowski 2006).

However, bulk adsorption tests do not provide direct measurements of the presence of polymer on the mineral surface, but rather infer it form differences in polymer concentration in solution. Emerging techniques such as ToF-SIMS are now able to provide such information that is specific to selected particle planes (such as basal planes and edges).

It is hypothesised that the adsorption of divalent calcium ions and monovalent potassium ions on the surface of talc has an effect on the surface charge distribution of talc particles and affect the adsorption characteristics of CMC. The adsorption characteristics of CMC are further complicated by the effect that metal cations have on the conformation of CMC macromolecules.

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3 Experimental Details

3.1 MATERIALS

3.1.1 New York Talc

New York talc, obtained from Wards Minerals, was used in the test work. The talc was dry ground in a titanium ring mill to yield a p50 of 23 µm with the top size not exceeding 100 µm. The cumulative size distribution plot is shown in Figure 3.1. The composition of talc was determined using electron microprobe analysis, with the details shown in Table 3.1.

Table 3.1 - Detailed microprobe analysis of the New York talc sample

Compound	% Composition	Standard Deviation
SiO_2	61.83	1.915
Na_2O	0.16	0.065
TiO_2	0.03	0.016
CaO	0.42	0.458
Al_2O_3	0.36	0.227
MgO	31.27	1.370
Cr_2O_3	0.02	0.010
FeO	0.19	0.153
MnO	0.25	0.217
Total	94.53	0.823

The BET isotherm analysis showed that the talc surface area was 10.25 m^2/g of talc.

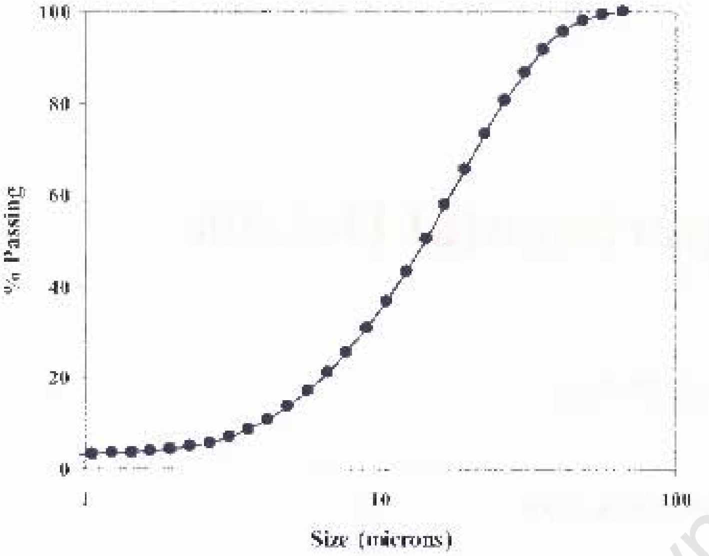

Figure 3.1 – Cumulative size distribution of the New York talc sample

3.1.2 Polymeric depressants

The CMC used in this study was DEP267, supplied by Akzo Nobel Industrial minerals. The purity of this polymer is ≈ 70%, with the molecular weight of ≈ 320 000 Dalton and the degree of substitution of 0.65.

The guar gum used in this study was CZD 519, supplied by Chemzyme. The purity of the polymer is ≈ 95% , with the molecular weight of ≈ 400 000 Dalton.

The detailed weight distribution of these polymers was determined by size exclusion chromatography and is shown in Appendix D.

3.1.3 Solution additives

In all tests, $CaNO_3$ and KNO_3 solutions were used as a source of Ca^{2+} and K^{+} ions respectively. The pH modification was performed with the use of nitric acid and potassium/calcium hydroxide, depending on which salt was present in solution.

3.2 ZETA POTENTIAL MEASUREMENTS

The zeta potential measurements were performed using the Malvern Zeta-sizer. Samples were prepared in 25 ml test tubes, using 0.50g of talc and 20 ml of solution, containing varying concentrations of electrolyte. The samples were allowed to settle overnight. The supernatant fluid was then withdrawn with a syringe and placed inside the analysis probe to perform the measurement. It was assumed that the particles present in the supernatant fluid were representative of the bulk solids sample due to the high purity and homogeneity of the New York talc samples.

The electrophoretic mobilities of the talc particles were used to calculate the zeta potentials using Smoluchovski's equation (Dukhin and Derjaguin 1976).

3.3 RHEOLOGICAL MEASUREMENTS

Talc suspensions of volumetric solids fraction (ϕ) of 0.42 were prepared in 20 ml aliquots at varying levels of Ca^{2+} and K^{+} ion concentrations and pH levels. The solutions were allowed to equilibrate for 1 hour before measurement. The solutions were all prepared at room temperature, which was measured to be 23 ± 0.5 °C. Each measurement point presented in the results in the following chapters represents an individually prepared and measured sample.

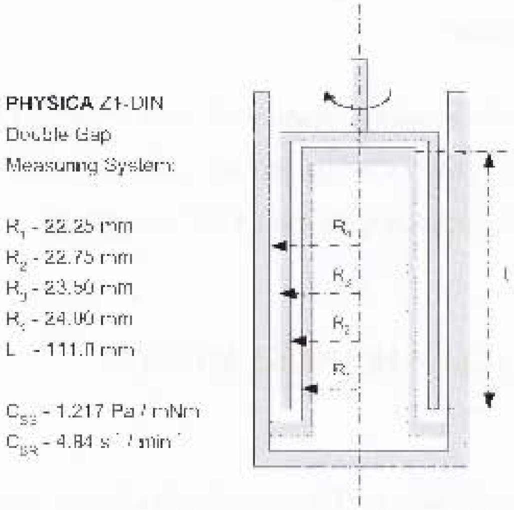

Figure 3.2 - Schematic representation of the double gap rheological measuring system

Yield stress measurements were performed using a Paar Physica MC 1+ rheometer. The measuring geometry used was a double gap curette cylinder, with a gap size of 0.5 mm, as shown in Figure 3.2. The measurements were performed in a shear rate controlling regime, with the shear rate ranging between 30 and 200 s^{-1}. The resulting curves were modelled using the Casson Equation (3.1) in order to calculate the Casson yield stress. Figure 3.3 shows the typical rheograms and Casson models used in the calculation.

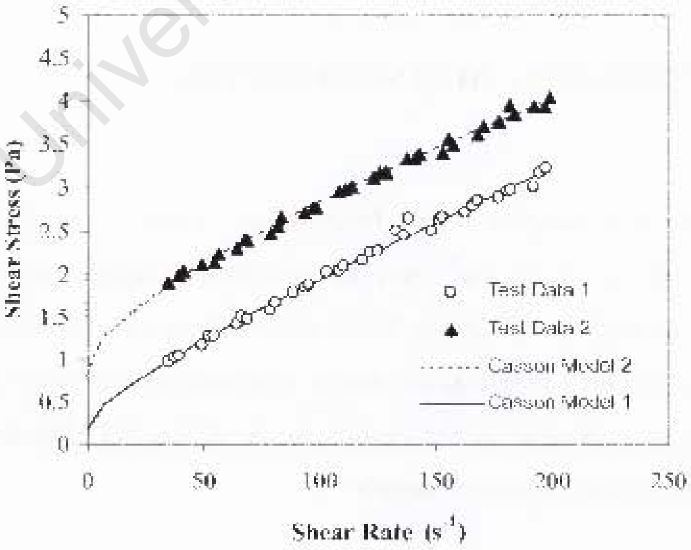

Figure 3.3 - Typical rheograms of talc suspensions, fitted with the Casson Model

$$\sqrt{\tau} = \sqrt{\tau_C} + \sqrt{\eta_C \cdot \gamma} \qquad (3.1)$$

τ – Shear stress (Pa)

τ_C – Casson yield stress (Pa)

γ Shear rate (s^{-1})

η_C - Casson viscosity (Pa s)

3.4 POTENTIOMETRIC TITRATION

The apparent point of zero charge of talc minerals was determined using the Roberts-Mular titration method (Mular and Roberts 1966). In this method the pH of a suspension is measured at different ionic strengths of the solution. Each measurement point presented in the results in the following chapters represents an individually prepared and measured sample.

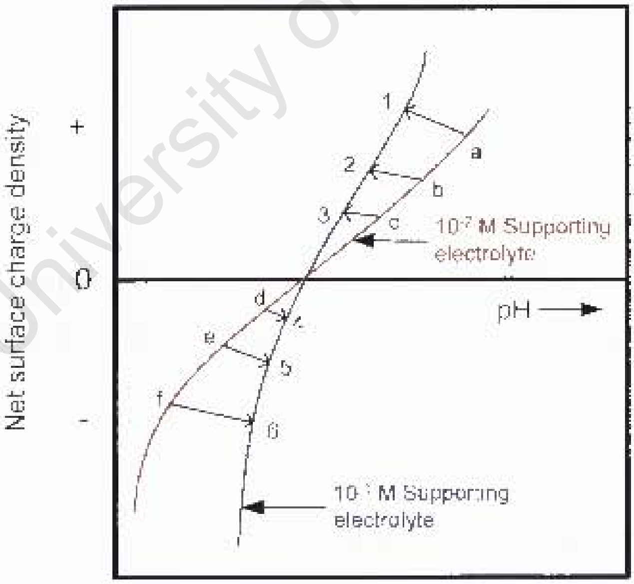

Figure 3.4 - Schematic representation of the Roberts-Mular potentiometric titration method (Mular and Roberts 1966)

The pH of the solutions was then measured again to yield a final pH The difference in the initial and final (after increasing ionic strength) pH values is calculated and plotted versus the final solution pH. The point where the ΔpH value equals zero indicates the pH of the apparent point of zero charge of the mineral. the schematic representation of the measurement principle is shown in Figure 3.4.

3.5 INTRINSIC VISCOSITY MEASUREMENTS

The intrinsic viscosity measurements were performed using a Lauda PVSI capillary viscometer, in conjunction with a three tube Ubbelohde capillary. The polymer solutions were made at varying concentrations, with 10^{-2} M KNO_3 as supporting electrolyte. The pH of the solutions was adjusted drop-wise with nitric acid and potassium hydroxide.

The reduced viscosity and intrinsic viscosity values were calculated using the Huggins equation (3.2) (Huggins 1942).

$$\eta_{red} = [\eta_{rel} - 1]/C \qquad (3.2)$$

$$\eta_{red} = [\eta] + k[\eta]^2C$$

η_{rel} – Relative viscosity

η_{red} – Reduced viscosity (l/g)

η – Intrinsic viscosity (l/g)

C – Solution concentration (g/l)

k – Huggins coefficient (l/g)

3.6 TOF-SIMS MEASUREMENTS

3.6.1 Sample preparation

Large talc flakes were manually picked out of a +150 μm talc sample, which had been ground in a titanium ring mill. Solutions of varying ionic strengths, pH values and concentrations of DEP 267 were made up in 10 ml sealable plastic test tubes. 0.5 g of talc particles were placed inside each test tube and allowed to equilibrate for 1 hour. After an hour the particles were filtered out using a vacuum funnel and gently rinsed with distilled water adjusted to pH 9, to prevent any bulk solution from adhering to the mineral surface. The particles were dried in a convection oven at 50° C. Out of the 0.5 g sample, six particles were randomly selected and manually placed on an adhesive surface (post note) such that the orientation of three of the particles was face-up, while the other three were edge-up. An example of the prepared samples is shown in Figure 3.5.

Figure 3.5 – Example of the New York talc particles prepared for ToF-SIMS analysis

3.6.2 ToF – SIMS analysis

The measurements were performed on the IONTOF Secondary Ion Mass Spectrometer, provided by TASCON GMBH, in Munster, Germany. The measurement analysis was performed by Kees van Leerdam (Akzo Nobel Functional Chemicals). The primary excitation ion was Bi^{+3}. The spectra and images were taken in bunched mode (focus: 3-

5 μm), with a mass resolution of 5000-10000. Cycling time of the instrument was set to 200 μs, allowing the acquisition of spectra up to a mass to charge ratio of 1800.

In order to make the measurements obtained for the different samples comparable, the ionic intensities were normalised with respect to the intensity of the silicon mass spectrum.

The detection of CMC was achieved by detecting the mass spectra of the charged carboxylic acid groups of CMC molecules ($C_3H_6O_2$ and $C_2H_4O_2$) as shown in Figure 3.6.

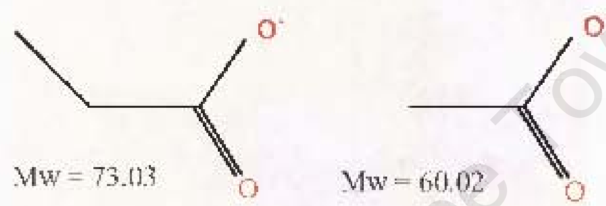

Figure 3.6 - Carboxylic acid groups used to detect CMC intensities by ToF-SIMS

3.7 MICROPROBE ANALYSIS

The chemical composition of talc was determined by mineral analysis of polished thin sections of New York talc with a Jeol Superprobe JXA8100. The probe power output was set at 15kV, 20nA with 10s peak and 5s background counting time. The beam size was approximately 5-10 microns. The analysis was performed by Megan Becker (Centre for Minerals Research, UCT).

The exact chemical formula of talc was determined by balancing the cations present in the sample (as detected by the microprobe) with the oxygen content of the oxide species containing these cations. This procedure is described in detail by Deer, Howie and Zussman, (Deer *et al.* 1997).

In order to determine the amount of crystalline water (OH^-) contained within the talc sample, several 2.00 g talc samples were dehydrated in a furnace at a temperature exceeding 950 °C, over a period of 48 hours. The amount of water was calculated the difference in the mass of the talc samples before and after roasting.

3.8 STATISTICAL TOOLS

The following statistical tools were used in the analysis of the experimental data.

3.8.1 Standard deviation

The true standard deviation (σ) represents the spread of the normal distribution of a sample population. This value can be estimated, as shown in Equation 3.3 (Napier-Munn 1994).

$$s = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}} \tag{3.3}$$

s – Estimated standard deviation
N – Number of observed values (data points)
x_i – i^{th} observed value
$\bar{x}$ – Average of all the observed values

3.8.2 Standard error

The standard error provides a confidence value of the mean of the dataset, as shown in Equation 3.4 (Napier-Munn 1994).

$$s_{\bar{x}} = \frac{s}{\sqrt{N}} \tag{3.4}$$

$s_{\bar{x}}$ – Standard error

s – Estimated standard deviation

N – Number of observed values (data points)

3.8.3 95% confidence limit

The 95% confidence limit represents the probability of the quoted value lying within the specified region (Napier-Munn 1994). For example, the true value μ, will lie in the region:

$$\left(\bar{x} - z \cdot s_{\bar{x}}\right) < \mu < \left(\bar{x} + z \cdot s_{\bar{x}}\right)$$

Where:

μ True value of the mean

$\bar{x}$ – Average of all the observed values

$s_{\bar{x}}$ – Standard Error

z – Probability value (from statistical tables)

3.8.4 95% confidence limit on linear regression parameters

The elliptical confidence intervals of regression lines represents the probability that the true regression line lies within the specified limits, as shown in Equation 3.5 (Weisberg 2005).

$$CL \Rightarrow y_0 \pm t_{(0.05,N-2)} \cdot \sqrt{MS_E \cdot \left(\frac{1}{N} + \frac{\left(x_0 - \bar{x}\right)^2}{Sxx}\right)} \qquad (3.5)$$

CL Confidence limits

N – Number of data points

y_0 – Predicted value of y at the intercept (x=0)

x_0 – Value of x at the intercept (x=0)

$\bar{x}$ – Average of all the x values

Sxx – Sum of the squares of Average of all the x values

MS_E – Mean square of residual errors

$t_{(0.05,\,N\text{-}2)}$ – Students t distribution at 95% confidence, with N-2 degrees of freedom

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4 Talc Surface Charge Distribution

4.1 INTRODUCTION

Surface charge is one of the key factors that influence the behaviour of the mineral particles in suspension. Talc surface charge is therefore an important variable which affects the behaviour of talc in flotation systems. This chapter seeks to infer the surface charge distribution of talc particles using a combination of various techniques such as potentiomteric titrations, rheology, ToF-SIMS analysis as well as electron microprobe analysis.

The majority of information regarding the surface charge distribution of talc has been obtained by means of electrophoretic zeta potential measurements. However, electrophoretic measurements are ill suited for the determination of the surface charge of plate like anisotropic minerals due to the complications arising from the complex hydrodynamics of such particles in aqueous suspensions (Dukhin and Derjaguin 1976; Lyklema 1995).

The crystallochemical structure of talc is similar to that of kaolinite, since they both originate from the same family of sheet silicate minerals. The main difference between the two is that kaolinite is a 1:1 sheet silicate composed of a Si - O tetrahedral layer and an octahedral Al - OH layer, while talc is a 2:1 sheet silicate in which the octahedral layer is sandwiched between two tetrahedral layers.

Similarly to talc, the basal planes of kaolinite were once considered completely neutral, however they have later been shown to carry a negative charge due to the isomorphic substitution of Si^{+4} ions with Al^{+3} ions in the tetrahedral layers (Van Olphen 1951; Swartzen-Allen and Matijevic 1974). It has recently been demonstrated (Carty 1999) that kaolinite is an asymmetric 1:1 sheet silicate and that the previously drawn conclusions apply to the tetrahedral plane only.

Talc particles have also been shown to contain random impurities including Al^{+3} ions that exhibit similar substitutions with Si^{+4} ions on the tetrahedral layers of talc (Deer *et al.* 1978; Deer *et al.* 1992). However, despite this fact, the basal planes of talc are continually believed to be electrically neutral by a majority of researchers.

This chapter compares available talc electrophoretic data to the rheological behaviour of talc suspension. It also examines the potentiomteric titration measurements of these suspensions in order to validate/invalidate the use of zeta potential measurements in studying talc surface charge distributions.

This chapter also investigates the possibility of the presence of a negative charge on the basal planes of talc due to the known substitutions of silicon ions in the tetrahedral layers of talc with ions of a lesser charge.

4.1.1 Hypotheses

The basal planes of talc carry a negative charge resulting from natural substitution of silicon ion with ions of a lesser valency on the talc basal planes, while the charge on the edges of talc changes as a function of pH. As a result the surface charge distribution of talc cannot be studied using electrophoretic measurements.

This hypothesis can be broken down into a number of more specific hypotheses:

- The currently accepted value of the isoelectric point of talc at pH ≈ 2.5 does not correspond to the point of zero charge of New York talc.
- The basal planes of New York talc carry a negative charge in entire pH range due to the isomorphic substitution of Si^{4-} ions with Al^{3-} ions in the tetrahedral layer of talc, resulting in an overall proton deficiency on the talc basal plane surface.

- The edges of talc undergo a change from positive to negative at a pH significantly higher than its electrophoreticaly determined isoelectric point of pH ≈ 2.5.

4.2 TALC RHEOLOGICAL BEHAVIOUR

As mentioned in previous chapters, yield stress is a good indicator of the degree of coagulation of a suspension, which is strongly related to the surface charge of the mineral in suspension.

It is important to note, that if the basal planes of talc do not carry a negative charge, then the rheological behaviour of talc should be similar to isotropic minerals when placed in a solution. In that case, if the measured apparent isoelectric point of talc does indeed represent a true isoelectric point, then the yield stress peak and the isoelectric point should converge on the same value (pH ≈ 2.5).

Rheological measurements were performed in a manner described in Chapter 3, where the obtained rheological curves were modelled using the Casson equation to obtain the Casson yield stress values for these suspensions.

The reproducibility of the rheological data was tested by performing replicate tests under a limited set of conditions and determining the 95% confidence interval for these measurements. The results of the reproducibility tests are shown in Table 4.1. The details of the analysis are shown in Appendix C.

Table 4.1 – Confidence limits of the rheological data

Measurement	**95% Confidence Interval**
Casson Yield Stress	± 0.05 Pa
pH	± 0.1

The results are shown in Figure 4.1 (please note that the line is drawn only to guide the eye). The results show that the rheological behaviour of talc is similar to that of other minerals (such as kaolinite and zircon), where the suspension yield stress changes as a function of pH, with the maximum occurring at pH ≈ 5.5. This trend is verified by the fact that the difference between the measurement points exceed ± 0.05 Pa, which makes them significant on the 95% confidence interval.

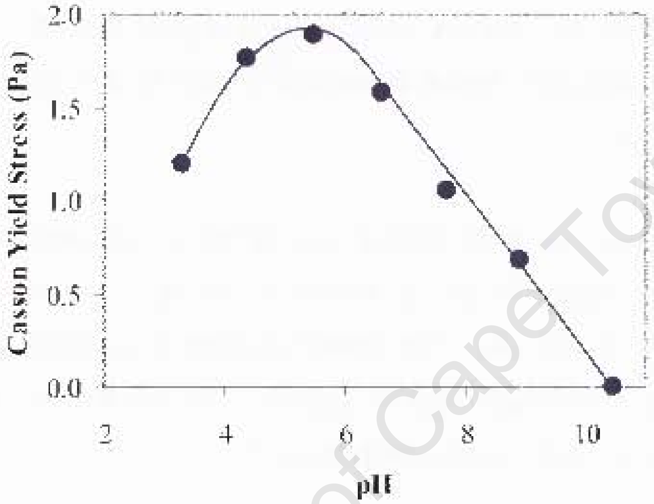

Figure 4.1 - Yield stress curve of talc suspensions as a function of pH

The rheological behavior of talc suspensions can now be compared to other available information, such as the zeta potential of talc as a function of pH, to see if the yield stress peak of talc suspensions coincides with the electrophoretic isoelectric point.

The results of the comparison are shown in Figure 4.2, which indicates that the point of maximum Casson yield stress of talc suspensions lies at a significantly higher pH than the isoelectric point of New York talc.

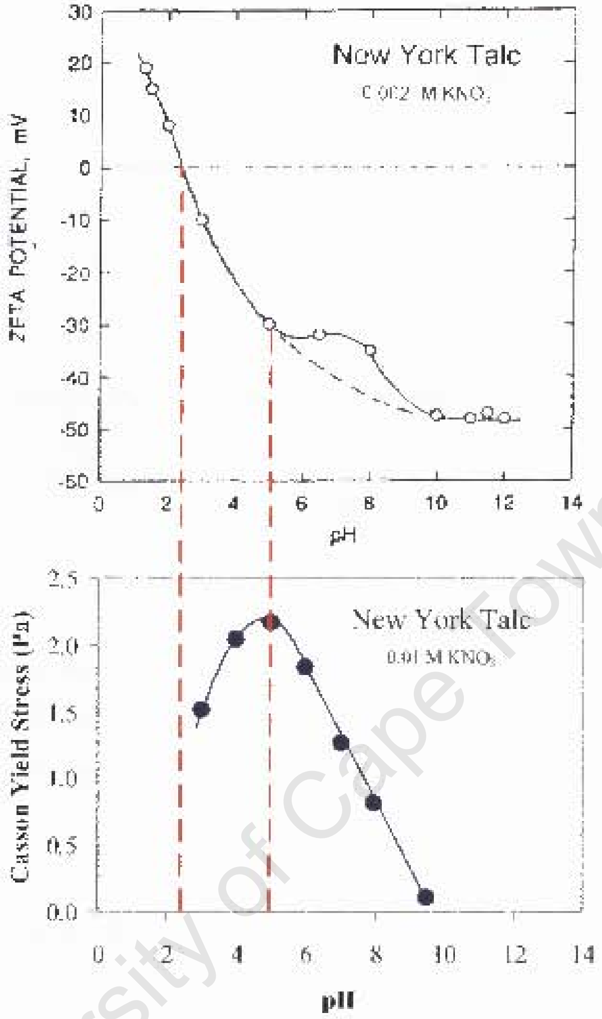

Figure 4.2 – Zeta potential of New York talc suspensions showing the suspension isoelectric point (Fuerstenau and Huang 2003), along with the yield stress curve of talc suspensions as a function of pH

At this stage, it is important to re-iterate that in the case of plate like minerals such as talc and kaolinite, electrophoretic zeta potential measurements do not provide adequate descriptions of minerals surface properties. Electrophoretic mobility of these particles is complexed by the hydrodynamics due to their irregular shape, and therefore Smoluchowski´s equation cannot be used to calculate the zeta potential value for such cases. Smoluchowski´s equation was derived for spherical or near-spherical particles with electrical charge evenly distributed over the surface of such particles. No model currently exists that can describe the movement of plate like anisotropic particles in an electrical field (Lyklema 1995).

4.3 POINT OF ZERO CHARGE OF TALC

Since electrophoretic measurements of plate like minerals should not be relied on when determining the charge distribution of these minerals, another method must be employed in order to estimate the point of zero charge of talc particles, so that it can be correlated with the yield stress values for talc suspensions.

In this thesis the point of zero charge of talc has been determined using the Roberts-Mular titration. Such titration methods have been successfully used to estimate the points of zero charge/isoelectric points of oxide mineral at the time when zeta meters were not yet commercially available (Mular and Roberts 1966; Laskowski and Sobeiraj 1969).

The R-M titration works on the principle of ion exchange in solution and is independent of the shape of the mineral particles. This eliminates the problems of the hydrodynamics of plate-like particles associated with electrophoretic mobility measurements. It is therefore expected that in the case of plate like minerals, the point of zero charge measured by titration will be different from the isoelectric point as measured by electrophoresis.

In the specific case of talc, if the basal planes of talc do not carry an electrical charge and are completely neutral, then the point of zero charge as measured by titration is expected to converge on the point of maximum yield of talc suspension. The titration results compared to both the zeta potential measurements and the rheological measurements are shown in Figure 4.3.

It is important to note that in the case of anisotropic minerals, the overall point of zero charge does not exist at any pH, it may only indicate the pH at which the charge of the positively charged sites is more or less identical to the charge of negative sites. Various sites of the crystal planes may still carry an electrical charge (see Figure 2.13 as an example). Therefore, the point of zero charge as determined by titration does not represent the point where the overall charge is zero, but rather the value where the net charge is equal to zero. In other words, the net point of zero charge occurs at a point where the magnitude of the positive charge on one of the particle planes is equal to that of a negative charge on a different particle plane.

The results show that the point of zero charge of talc (pH 7.7 ± 0.45) does not correspond to the electrophoretic isoelectric point of talc (pH 2.5). This demonstrates the disparity between electrophoretic and titration measurements, indicating that the former is impaired by problems arising from the complex hydrodynamics of the plate-like particles in solution. Therefore, the electrophoretic isoelectric point should not be used as an adequate representation of the point of zero charge of the mineral and must be referred to as an "apparent" isoelectric point.

Furthermore, the measured net point of zero charge (pH 7.7 + 0.45) does not converge with the point of maximum Casson yield stress (pH 5.5 ± 0.1). The shift of the maximum coagulation point away from the point of zero charge indicates that talc does not behave in a manner consistent with an isotropic mineral.

The results shown in Figure 4.3 indicate that there exists an attractive force between talc particles other than the van de Waals force, which causes the suspensions to coagulate at a point where the charge of the particles is non-zero. This behaviour is consistent with the presence of an attractive electrostatic force between mineral particles, which causes the suspensions of talc to coagulate in a pH range where two oppositely charged particle planes are present, i.e. heterocoagulation is taking place. These observations point to a strong possibility that the basal planes of talc are not neutral, but carry a negative charge.

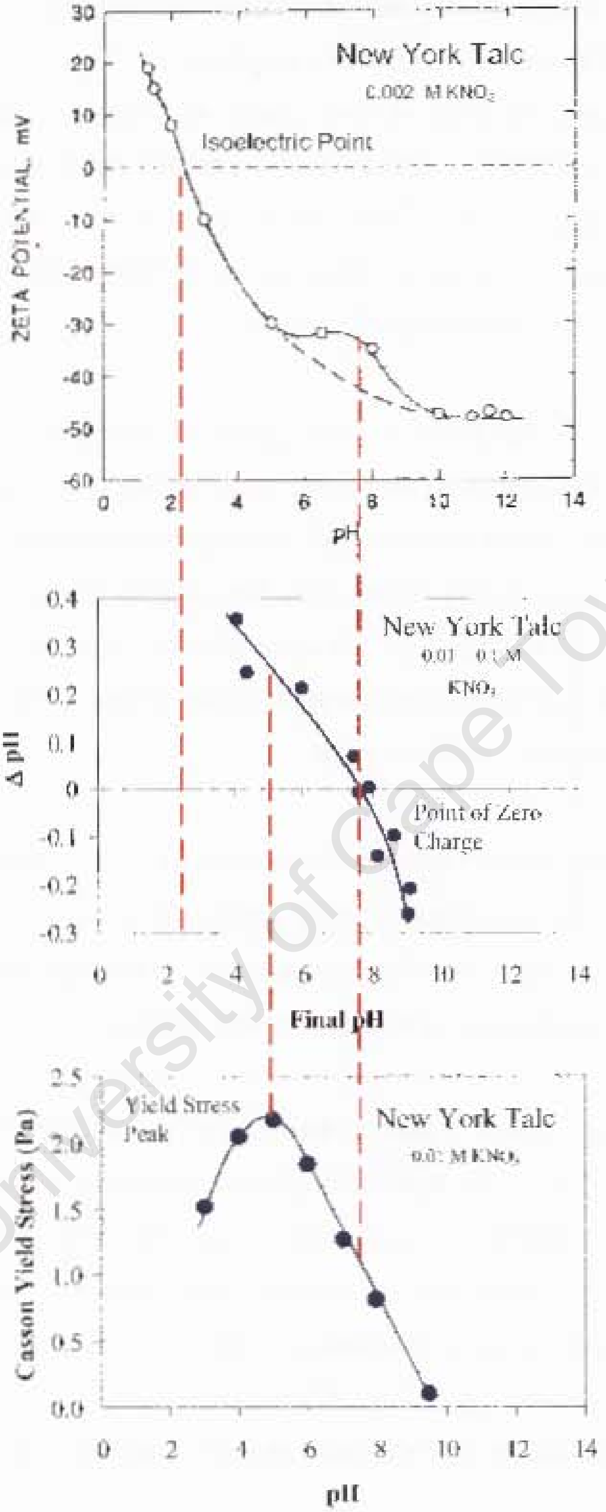

Figure 4.3 – Potentiometric titration of talc compared to the zeta potential of New York talc suspensions (Fuerstenau and Huang 2003), along with the yield stress curve of talc suspensions as a function of pH

4.4 COMPARISON WITH OTHER MINERALS

In order to re-emphasise the findings of the previous sections, the behaviour of talc can be compared to other minerals, both isotropic and anisotropic. Zircon and kaolinite were chosen to represent isotropic and anisotropic minerals respectively; the results are shown in Table 4.2.

The values presented in Table 4.2 show that for isotropic zircon, all three mineral properties converge on a single value (Subbanna *et al.* 1998; Johnson *et al.* 1999; Burdukova *et al.* 2006; Tombacz and Szekeres 2006), with slight variations depending on the source of zircon.

Table 4.2 - Comparison between the characteristics of suspensions of talc, kaolinite and zirconia, reflecting their surface properties

Mineral Properties	**pH – Zircon**	**pH - Kaolinite**	**pH – Talc**
Electrophoretic Isoelectric Point	6 – 7	3.5	2.5
Titration Point of Net Zero Charge	6.5	6.5	7.7
Yield Stress Peak	6	6	5.5

These values show that in the range between pH 6 and 7, zircon particles reach a point of zero charge, as measured by both titration and electrophoresis. At this point the only inter-particle forces present are the attractive van de Waals forces. This causes the suspension to coagulate, resulting in a peak in the yield stress of the suspension.

On the other hand, in the case of anisotropic kaolinite, isoelectric point and yield stress do not converge but **diverge**. The point of maximum coagulation does not occur at the point where the electrophoretic mobility is zero, but rather at the point where the attractive force between two oppositely charged particle planes occurs, causing the suspension to heterocoagulate.

Table 4.2 shows that the behaviour of talc closely resembles that of anisotropic kaolinite, because its point of maximum coagulation and its isoelectric point diverge from one another as opposed to converging as is the case with isotropic zirconia. This is a further indication that the basal planes of talc could carry a negative charge. It follows that the edges of talc serve as a source of positive charge that is responsible for the shift of the point of maximum aggregation away from both the isoelectric point and the point of zero charge.

4.5 PROPOSED TALC SURFACE CHARGE DISTRIBUTION

Based on the observations made in Section 4.4, it is proposed that the basal planes of talc carry a negative charge in the majority of the pH range. It is also proposed that the edges of talc undergo a change from positive to negative at a pH below 7.7 (point of net zero charge).

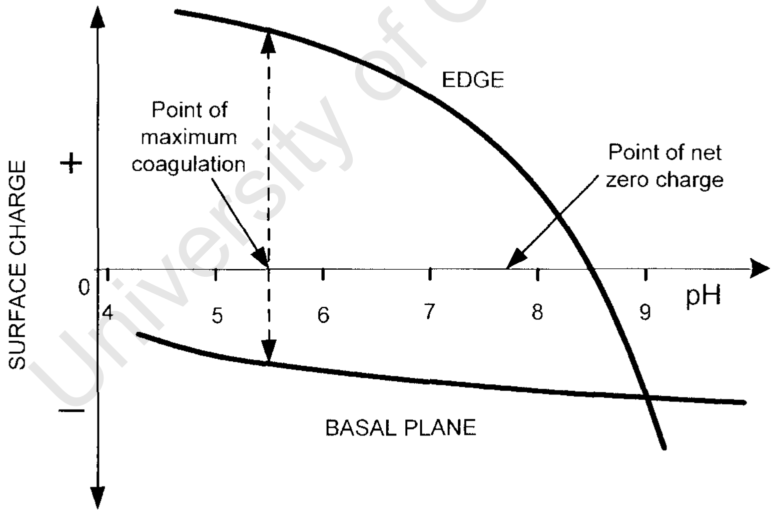

Figure 4.4 – Proposed charge distribution on the surface of talc

A schematic representation of the proposed surface charge distribution of talc is shown in Figure 4.4. This analysis is similar to that applied to Kaolinite by Johnson *et al* (1999). It is important to note that no attempt has been made to quantify the magnitudes of the surface charge on either basal planes or edges of talc. The diagram is merely a representation of the possible charge configuration.

4.1 POSSIBLE SOURCES OF NEGATIVE CHARGE

If the basal planes of talc carry a negative charge as suggested in the previous sections, the most likely source of that charge is the substitution of Si^{4+} ions with Al^{3+} ions in the tetrahedral layer of talc. Such substitution occurs in the tetrahedral layers on the basal planes of kaolinite (Van Olphen 1951; Swartzen-Allen and Matijevic 1974). Similar substitutions have also been demonstrated for talc from various mineralogical sources (Deer *et al.* 1997).

4.5.1 Distribution of aluminium on the surface of talc

The microprobe analysis of New York talc (see section 3.1.1) showed that the analysed samples contained 0.03 % of aluminium. A ToF-SIMS analysis of New York talc was performed in order to see whether or not this aluminium content forms part of the crystal lattice of talc and is not a part of a cluster of contaminating particles.

ToF-SIMS analysis allows one to obtain a semi-quantitative indication of which ionic species are present in the top monolayer of a mineral surface. Unfortunately, in the case of phyllosilicates the crystal lattice is loosely structured, with large gaps in the tetrahedral layers. This structure is illustrated in Figure 4.5.

The large gaps in the tetrahedral layer allow the ionic species present in the deeper layers of the mineral to escape the lattice and be detected by the ToF-SIMS instrument. This means that it is impossible to tell whether the ionic spectrum seen on a ToF-SIMS image corresponds to the ions inside of the tetrahedral layer, or to deeper octahedral layers.

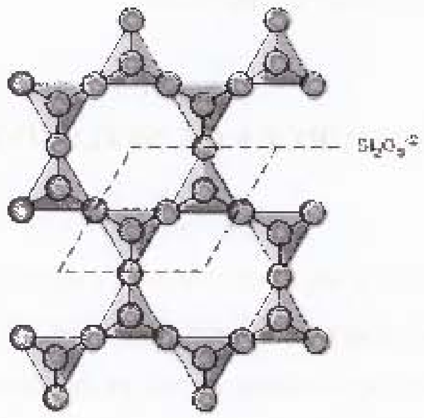

Figure 4.5 – Top view of the crystallographic structure of a phylosilicate mineral, showing large gaps in the topmost tetrahedral layer (Nesse 2000)

Furthermore, ToF-SIMS detection of Al^{3+} ions is particularly difficult in case of minerals containing large amount of MgH^{+} ionic species (as is the case with talc). These ions have a very similar molecular mass to Al^{3+} (they both have a molecular mass of 13 g/mol) and tend to obstruct the aluminium peak, making it difficult to isolate. For this reason, ToF-SIMS images of aluminium on talc should not be viewed in isolation, but rather be corroborated by another technique.

ToF – SIMS measurements were performed on a sample of talc that was dry ground in a titanium ring mill and washed in distilled water to prevent any contamination of the surface. In order to perform the measurements the sample particles were placed onto an adhesive surface with their basal planes facing up. The sample preparation procedure is outlined in detail is prepared Chapter 3.

The SEM image of a talc basal plane and the corresponding ToF-SIMS spectrum are shown in Figure 4.6. The advantage of having both the SEM and ToF-SIMS image of the same particle from the same vantage point is the consequent ability to superimpose the two images. This allows one to judge the distribution of the spectrum with regards to the surface features of the particle.

It is important to note that the superimposition is not exact and should only be used as a general guideline in determining whether or not a spectral image corresponds to a desired particle plane.

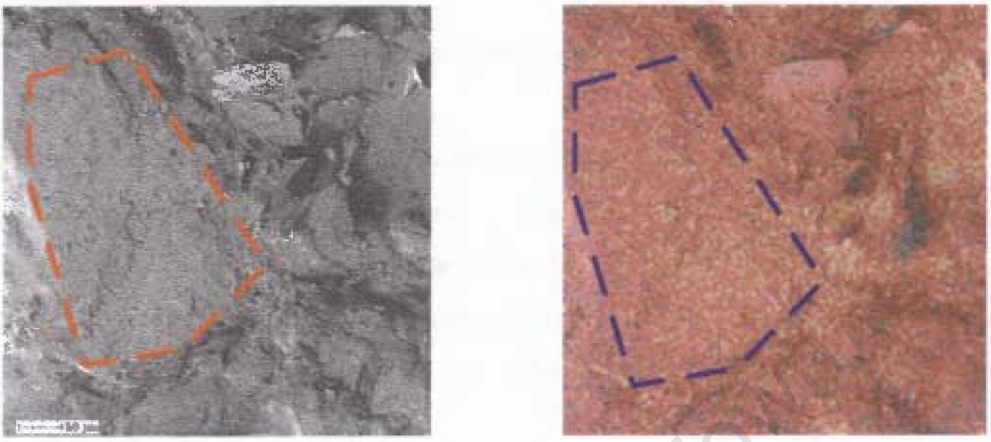
(A) (B)

Figure 4.6 - (A) SEM image of a basal plane of a talc particle, (B) Corresponding ionic spectrum of aluminium ions, superimposed onto the original SEM image of the talc particle, with selected areas of analysis.

Figure 4.6 (A) shows that the particle in question does not consist of an ideal basal plane surface, but rather of a basal plane surface that shows a lot of damage through sample preparation. For that reason, the area of analysis was selected such that it only contains the section of the particle that displays an undamaged basal plane.

Figure 4.6 indicates that the aluminium spectrum is evenly distributed throughout the basal plane of the talc particle. This implies that the ions form part of the crystal lattice, rather than coming form a single cluster of contaminating mineral. As mentioned previously, ToF-SIMS is only a semi-quantitative technique and the spectra cannot be used to estimate the exact quantity of ions present on the surface.

4.5.2 Quantity of aluminium in New York talc

In order to estimate the exact amount of aluminium ions present in New York talc, as well as determine whether or not they are substituting for silicon ions in the tetrahedral layers, the exact crystalline formula of New York talc had to be calculated. The formula was determined by using electron microprobe analysis.

Microprobe analysis works by focusing a beam of electrons onto the mineral surface The result is the emition of X-rays with a wave length specific to every individual compound (with the exception of hydrogen, helium and lithium). This technique is a standard one in geological applications and has been widely used to characterise talc (Deer *et al.* 1978; Bose and Ganguly 1994).

The microprobe analysis was carried out on a polished thin section of New York talc. The detailed information is shown in the Appendix, the summary of the key constituents is presented in Table 4.3.

Table 4.3 shows that the majority of the New York talc sample (ideal formula $Mg_6Si_8O_{20}(OH)_4$) consisted of silicon oxide and magnesium oxide species, as expected. The results also show that the talc sample contains small amount of aluminium and titanium oxide species.

Table 4.3 – Electron Microprobe Analysis of New York Talc, $Mg_6Si_8O_{20}(OH)_4$

Compound	Weight %	Standard Deviation
SiO_2	61.83	1.92
TiO_2	0.03	0.02
Al_2O_3	0.36	0.23
MgO	31.27	1.37
Total	94.53	0.823

The results also show that the total weight fraction of the sample does not add up to 100 %. This is due to the fact that microprobe analysis is unable to detect hydrogen ions and is therefore unable to estimate the amount of water present in the crystal lattice. By difference, the talc sample should contain 5.47 ± 0.823 % water to make up 100% of the sample weight (the error shown is the standard deviation of the sample population).

The actual amount of water contained within New York talc was experimentally measured by dehydrating the talc samples in a furnace at 950 °C for 48 hours. The samples were first pre-dried in an oven at 110 °C overnight to remove any non-crystalline moisture from the sample. The proportion of crystalline water was found to be 4.52 ± 0.14 % and this value is in close agreement to those obtained in similar studies of New York talc (Bose and Ganguly 1994), as well as with the expected value from the microprobe analyses.

From the available mineral and dehydration data, the exact chemical formula of the non-ideal sample of New York talc can be calculated, The formula calculation procedure is simple but an involved one and consists of a number of steps, which are described in detail in the Appendix A. This analysis is also described in detail by Deer, Howie and Zussman (Deer *et al.* 1992).

The error in the analysis is expressed as a standard deviation of the sample populations. Due to the complex, multi-step analysis of the data, the conventional method of calculation of the propagated error through a mathematical formula by differentiation was not feasible. The error analysis was performed by means of a numerical "re-sampling" method. In this method the calculation is performed multiple times with the values of the input parameters varying randomly within the experimentally determined standard deviations (some of the standard deviation values of the input variables are shown in Table 4.3).

The mean and standard deviation of the output parameters was then calculated from the population of possible calculation outcomes. This method provides a close estimate of the mean and standard deviation of the output as long as a sufficiently large number of points is sampled. In these calculations the input parameters were sampled 10 000 times. The results of the calculation for the key constituents are shown in Table 4.4. The details of the calculation as well as the remainder of the calculation results are shown in the Appendix A.

Table 4.4 – Calculated number of cations in a single crystalline cell of New York talc

$Mg_6Si_8O_{20}\,(OH)_4$

Cation	**Mean Number of Cations**	**Standard Deviation**
Si	7.96	0.12
Ti	0.00	0.00
Al	0.03	0.02
Mg	6.00	0.23

The results presented in Table 4.4 can now be re-arranged according to the following categories: those in the tetrahedral layer and octahedral layer of talc. According to the ideal chemical formula of New York talc, $Mg_6Si_8O_{20}\,(OH)_4$, the various cations can be arranged in a manner shown in Table 4.5.

Table 4.5 – Ideal distribution of cations in New York talc $Mg_6Si_8O_{20}\,(OH)_4$

	Number of Cations
Tetrahedral layer (Si)	8
Octahedral layer (Mg)	6

In real mineral samples, these values rarely add up to the ideal amounts due to substitution with other ions. Therefore by comparing the actual values to the ideal values, the degree of substitution taking place within every layer can be calculated. Due to the similarity in size and charge, Al and Ti ions substitute for silicon, while Ca ions substitute for magnesium (Deer *et al.* 1978). The rearranged values are shown in Table 4.6.

Table 4.6 shows that the number of Si^{+4} ions present in the tetrahedral layer is insufficient to completely fill the available cation sites. A small proportion of the sites is therefore taken up by Al^{+3} ions. This means that there is a small but definite deficiency in the number of protons available in the tetrahedral layers of talc, which will result in a definite presence of a negative charge on the basal planes of talc.

Table 4.6 – Distribution of cations in New York talc samples

	Cation	Mean Number of Cations	Standard Deviation
Tetrahedral layer	Si	7.96	± 0.123
	Al	0.03	± 0.017
	Ti	0.00	± 0.002
	Total	**7.99**	**± 0.124**
Octahedral layer	Mg	6.00	± 0.232

However, the results also show that the amount of substitution is very small, only 0.03 ± 0.017 cations out of eight. This amounts to 0.35 ± 0.21 % of the cations in the tetrahedral layer. It is arguable whether such an amount (viewed in isolation) would be sufficient to significantly alter the surface charge of the talc basal planes.

In order to ascertain whether or not such a small amount of substitution would be sufficient to cause major changes in charge of mineral planes, the obtained substitution values can be compared to that of kaolinite. The strong negative charge on the tetrahedral planes of kaolinite is well attested to, as well as measured by a number of researchers (Van Olphen 1951; Schofield and Samson 1954; Swartzen-Allen and Matijevic 1974; Williams and Williams 1977; Johnson *et al.* 1999).

The degrees of substitution of silicon with aluminium in kaolinite for a number of different kaolinite deposits have been reported to range between 0.5% and 1.5% (Deer *et al.* 1978; Deer *et al.* 1992). These values are of a similar magnitude and are therefore comparable to the value obtained for talc (0.35 ± 0.21 %). This means that the magnitude of substitution of silicon ions with aluminium ions in the tetrahedral layers of talc is sufficient to produce a significant negative charge.

Furthermore, the rheological and titration evidence presented in earlier sections confirms this. The results discussed in Section 4.4 show that the behaviour of talc is consistent with the presence of oppositely charged surfaces on the particles of this mineral. The presence of a negative charge on the basal planes is required to produce the kind of heterocoagulation behaviour shown in Figure 4.1, where the yield stress peak of the mineral suspension is shifted away from the point of net zero charge.

Therefore, even though the degree of substitution of silicon ions with aluminium ions is very small (0.35 ± 0.21 %), it is clearly sufficient to alter the solution behaviour of talc, to the extent that it significantly differs from the expected behaviour of a mineral that carries no charge on its basal planes.

4.6 SECTION KEY FINDINGS

From the results presented in this section, the following key findings can be identified:

- Rheological behaviour of talc suspensions was studied as a function of pH. It was found that the point of maximum coagulation of talc suspensions lies at pH ≈ 5.5, which does not coincide with the accepted electrophoretic isoelectric point of talc at pH ≈ 2.5. This finding supports the hypothesis that the electrophoretic isoelectric point of talc does not represent the true anisotropic surface charge characteristic of the structure of New York talc.

  The point of zero charge of talc was determined using potentiomteric titration, and was found to lie at pH ≈ 7.7. This point does not coincide with the electrophoretic isoelectric point of talc.

- The fact that the point of maximum coagulation of talc as a function of pH does not correspond to neither the point of zero charge nor the electrophoretic isoelectric point indicates that coagulation of particles occurs as a result of the presence of oppositely charged particle planes, i.e. the suspension heterocoagulates.

  In this respect, the behaviour of talc was found to closely resemble that of kaolinite, which carries a negative charge on its tetrahedral basal planes, while the edges undergo a change from positive to negative at a pH range between 7 and 8.

This indicates that the basal planes of talc carry a negative charge, while the edges of talc undergo a change from positive to negative at a pH below the point of zero charge of talc as measured by potentiomteric titration (pH ≈ 7.7).

- The surface of talc was found to contain aluminium ions as indicated by ToF-SIMS measurements. The ToF-SIMS images indicated that aluminium ions are evenly spread out over the surface and not occurring as a cluster. This is an indication that aluminium ions occurs as part of the talc crystal lattice as opposed to random contamination by another mineral.

- Electron microprobe analysis of New York talc showed that the amount of silicon present in the samples was insufficient to fill all the available tetrahedral sites on the surface of talc, as it took up 99.46 ± 0.153 %. The remaining 0.35 ± 0.21 % and 0.04 ± 0.02 % of the sites were filled by aluminium and titanium ions respectively. This shows that there exists a small but definite proton deficiency in the tetrahedral layers of talc, which results in a definite negative charge.

  The magnitude of substitution of silicon with aluminium (0.35 ± 0.21 %) is similar to that of kaolinite (1.5 % - 0.5 %), which has been shown to possess a strong negative charge on its tetrahedral planes. A small magnitude of substitution in the talc basal planes is therefore sufficient to alter the behaviour of talc to the extent that it significantly differs from the expected behaviour of a mineral that carries no charge on its basal planes.

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5 Effect of Talc Surface Charge on Polymer Addition

5.1 INTRODUCTION

Polymeric depressants are important reagents in the mineral processing industry, as they are used to depress gangue such as talc out of flotation concentrates. This chapter investigates the adsorption characteristics of two such depressants, non ionic guar gum and anionic carboxymethyl cellulose (CMC).

In previous chapters, the surface charge distribution of talc particles was investigated and discussed. As a result, it was proposed that the basal planes of talc carry a negative charge due to substitution of Si^{4+} ions with metal ions of a lesser charge. It was also proposed that the edges of talc undergo a change from positive to negative at a pH below the point of net zero charge, at pH $\approx$ 7.7.

This chapter investigates the effect of talc surface charge on the adsorption characteristics of polymeric depressants, both anionic CMC and non ionic guar gum.

The effect of surface charge on polymer adsorption, for both guar gum and CMC is demonstrated with the use of rheological measurements as a function of varying concentration of potential determining ions (pH). The effect of pH on the conformational changes of both polymers is shown by means of intrinsic viscosity measurements of these polymers in solution. This is done to ensure that the changes in polymer adsorption (as indicated by rheological measurements) occur as a function of particle surface charge and not changes in polymer conformation.

5.1.1 Hypotheses

Rheological measurements of talc suspensions in the presence of polymeric depressants provide important information regarding the adsorption mechanism of these depressants. Rheological behaviour of talc suspensions in the presence of guar gum will be consistent with the adsorption of guar gum onto the basal planes of talc. Rheological behaviour of talc suspensions in the presence of CMC will be consistent with electrostatic attraction playing a major role in the adsorption of CMC onto talc, with the adsorption taking place primarily on talc edges.

This general hypothesis can be broken down into a number of more specific hypotheses:

- The rheological behaviour of talc as a function of pH will be strongly affected by the presence of guar gum in the entire pH range tested.
- The effect of CMC addition on the rheological behaviour of talc as a function of pH will be significantly stronger in the acidic pH range than in the alkaline pH range.
- The differences in the rheological measurements of talc suspensions as a function of polymer dosage will arise due to changes in talc surface charge distribution and not due to changes in polymer conformation.

5.2 TALC SURFACE CHARGE AND POLYMER ADSORPTION

This section examines the effect of the surface charge distribution of talc particles on the adsorption characteristics of polymeric depressants, both guar gum and CMC. These effects will be analysed using rheological measurements.

As shown in previous sections, rheological measurements provide information regarding the change in the surface characteristics of a mineral in suspension. In the case of polymeric depressants, the change in the yield stress of the suspension with the addition of polymer can be indicative of the degree of adsorption of these polymers onto the talc surface. These measurements are not as sensitive as measuring adsorption using conventional total carbon analysis (ToC) methods, but they do provide extra information regarding the forces acting in the suspension as a result of polymer adsorption.

The behaviour of the polymer macromolecules will also be examined in order to evaluate the conformational changes within the polymer structure (coiled vs. uncoiled) as a function of the changes in solution chemistry. These effects will be studies using capillary viscometry.

5.2.1 Effect of surface charge on guar gum adsorption

Rheological tests were performed on samples of New York talc as a function of changing guar gum dosage and pH. The guar gum used was CZD 519 with the dosage of polymer varied between 0 and 400 g/ton of solids. The tests were performed with the 10^{-2} M KNO_3 as background electrolyte. The rheological indicator used was Casson yield stress, which was obtained by modelling the shear rate/shear stress relationship of a given suspension using the Casson model for pseudo-plastic rheological behaviour (see Chapter 3 for details).

The reproducibility of the rheological data was tested by performing replicate tests under a limited set of conditions and determining the 95% confidence interval for these measurements. The results of the reproducibility tests are shown in Table 5.1. The details of the analysis are shown in Appendix C. The results are shown in Figure 5.1.

Table 5.1 – Confidence limits of the rheological data

Measurement	95% Confidence Interval
Casson Yield Stress	± 0.05 Pa
pH	± 0.1

Figure 5.1 shows that the addition of guar gum has an effect of increasing the Casson yield stress of the suspension. This is indicative of the increased degree of aggregation of particles. This result is expected since guar gum is known to have coagulant/flocculant properties. The adsorption of guar gum is thought to "mask" the charge on the surface of particles and hence decrease the electrostatic repulsion between them, causing the suspension to coagulate. This trend is verified by the fact that the differences between the measurement points exceed ± 0.05 Pa, which makes them significant on the 95% confidence interval.

The results also demonstrate that addition of guar gum had an effect on talc rheological behaviour in the entire pH range tested. This is consistent with the observations made by Wang (Wang *et al.* 2005) and is therefore consistent with the premise that guar gum adsorbs onto talc by means of hydrogen or hydrophobic bonding as opposed to electrostatic attraction. This makes guar gum adsorption independent of the nature of the surface charge of the host mineral.

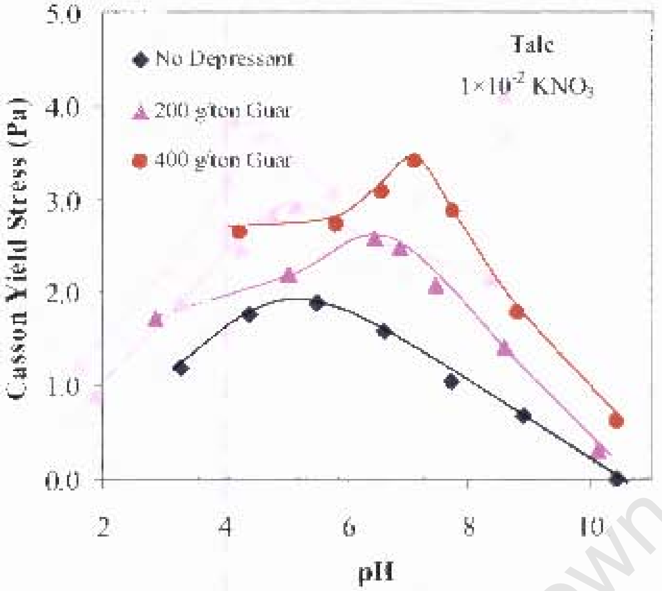

Figure 5.1 - Effect of guar gum addition on the Casson yield stress of talc suspensions

Although the adsorption of guar gum are independent of surface potential, the rheological behaviour of a mineral in suspension in the presence of this polymer is still indicative of the nature of the surface charge distribution of that mineral. It is important to note the shift of the point of maximum aggregation of talc suspensions with increasing guar gum dosage. At a very high dosage (400 g/ton), the point of maximum aggregation begins to approach the measured point of net zero charge (pH ≈ 7.7).

As stated in the previous chapters, the rheological behaviour of isotropic minerals is such that the suspensions yield stress reaches a maximum value at the point of zero charge of the mineral. This is unlike anisotropic mineral such as talc and kaolinite, where the point of maximum coagulation lies at the point of the maximum difference between oppositely charged particle planes.

The shift of the yield stress peak of talc suspensions indicates that the adsorption of guar gum occurs preferentially on one of the particle planes, eliminating its electrical charge. This preferential "masking" brings the mineral closer to the state of isotropy. Therefore, at high dosages of guar gum, the rheological behaviour of talc begins to approach that of an isotropic mineral, as illustrated in Figure 5.2.

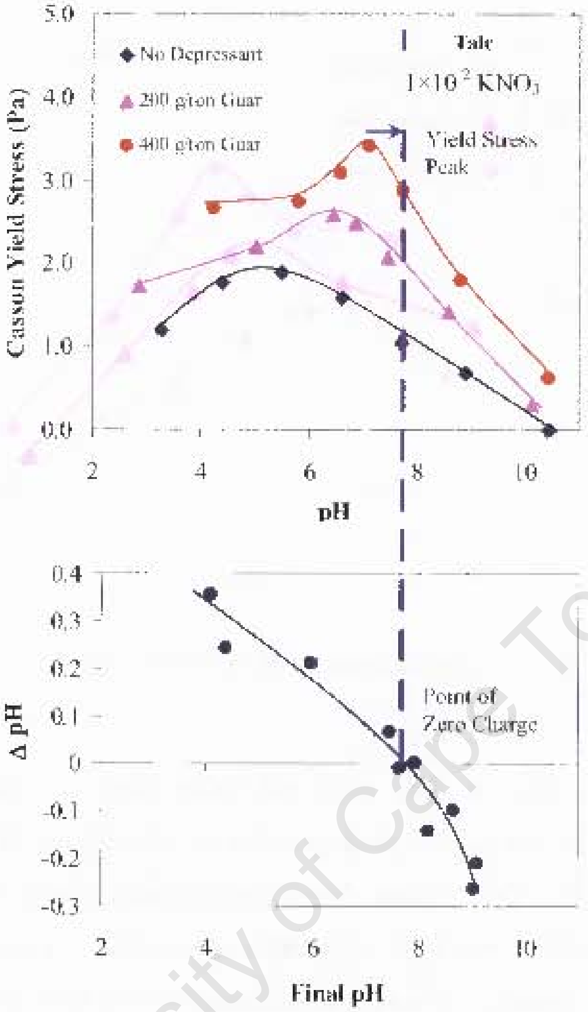

Figure 5.2 – Casson yield stress of talc suspensions as a function of guar gum dosage along with the potentiometric titration of talc

These results are consistent with the surface charge distribution of talc proposed in Chapter 4, which state that the basal planes of talc carry a negative charge, while the edges of talc undergo a change from positive to negative at a high pH. The results shown in Figure 5.2 indicate that the adsorption of guar gum takes place primarily on the basal planes of talc rather than the edges.

The "masking" of the negative charge on the basal planes would then dampen the effect of the particle anisotropy on suspension rheological behaviour. This is consistent with the findings of Steenberg (Steenberg and Harris 1984) as well as Wang (Wang *et al.*

2005) who stated that the adsorption of guar gum onto talc takes place primarily on talc basal planes.

5.2.2 Effect of surface charge on CMC adsorption.

Similar tests were performed with varying the dosage of CMC. The dosage of polymer was once more varied between 0 and 400 g/ton of solids. The CMC used was DEP 267 and the tests were performed with the 10^{-2} M KNO_3 as background electrolyte.

The results shown in Figure 5.3 indicate that the addition of CMC decreases the yield stress of the suspension, which is indicative of an increased degree of dispersion. It is likely to result from the adsorption of CMC and increasingly negative electrical charge of the interacting particles.

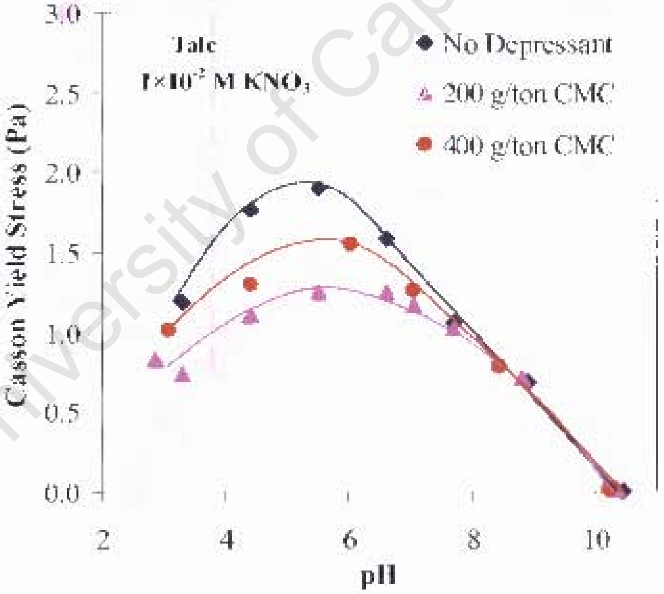

Figure 5.3– Effect of CMC addition on the Casson yield stress of talc suspensions

It should be noted that the dosage of 200 g/ton of CMC caused a greater degree of dispersion than that at 400 g/ton. This effect is unexpected and will not be discussed further at this time.

The results also indicate that the colloidal behaviour of talc was only affected by the addition of CMC at pH below ≈ 8. This pH value coincides with the point of net zero charge of talc found by means of a potentiometric titration, as is illustrated in Figure 5.4. This trend is verified by the fact that the difference between the measurement point exceed + 0.05 Pa, which makes them significant on the 95% confidence interval.

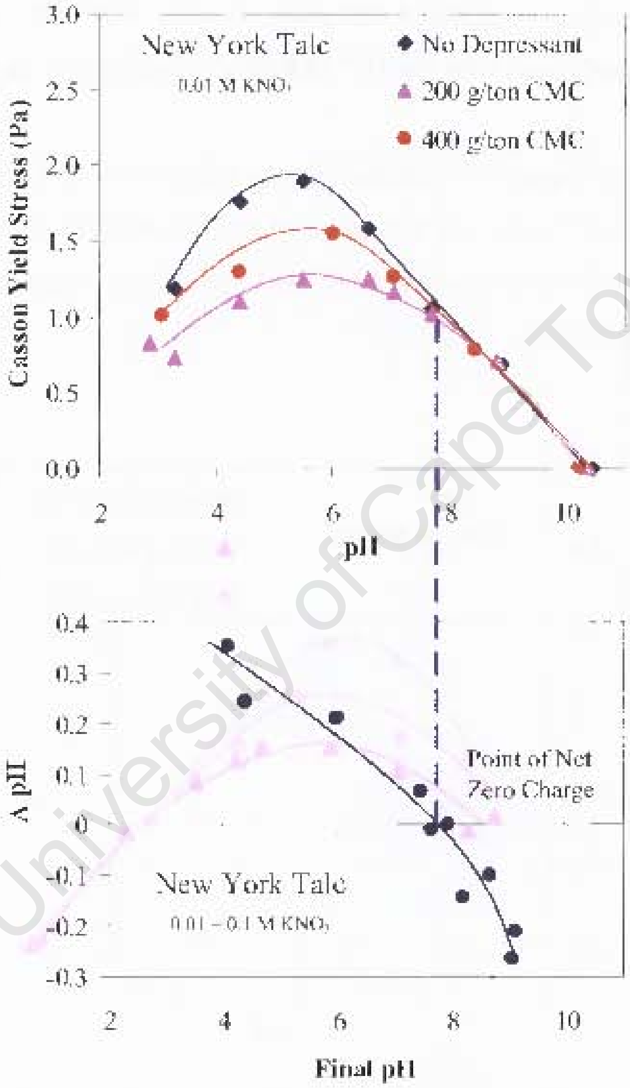

Figure 5.4 –Casson yield stress of talc suspensions as a function of CMC dosage along with the potentiometric titration of talc

This finding is once again consistent with the proposed distribution of charge on the surface of talc, described in detail in Chapter 4 and suggests that adsorption of CMC takes place largely in the pH range where the edges of talc particles carry a positive charge, i.e. a lower pH. These findings indicate that electrostatic attraction could play a large role in the mechanism of CMC adsorption onto talc.

This is consistent with the observations made by Morris et al. (2002), who showed that the adsorption of CMC increases dramatically at low pH values (although it was pointed out that this may result from the fact that over lower pH ranges the CMC macromolecules are not ionized and coil).

It is important to note, that in the case of talc suspensions, although polymer addition has little effect on the rheology of the suspensions in the region where the particle edges are thought to carry a negative charge (e.g. pH 9), previous research has shown that CMC does adsorb onto talc in that pH region (Parolis *et al.* 2004). The floatability of talc was also shown to be reduced (Steenberg and Harris 1984; Shortridge *et al.* 2000).

5.2.3 Summary of the results

The differences in the rheological behaviour of talc suspensions in the presence of guar gums and CMCs are summarised in Table 5.2.

The results show that clear differences exist between the rheological behaviour of talc as a function of the addition of non-ionic and anionic polymers. These differences are indicative of the different adsorption mechanism of these two polymers as well as their properties.

Table 5.2 – Summary of the rheological response of New York talc suspensions to the addition of polymeric depressants

Effect of Polymer Addition	Guar Gum	CMC
Affected pH Range	Entire tested range	Below pH ≈ 8 (net p.z.c of talc)
Yield stress	Increase (coagulation/flocculation)	Decrease (dispersion)
Yield stress peak	Shift towards pH ≈ 8 (net p.z.c of talc)	No shift

The addition of guar gum causes an increase in the yield stress of the suspensions, indicative of suspension coagulation or flocculation. The yield stress of the suspensions is affected in the entire pH range, which indicates that the adsorption of guar gum is independent of surface charge. Finally, the yield stress peak of the suspensions shifts towards a point of zero charge of New York talc as a function of guar gum addition, which indicates that guar gum adsorbs primarily on the basal planes of talc.

The addition of CMC caused the yield stress of the suspensions to decrease, indicative of suspension dispersion. The addition of CMC caused the change in the yield stress of the suspensions in the pH range below the point of zero charge of New York talc. This indicates that the adsorption of CMC is dependent on both the surface charge of the talc particles, as well as the ionisation of the metal hydroxide species present on the surface of talc particles. The addition of CMC did not cause a shift in the yield stress peak, indicating that the adsorption took place primarily on the edges of talc.

5.3 EFFECT OF PH ON POLYMER CONFORMATION

Many researchers have explained the differences in the adsorption characteristics of polymeric depressants onto minerals as a function of pH by the effect that pH might have on the conformation of the polymer molecules. The change in conformation is then responsible for the change in adsorption density, due to the resulting decrease in effective molecule size (Morris *et al.* 2002; Pawlik *et al.* 2003; Parolis *et al.* 2006).

Therefore, it is important to measure the degree of coiling of the polymer molecules as a function of pH to make sure that the differences in rheological measurements shown in the previous sections do not arise due to changes in polymer conformation.

5.3.1 Conformation of guar gum

Intrinsic viscosity measurements were used to determine the degree of coiling of both guar gum and CMC molecules in the pH range used in the rheological experiments. All tests were performed with 10^{-2} M KNO_3 as background electrolyte.

Figures 5.5 and 5.6 show the reduced viscosity of the solutions of guar gum and CMC as a function of decreasing solution concentration. According to the Huggins equation (Equation 3.2), the intrinsic viscosity is equal to the reduced viscosity of the solution as the polymer concentration approaches zero. Therefore, the intrinsic viscosity can be approximated by the intercept of the straight line fit of the reduced viscosity data.

Figure 5.5 shows that the reduced viscosity vs. concentration lines remain virtually unchanged as a function of pH. The intercepts of the regression lines extrapolated from the experimental data are shown in Figure 5.6

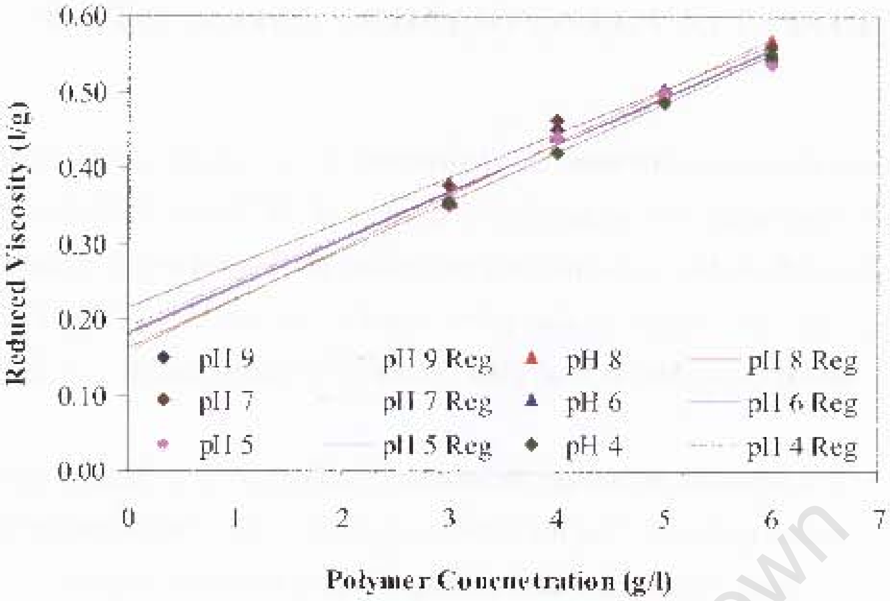

Figure 5.5 Effect of pH on the reduced viscosity of guar gum solutions

The results shown in Figure 5.6 clearly indicate that the intrinsic viscosities of guar gum remain unchanged as a function of pH, with none of the differences between the values being significant on the 95% confidence limit. This result is expected, since guar gum is an non-ionic polymer and does not contain negatively charged carboxylic acid groups that are responsible for the coiling/uncoiling of the molecules under varying ionic strength conditions.

The results presented in Figure 5.6, indicate that the differences in rheological behaviour of talc as a function of pH and guar gum addition arise from the differences in talc surface charge distribution, and not polymer conformation.

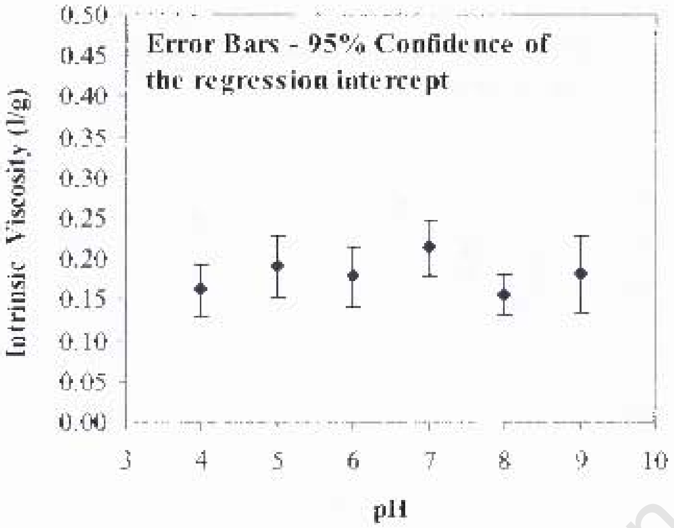

Figure 5.6– Intrinsic viscosity of guar gum as a function of pH

5.3.2 Conformation of CMC

Similar tests were performed with CMC, where once again all tests were performed with 10^{-2} M KNO_3 as background electrolyte. The results of the tests are shown in Figure 5.7. The results show that the variation in the reduced viscosity curves of CMC does not greatly differ as a function of pH, however the variation is greater than in the case of guar gum. This is specifically the case in the pH range below 5. The 95% confidence intervals on the intercepts of these curves were once more calculated. The results are shown in Figure 5.8.

The results show that although the variation with pH in intrinsic viscosity of CMC varies to a greater extent than that of guar gum, none of the differences are significant on the 95 % confidence limit. This indicates that no significant amount of polymer coiling takes place in the pH range indicated.

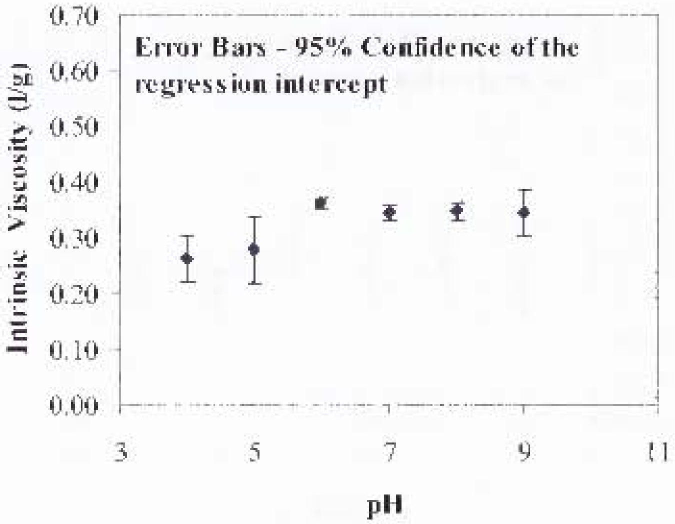

Figure 5.7 – Effect of pH on the reduced viscosity of CMC solutions

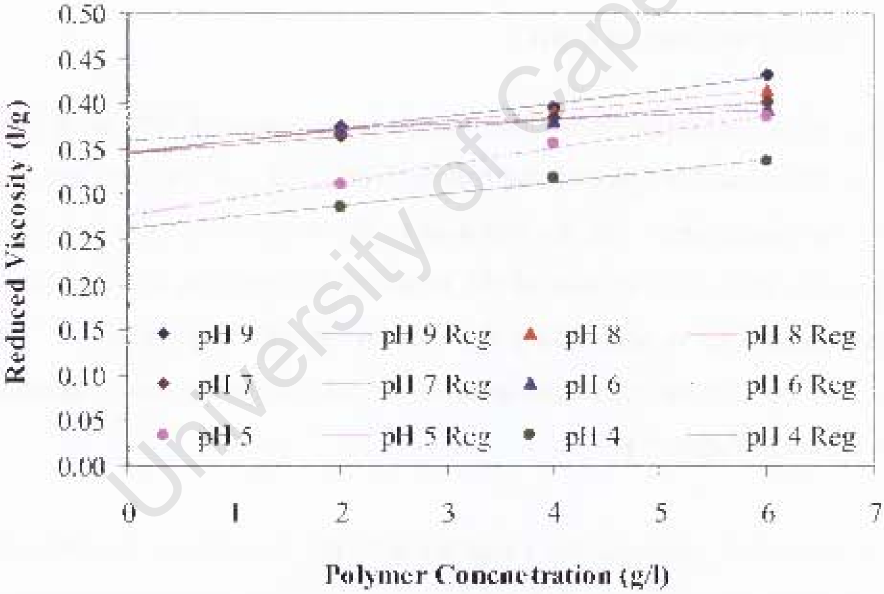

Figure 5.8 – Intrinsic viscosity of CMC as a function of pH

This again is not surprising, since the combined ionic strength of both hydrogen (H^+) and hydroxide (OH^-) ions varies between 10^{-5} and 10^{-4} M in the pH range in which the tests were conducted. The relatively high concentration of background electrolyte serves as a sufficient buffer to prevent ionic strength fluctuations as a function of pH, preventing significant conformational changes.

As in the case of guar gum, these results strongly indicate that the differences in rheological behaviour of talc as a function of pH and CMC addition arise from the differences in talc surface charge distribution, and not polymer conformation.

5.4 SECTION KEY FINDINGS

From all the results presented in this section, the key findings can be identified:

- The addition of guar gum caused a strong coagulation of talc suspensions in the entire pH range tested (pH 9 - 4), manifested by the increase in the Casson yields stress of these suspensions. The change in the rheological behaviour is indicative of the adsorption of guar gum onto talc irrespective of the talc surface charge. These results are in agreement with the premise that guar gum adsorbs onto talc by means of hydrogen and hydrophobic bonding and is therefore independent of particle surface charge.

  The results also showed that the yield stress peak of talc suspensions shifted towards a higher pH. At high dosages, the Casson yield stress began to approach the measured point of net zero charge of talc (pH ≈ 7.7). This indicates that the talc suspension begins to act in a manner similar to isotropic particles, where the yield stress peak coincides with the point of zero charge of the mineral. These findings support the premise that guar gum preferentially adsorbs on the basal planes of talc, effectively "masking" the surface charge.

- The adsorption of CMC onto talc occurred mainly in the pH region below the measured point of net zero charge of talc, manifested by a decrease in the Casson yield stress of talc suspensions. In other words, the adsorption of CMC mainly took place in the pH region where the talc surface exhibits a net positive charge. These results are consistent with the premise that electrostatic attraction plays an important role in the adsorption of CMC onto talc.

The results are also consistent with the mechanism whereby CMC molecules interact with metal hydroxide species present on the talc edges, which become activated in acidic pH.

- The intrinsic viscosity of guar gum was completely unaffected by solution pH. This indicates that no conformational changes took place in the guar gum molecule. This result indicates that the differences in rheological behaviour of talc as a function of pH and guar gum addition arise from the differences in talc surface charge distribution, and not polymer conformation.

- The intrinsic viscosity of CMC molecules was largely unaffected by solution pH. This indicates that no conformational changes took place within the CMC molecules. This result indicates that the differences in rheological behaviour of talc as a function of pH and CMC addition arise from the differences in talc surface charge distribution, and not polymer conformation.

5.5 REFERENCES

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6 Effect of Calcium and Potassium Ions on the Surface Charge of Talc and Polymer Adsorption

6.1 INTRODUCTION

The presence of metal cations in the water used in flotation processes has been found to have a strong effect on the performance of flotation systems. The presence of metal cations in the aqueous phase of flotation pulps has been shown to have a strong effect on both the surface charge of mineral species (Fuerstenau *et al.* 1988), adsorption characteristics of reagents (Morris *et al.* 2002; Parolis *et al.* 2004; Ma and Pawlik 2005) as well as an effect on the conformational structure of polymeric depressants (Pawlik and Laskowski 2004; Parolis *et al.* 2006).

In previous chapters, the surface charge distribution of talc particles was discussed. An alternative surface charge distribution model of talc particles was put forward, where talc basal planes carry a negative charge, while the edges of talc undergo a change from positive to negative at pH above 7.7.

In Chapter 5, the adsorption of anionic CMC depressants was shown to be affected by the surface charge distribution of the mineral surface to a much greater extent than guar gum. For this reason, this chapter focuses on the effect of metal cations on the anionic

CMC molecules. Furthermore, guar gum is a non-ionic polymer and is therefore not amenable to analysis with techniques such as ToF-SIMS.

The study focuses on two specific metal cations: monovalent potassium ions and divalent calcium ions. Monovalent potassium ions were chosen because they are commonly used as a background electrolyte for laboratory studies of mineral behaviour. On the other hand, divalent calcium cations are commonly present in the water used in industrial flotation circuits due to high levels of lime addition for pH control purposes.

This chapter sets out to examine the adsorption of both monovalent potassium ions and divalent calcium ions on talc as a function of particle morphology (basal plane vs. edge) and pH, as well as investigating the effect that ion adsorption has on the magnitude of the surface charge of the talc particles.

The adsorption behaviour of anionic CMC onto talc is then investigated as a function of the presence of both monovalent potassium and divalent calcium cations in solution. The adsorption characteristics as well as the solution interactions between CMC molecules and these cations are investigated using ToF-SIMS measurements.

6.1.1 Hypotheses

It is hypothesised that the adsorption of divalent calcium ions and monovalent potassium ions on the surface of talc has an effect on the surface charge distribution of talc particles and affect the adsorption characteristics of CMC. The adsorption characteristics of CMC are further complexed by the effect that metal cations have on the conformation of CMC macromolecules.

This general hypothesis can be broken down into a number of specific hypotheses:

- It is hypothesised that the combination of ToF-SIMS and SEM images can provide the measurement of the adsorption characteristics of metal cations as a function of particle morphology, by means of isolating the particle basal planes and edges.

- It is hypothesised that both monovalent potassium ions and divalent calcium ions will adsorb onto the surface of talc particles, but will have different effects on the magnitude of the surface charge of talc.

- It is hypothesised that the adsorption density of CMC molecules onto the basal planes of talc will be different in the presence of calcium ions than in the presence of potassium ions in solution due to the differences in the magnitude of the surface charge in the presence of these two ions.

- It is hypothesised that the solution interactions between monovalent potassium ions and divalent calcium ions and CMC macromolecules will take place to a different extent in the presence these two ions.

6.2 IONIC ADSORPTION ONTO TALC AS A FUNCTION OF PH AND PARTICLE MORPHOLOGY

This section examines the adsorption characteristics of both monovalent potassium ions and divalent calcium ions on the different crystalline planes of talc. The relative degree of ion adsorption is measured by means of ToF-SIMS measurements. The ToF-SIMS measurements are shown for both the basal planes and edges of talc. The validity of the measurements is evaluated by looking at the ToF-SIMS images in conjunction with SEM images of the particle planes.

6.2.1 ToF-SIMS measurements

ToF-SIMS is a semi quantitative technique that enables the measurements of the presence of ionic species on the top-most surface of a mineral. However, as discussed in the previous chapter, phyllosilicate minerals have a very open crystal structure with large gaps in the top most tetrahedral layers. This allows the ions from deeper layers within the crystal lattice to escape the mineral and therefore be detected. This makes it difficult to study the inherent molecular composition of the mineral surface.

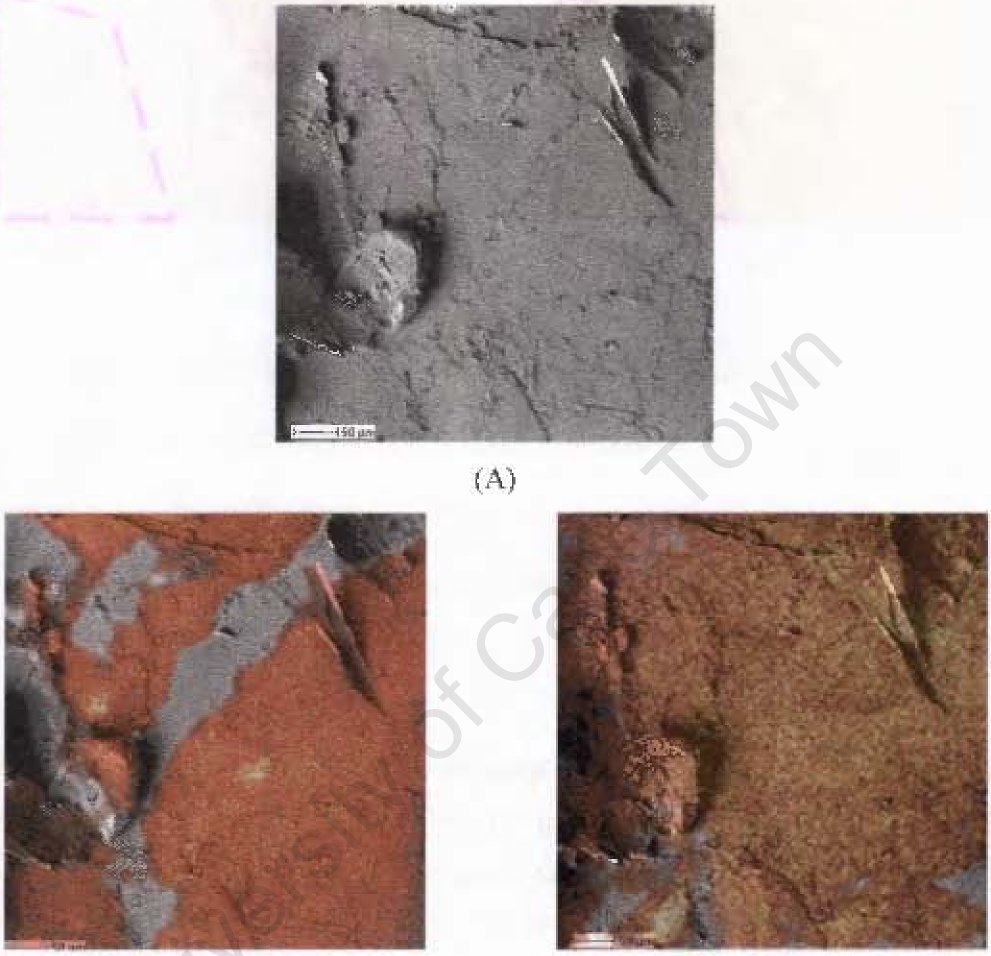
For this reason, when evaluating the degree of adsorption of ionic species on the mineral surface, the obtained measurement should always be compared to the measurement of a blank mineral surface in the absence of the adsorbed ionic species. Such a blank surface would then act as a base line with reference to which the rest of the measurements can be evaluated.

Sample preparation is also crucial to the success of the measurement. When measuring the degree of adsorption of ionic species, care must be taken that the sample being measured contains only the adsorbed ions. If samples are not prepared properly, residual supernatant solution might be deposited and dried on the sample surface and therefore be mistaken for adsorbed species. For this reason, all samples should be rinsed in de-ionised water after being contacted with the solution containing ions, before being dried.

The absolute magnitudes of the peaks are also not comparable between samples and therefore elemental ratios must be used as a basis of comparison. In this case, silicon ions were chosen as the ion against which all other ions were normalised so as to enable direct comparison between different samples.

6.2.2 Adsorption of calcium and potassium ions on the basal planes of talc

In order to ascertain whether or not cation adsorption takes place on the basal planes of talc particles, ToF-SIMS measurements were performed. In order to confirm that the measurements correspond to the basal planes of the measured talc samples, ToF-SIMS measurements were performed in conjunction with low resolution SEM images of the talc particles. Such images can then be superimposed onto the ToF-SIMS spectral images to determine which particle morphology is responsible of the resulting ToF-SIMS measurement. Examples of such images for both calcium hydroxide, calcium and potassium ions are shown in Figure 6.1 and Figure 6.2. Similar images for the remainder of the samples can be viewed in Appendix B.



(A)

(B) (C)

Figure 6.1 - (A) SEM image of a basal plane of a talc particle, (B) Corresponding ionic image of calcium hydroxide ions, (C) Corresponding ionic image of calcium ions superimposed onto the original SEM image of the talc particle at the ionic strength of 0.01 of calcium nitrate solution, at pH 9


(A) (B)

Figure 6.2 - (A) SEM image of a basal plane of a talc particle, (B) Corresponding ionic image of potassium ions, superimposed onto the original SEM image of the talc particle, with selected analysis area, at the ionic strength of 0.01 of potassium nitrate solution, at pH 9

The images show that the particles in question do not always consist of an ideal basal plane surface, but rather surface that shows a degree of damage through sample preparation. For this reason, in the case of particles where such damage is extensive, a specific area of analysis was selected. Such selections only contain the particle sections that contain an undamaged basal plane. These images confirm that the adsorption of both monovalent and divalent cations inferred by the normalised ToF-SIMS intensities corresponds to the basal planes of talc.

In the case of the adsorption of calcium ions, it is important to establish not only the location of the adsorption (basal plane vs. edge), but also the ionic form in which the adsorption takes place. The adsorption of calcium ions could potentially take place in two forms, Ca^{+2} ions and hydrolysed $CaOH^{+}$ ions. As was discussed in detail in Chapter 2, the adsorption of Ca^{+2} ions onto talc is thermodynamically unfavourable, due to their high energy of hydration which results in their structure making properties. It is therefore more likely that the adsorption would take place in the form of $CaOH^{+}$ ions.

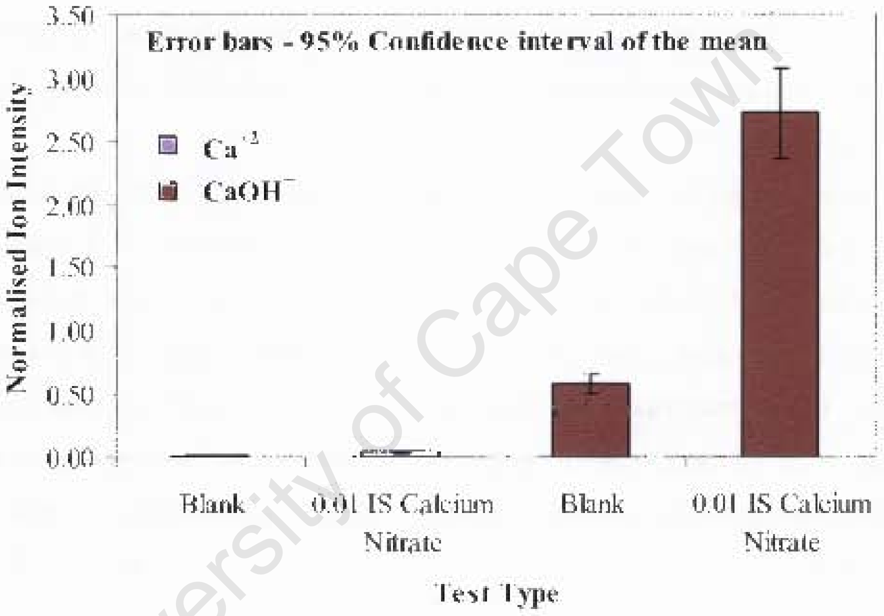


Figure 6.3 – Normalised Intensities of both Ca^{+2} and $CaOH^{+}$ ions on the basal planes of talc at pH 9

The normalised intensities of both Ca^{+2} and $CaOH^{+}$ ions on the surface of talc are shown in Figure 6.3. The results show that the normalised intensities of both Ca^{+2} and ions $CaOH^{+}$ on the basal planes of talc in the presence of calcium nitrate solution are significantly larger than that for a blank reference samples. This indicates that both ion species adsorb on the basal planes of talc. The results also show that the adsorption of Ca^{+2} can be considered negligible in comparison to the magnitude of adsorption of $CaOH^{+}$ ions.

This result contradicts the findings of Fuerstenau *et al*, who stated that the adsorption of $CaOH^+$ ions does not take place on the basal planes of talc. However, in their work, the presence or absence of ionic species on the basal planes of talc was never directly detected or measured, but inferred though floatability measurements. These results suggest that the presence of metal hydroxide ionic species on the basal planes of talc may not necessarily affect its floatability.

Similar techniques can be used to study the adsorption characteristics of monovalent potassium ions on the basal planes of talc. Potassium ions adsorb onto the surface of negatively charged mineral species by means of electrostatic attraction. The adsorption of K^+ ions is thermodynamically favourable, due their large ionic radius and a low level of hydration, which results in these ions exhibiting water structure breaking properties.

The electron microprobe analysis of talc showed that there is a deficiency of silicon ions in the tetrahedral layers of talc, compensated by the substitution of aluminium and titanium ions (see Chapter 4 for details). This substitution results in a proton deficiency on the talc basal planes, causing them to carry a negative charge in the majority of the pH range. It is therefore expected that potassium ions will adsorb onto talc basal planes. The adsorption characteristics of potassium ions onto the basal planes of talc were investigated using surface specific ToF-SIMS measurements, in the presence of 10^{-2} M solution of KNO_3, and a constant pH of 9. The normalised intensities of K^+ ions are shown in Figure 6.4

Figure 6.4 shows that the normalised intensities of potassium ions on the basal planes of talc in the presence of potassium nitrate solution are significantly larger than that for a blank sample. This indicates that the adsorption of K^+ ions takes place on the basal planes of talc. This result is a further confirmation of the presence of a negative charge on talc basal planes.

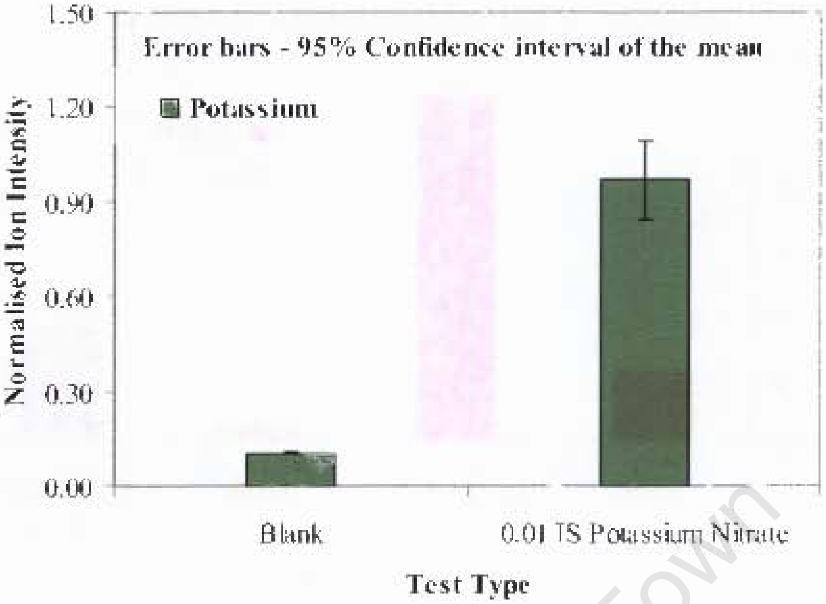


Figure 6.4 – Normalised intensities of potassium ions on the basal planes of talc, at the ionic strength of 0.01 of potassium nitrate solution, at pH 9

The results presented above showed that both K^+ and $CaOH^+$ ions adsorb onto the basal planes of talc. The magnitudes of their adsorptions are compared in Figure 6.5. The results show, that at the same solution ionic strength, at pH 9, the normalised intensities of calcium hydroxide ions are significantly larger than the normalised intensities of potassium ions. This indicates, that under a similar set of conditions, calcium hydroxide ions may tend to adsorb more densely onto the basal planes of talc than potassium ions.

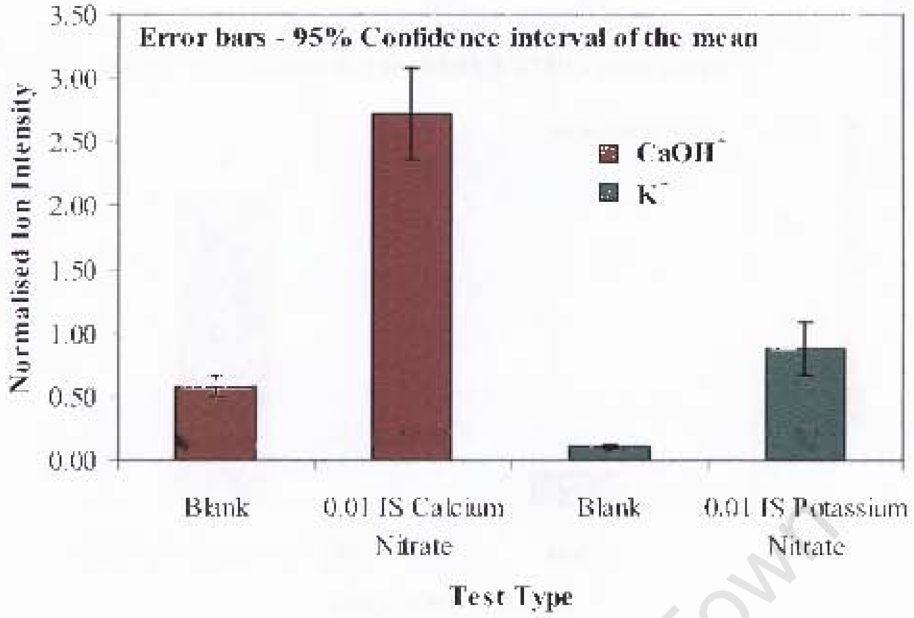


Figure 6.5 – Normalised intensities of K^+ and $CaOH^+$ ions on the basal planes of talc, at the ionic strength of 0.01 of calcium and potassium nitrate solutions respectively, at pH 9

6.2.3 Adsorption on the edges of talc

As in the case of talc basal planes, ToF-SIMS measurements were performed in conjunction with low resolution SEM images of the talc particles in order to confirm that the measurements correspond to the edges of the measured talc samples. An example of such an image is shown in Figure 6.6. The images for the remainder of the samples can be viewed in Appendix B. Unlike the images of the basal planes of talc, the edge images display the total ion image instead of the calcium image, in order to make the images more clearly visible.

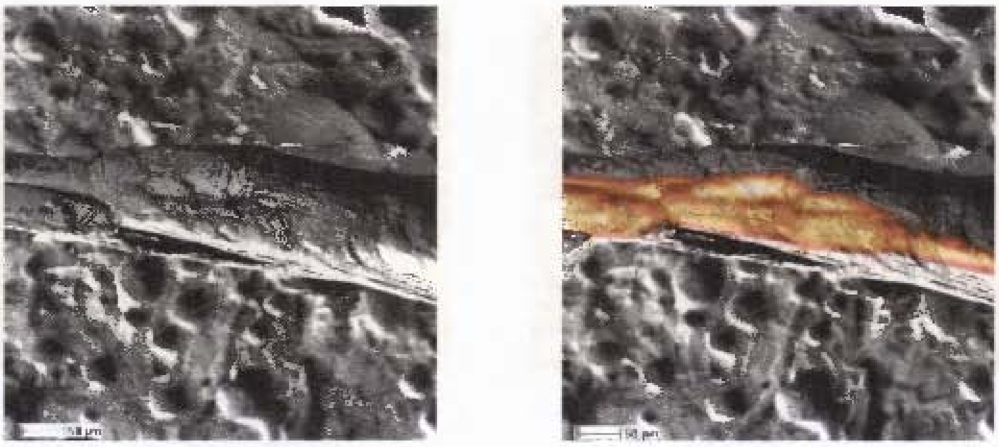

(A) (B)

Figure 6.6 - (A) SEM image of an edge of a talc particle, (B) Corresponding image of the total ion spectrum, superimposed onto the original SEM image of the talc particle.

The images shown in Figure 6.6 indicate that the ToF-SIMS measurements may not correspond to the edges of talc. The images show that the talc edges are largely obstructed by the overlapping basal planes of the talc particles.

This means that the obtained ToF-SIMS images originate from the bent basal planes rather than the particle edges. In order to show a clearer image of particle edges, high resolution SEM images were obtained. The images of an edge of an ideal talc particle obtained by manual cleavage and a talc particle obtained by milling in a ring mill are shown in Figure 6.7.

The images presented in Figure 6.7 show a contrast between an ideal edge of talc particles and those obtained though a milling process. Figure 6.7 (B) clearly shows that the impact of talc particles against the surface of the mill causes the edges of the thin particles to curl up onto themselves, resulting in the edges being completely obstructed by the overlapping basal planes. The comparison of the obtained ToF-SIMS data for both basal planes and edges is shown in Figure 6.8.

(A) (B)

Figure 6.7 - (A) High resolution SEM image of an edge of an ideal talc particle obtained by manual cleavage. (B) High resolution SEM image of an edge of a talc particle obtained by milling (images by Peter von Blokland, Akzo Nobel)

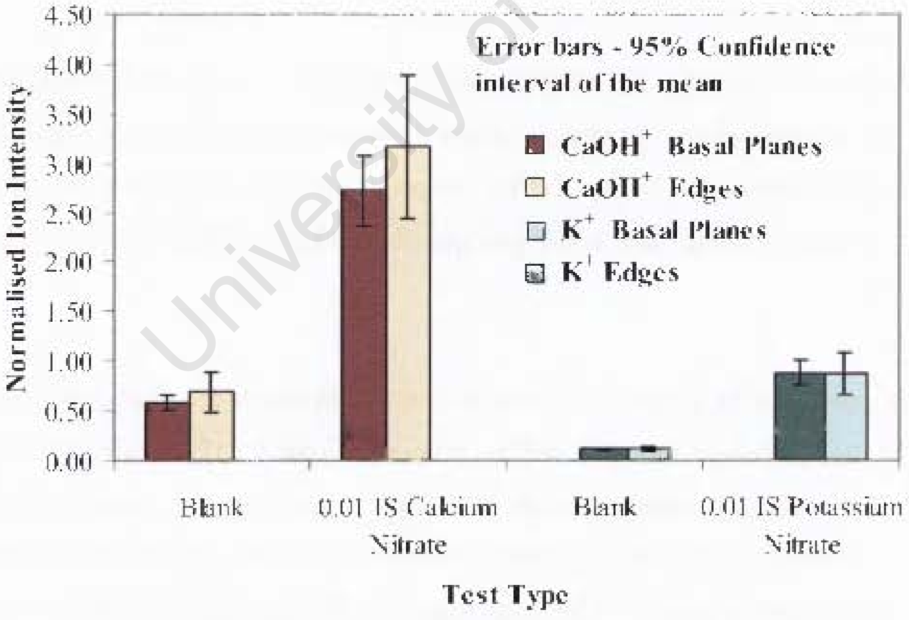


Figure 6.8 - Normalised intensities of $CaOH^{+}$ and K^{+} on the basal planes and edges of talc at the ionic strength of 0.01 of calcium and potassium nitrate solutions. at pH 9

The results show that there is no significant difference between the normalised intensities of ionic species adsorbed on the basal planes and edges of talc respectively. This applies to both blank and non-blank samples, of both types of ions. This confirms that edges of talc are obscured by basal planes.

This problem originates from the sample preparation procedure and is similar to that experienced by Nalaskowski (Nalaskowski *et al.* 2006), where talc edges were obscured by cutting with a diamond blade, causing the streaming electric potential readings of talc edges and faces to appear similar to one another.

This means that the method of sample preparation of talc edges rendered the ToF-SIMS measurements unable to pick up the differences in the adsorption of calcium ions between the different surfaces of talc particles. Therefore the adsorption properties of calcium onto the edges of talc particles remain unknown.

6.2.4 Effect of metal cations on talc surface charge magnitude

In order to estimate the effect that both monovalent and divalent metal cations have on the surface charge magnitude of the talc surface, the surface potential of talc particles needs to be estimated. A common method for measuring surface potential is by zeta potential measurements.

As discussed in previous chapters, zeta potential measurements are not appropriate for the use with plate like anisotropic minerals such as talc and kaolinite. The values obtained form these measurements should not be used as absolute quantities and should be treated and referred to as "**apparent**".

However, apparent zeta potential measurements can be used as a basis of comparison of mineral behaviour as a function of changing solution chemistry, such as type and concentration of metal cations in solution. It is important to note that the obtained zeta potential values should not be treated as absolute values and as such should not used to model the electrostatic adsorption energies of the metal cations, because they do not represent the actual surface potential of talc particles.

Apparent zeta potential measurements of talc particles as a function of concentration of both calcium and potassium ions were performed at pH 9, as this pH is common in industrial flotation systems of base metal sulfide ores. By keeping the pH constant, the amount of potential determining ions on the surface of talc is kept consistent throughout the experiments. This makes certain that the changes in the apparent zeta potential measurements are due to adsorption of metal cations calcium ions and not from the changes in the adsorption of potential determining ions. The results of the apparent zeta potential measurements are shown in Figure 6.9.

Apparent zeta potential measurements shown in Figure 6.9 are represented as a function of ionic strength as opposed to ionic concentration. This is done in order to eliminate variation in apparent zeta potential as a function of the thickness of the double electrical layer around the talc particles, as double layer thickness is a function of the ionic strength of the solution.

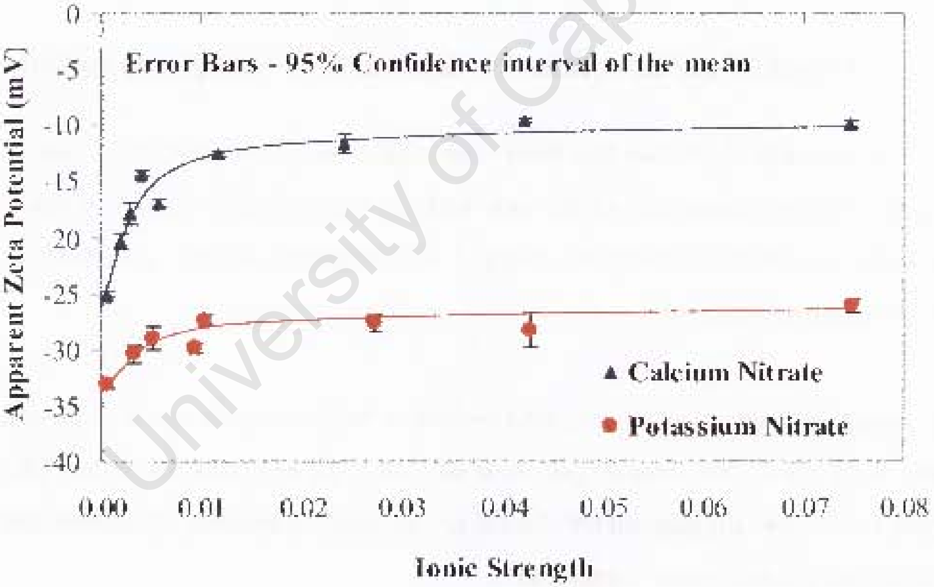


Figure 6.9 – Zeta potential measurements of New York Talc as a function of increasing ion concentration of both calcium and potassium ions at pH 9

The results show that the apparent zeta potential measurements change significantly as a function of ion concentration for both calcium and potassium ions at a constant pH. This means that the adsorption of both of these ions causes significant changes to the surface charge of talc particles, making them less negative.

Figure 6.9 also shows that in the presence of calcium ions, the apparent zeta potential of talc particles is reduced to a significantly greater degree than in the presence of potassium ions. This indicates that at the same level of ionic strength (and hence at the same double layer thickness), the adsorption of $CaOH^+$ ions onto the surface of talc causes a much greater reduction in surface potential of talc than that of K^+ ions.

These results are in agreement with the ToF-SIMS measurements of the density of ion adsorption, which showed that $CaOH^+$ ions adsorb more densely onto the basal planes of talc than K^+ ions. Furthermore, it has been previously shown that the adsorption of monovalent ions onto mineral surfaces has a relatively small effect on the surface charge of minerals (Ma and Pawlik 2005). However, the adsorption of hydrolysable polyvalent cations onto the surface of talc causes dramatic charges to the magnitude of the surface charge (Fuerstenau *et al.* 1988).

6.3 EFFECT OF CATIONS ON CMC ADSORPTION

This section examines the effect of the presence of both calcium and potassium metal cations in solution on polymer adsorption.

The results of the previous chapter showed that CMC adsorption characteristics strongly depend on the surface charge distribution of the minerals. The results of the previous section showed that the adsorption of metal cations onto talc causes significant changes to the surface potential of the talc particles. Work by Parolis (Parolis *et al.* 2006) has also shown that CMC macromolecules are highly susceptible to conformational charges as a function of both the ionic strength as well as the valency of the metal cations present in solution. This section focuses on combined effect that metal cations have on the surface charge of talc as well as the conformational structure of CMC macromolecules to investigate the adsorption characteristics of anionic CMC onto talc.

6.3.1 Detection of CMC molecules using ToF-SIMS

The adsorption of CMC molecules onto talc is studied by means of ToF-SIMS surface measurements. In the previous chapter, ToF-SIMS measurements were used to estimate the adsorption characteristics of metal cations on the surface of talc as a function of particle morphology.

The results presented in Chapter 5 showed that the basal planes of talc could be successfully isolated for measurement, while the talc edges were inaccessible due to obstruction by basal planes during the sample preparation process. This section is therefore limited to the study of the adsorption characteristics of CMC molecules on the basal planes of the talc particles.

As mentioned in previous chapters, ToF-SIMS is a semi-quantitative technique that allows the detection of ionic species on the surface of a mineral. Because the technique is only semi-quantitative, the absolute magnitudes of adsorption cannot be ascertained from the normalised intensity data. For this reason, the intensities are always compared to a blank sample, which serves as a reference baseline.

It is important to note that the all the intensities shown in the figures that follow are normalised against the intensities of silicon ions in order to make the data comparable between samples. The detection of polymers with ToF-SIMS is more complex than the detection of simple ions. Due to the size of the long chain polymer molecules, the entire molecule cannot be detected by the instrument. The detection occurs by means of identifying the carboxylic acid groups that carry the negative charge on the polymer molecules, as shown in Figure 6.10

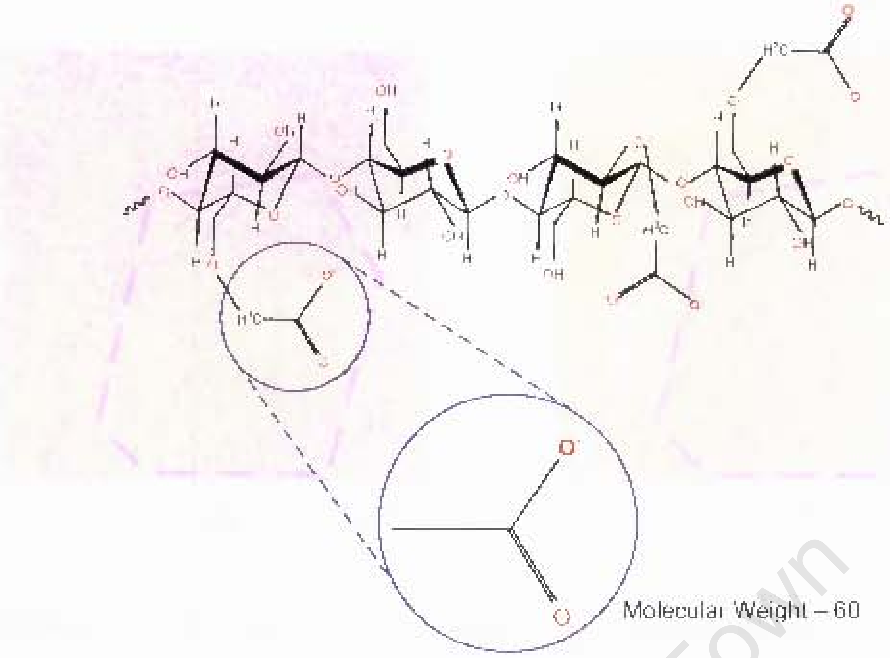
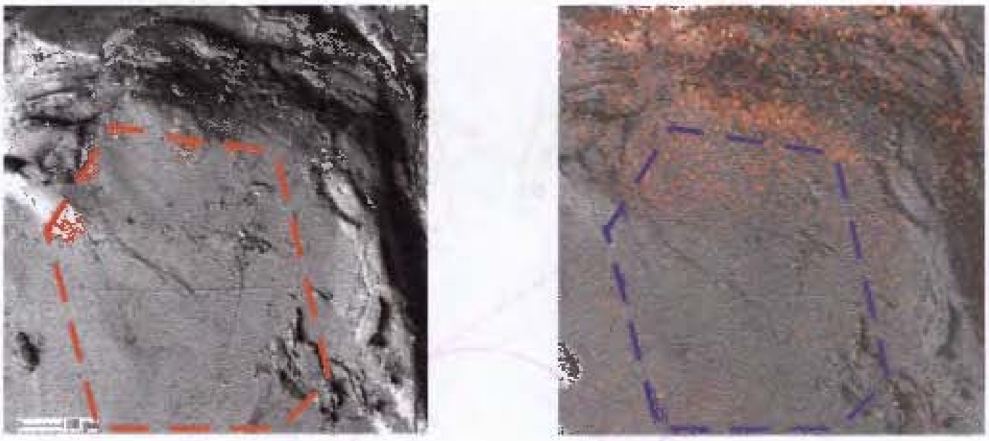


Figure 6.10 Schematic representation of a CMC macromolecule, showing the negatively charged carboxylic acid group, with a molecular weight of 60

6.3.2 Effect of cation type and concentration on CMC adsorption

ToF-SIMS measurements were performed on basal planes of talc particles in order to measure CMC adsorption as a function of both concentration and type of metal cations. The CMC used was FF10, because its bulk adsorption characteristics as well as solution behaviour have been well characterised by Parolis *et al* (2006), see Chapter 2 for details. The measurements were performed at a constant pH of 9, with the ionic strength of 10^{-2} for both calcium nitrate and potassium nitrate solutions.

The SEM images of talc basal planes with corresponding ToF-SIMS images of CMC ions in the presence of both potassium and calcium ions are shown in Figure 6.11 and Figure 6.12. Similar images for the remainder of the samples can be viewed in Appendix A. The normalised intensities of CMC in the presence of both potassium and calcium ions at pH 9 are shown in Figure 6.13.



(A) (B)

Figure 6.11 - (A) SEM image of a basal plane of a talc particle, (B) Corresponding ionic image of CMC in the presence of potassium ions, superimposed onto the original SEM image of the talc particle, with selected analysis area

(A) (B)

Figure 6.12 - (A) SEM image of a basal plane of a talc particle, (B) Corresponding ionic image of CMC in the presence of calcium ions, superimposed onto the original SEM image of the talc particle

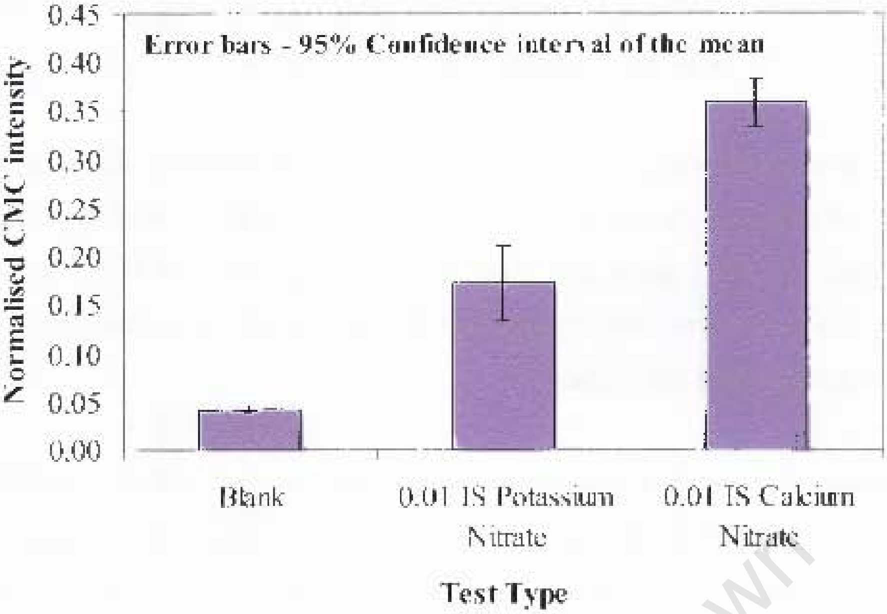


Figure 6.13 – Normalised intensities of CMC in the presence of both calcium and potassium ions on the basal planes of talc, at the ionic strength of 0.01, at pH 9

The results show that in the case of both monovalent potassium ion solutions and polyvalent calcium ions solutions, the normalised intensities of CMC are greater than the reference baseline sample. This indicates that the adsorption of CMC molecules takes place on the basal planes of talc at pH 9 in the presence of both these ion types.

Figure 6.13 also shows that the normalised intensities of CMC in the presence of calcium solutions are significantly higher than those in the presence of potassium solutions at the same ionic strength. This indicates that CMC adsorbs more strongly onto talc basal planes in the presence of calcium than it does in the presence of potassium at the same ionic strength. These findings are once again in agreement Parolis (Parolis *et al.* 2004; Parolis *et al.* 2006) who produced similar results using bulk adsorption techniques.

These differences can be attributed to three factors: The decreased magnitude of electrostatic repulsion between the anionic polymer and the negatively charged basal plane, denser adsorption of polymer due to a greater degree of polymer coiling and the presence of metal hydroxide ion species on the basal planes of talc enabling acid/base interactions between the polymer molecules and the talc surface.

It was shown in the previous sections that the presence of different cations in solution has a different effect on the magnitude of the surface charge of talc minerals. Therefore, the magnitude of CMC absorption onto talc in the presence of both calcium and potassium ions at the same ionic strength can be compared to the relative magnitude of the surface charge on the talc surface.

It is important to note that the relative magnitudes of talc surface potential were obtained by apparent zeta potential measurements. While these measurements provide an adequate comparison between mineral behaviour under different chemical conditions, they cannot be treated as absolute values of surface potential (see Chapter 2 for details).

Table 6.1 shows the normalised intensities of CMC molecules in the presence of different cations in conjunction with the apparent zeta potential of talc surface in the presence of these cations.

Table 6.1 – Normalised intensities of CMC vs. the apparent zeta potential of talc in the presence of calcium and potassium solutions at the same ionic strength

	Normalised CMC Intensity	**Apparent Zeta Potential (mV)**
0.01 IS, KNO_3	0.17 ± 0.04	-27.73 ± 1.08
0.01 IS, $Ca(NO_3)_2$	0.36 ± 0.03	-14.40 ± 0.35

Note that the error values shown represent the 95% confidence intervals of the values

The results shown in Table 6.1 indicate that in the case of potassium solutions, the low degree of CMC adsorption corresponds to a high negative apparent zeta potential of talc particles. This indicates that in the presence of potassium ions, there exists a large electrostatic repulsive force between negative talc surface and anionic polymers.

In the case of calcium ions, the negative apparent zeta potential is much lower and corresponds to a higher degree of CMC adsorption. This indicates that the magnitude of electrostatic repulsion between the CMC molecules is much lower, which results in denser CMC adsorption. These results indicate that electrostatic forces play an important role in the adsorption mechanisms of CMC onto mineral basal planes. The results obtained by ToF-SIMS measurements have shown a high degree of adsorption of $CaOH^+$ ions on the surface of talc particles, which then potentially interact with CMC molecules.

However, these results do not take into account the effect that metal cations have on the degree of coiling of CMC macromolecules. Therefore, the effect of CMC-cation interaction within the suspension medium still needs to be examined.

6.3.3 Interaction between CMC and calcium and potassium ions

The solution interactions between CMC macromolecules and calcium and potassium ions present in solution have been extensively studied by Parolis *et al* (2004, 2006) using intrinsic viscosity techniques. It was found that the CMC molecules underwent conformational changes as a function of the ionic strength of the cations present in solution. However, it was also found that Ca^{2+} ions had a significantly greater effect on polymer coiling than K^+ ions. This is due to the high affinity that calcium ions have for anionic carboxylic acid groups present on the polymers, which is conducive to gel formation (Kastner *et al.* 1997).

This section examines the same phenomenon by means of interrogating the adsorption data of CMC molecules onto the surface of talc obtained by means of ToF-SIMS measurements.

The combination of SEM images with ToF-SIMS ionic spectra has been previously used in this work in order to establish whether or not the adsorption of a given ionic species occurs on a specific particle plane. This technique can also be applied for examining the distribution of ionic spectral images of specific ions in spatial relation to one another. Figure 6.14 shows an SEM image of a single basal plane of a talc particle with the ToF-SIMS ionic spectral images of potassium ions, calcium ions and CMC respectively.

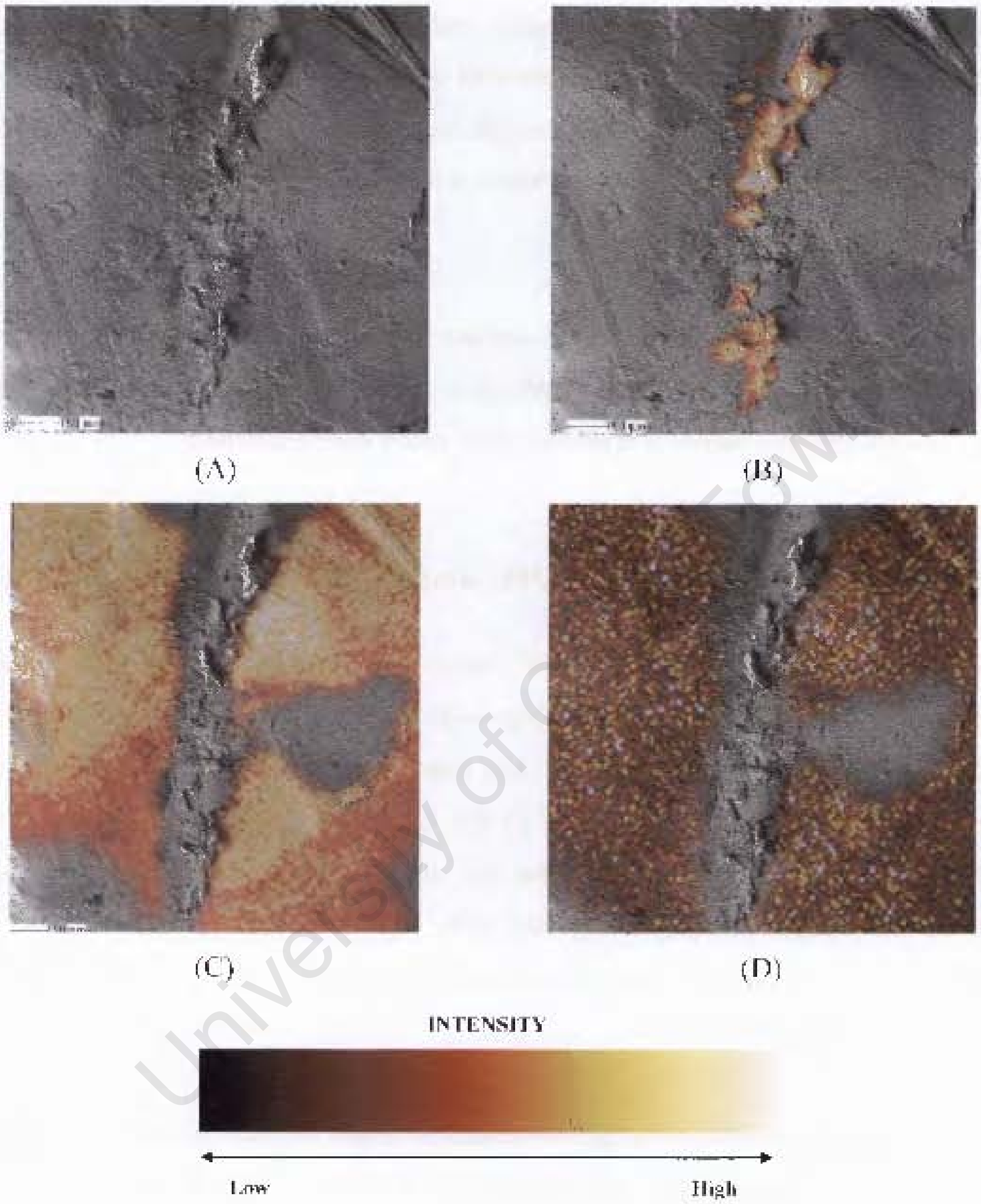


Figure 6.14 Images of talc basal planes, (A) SEM image of the basal plane of a talc particle, (B) Corresponding ToF-SIMS image of potassium ions, (C) Corresponding ToF-SIMS image of calcium ions. (D) Corresponding ToF-SIMS image of CMC.

Figure 6.14 (B) and (D) show the images of the distribution of potassium ions and CMC molecules respectively. The image shows that the distribution of CMC on the particle plane does not correlate to the distribution of potassium ions on the same particle. While potassium ions occur in a thin grouping across the centre of the image, the CMC molecules take up the remainder of the space on the basal plane surface.

On the other hand, Figure 6.14 (C) and (D) show the images of the distribution of calcium ions and CMC molecules respectively. The images show that the distribution of CMC molecules on the basal plane of the talc particle closely corresponds to that of calcium ions. This indicates that there might exist a strong relationship between the presence of calcium ions and CMC adsorption.

Its is difficult to judge whether or not a correlation exists between CMC and metal cations by looking at a small number of images. Numerical correlations can be obtained by comparing the normalised intensities of metal cations and CMC molecules in a large number of samples.

Figure 6.15 shows a plot of the normalised CMC intensities versus the normalised intensities of potassium ions on the basal planes of talc at various solution conditions. The results were plotted on a log-log scale in order to account for a bias in number of samples with the ionic intensities towards lower magnitudes.

The results presented in Figure 6.15 show no significant correlation between CMC adsorption onto talc basal planes and the presence of potassium ions in solution exists. The coefficient of determination (R^2) was calculated to have a low value of 0.031, which carries a confidence of 81.2 % that a correlation exists. This indicates that a linear relationship between CMC adsorption and the presence of potassium ions is not significant.

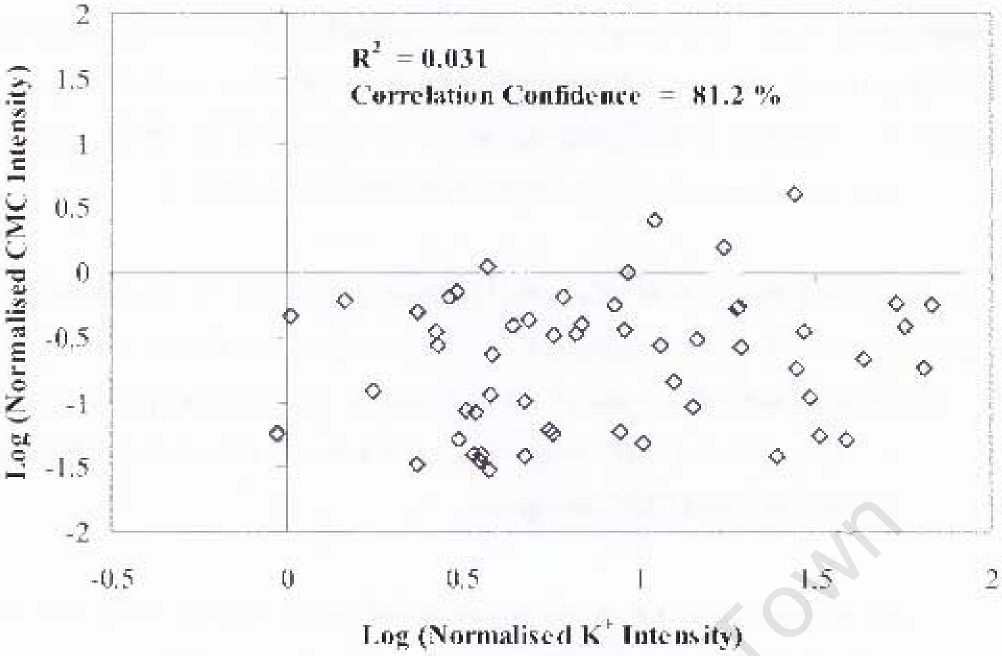


Figure 6.15 – Normalised intensities of CMC molecules shown versus normalised intensities of potassium ions on a log – log scale

Similar correlations can be drawn between the normalised intensities of CMC molecules on the surface of talc and the normalised intensities of $CaOH^+$ present on the surface. The results are shown in Figure 6.16.

The results presented in Figure 6.16 show that a statistically significant linear relationship exists between the adsorption density of CMC molecules and the amount of calcium hydroxide ions adsorbed onto the surface of talc basal planes. The R^2 value for the relationship is 0.86, which corresponds to a 100.00% confidence in the linear relationship. The residual plots of the data are shown in Appendix B.

The data shown in Figure 6.16 demonstrates that there exists a strong relationship between the amount of CMC adsorbed on the surface of talc and the amount of $CaOH^+$ ions adsorbed on the surface of talc.

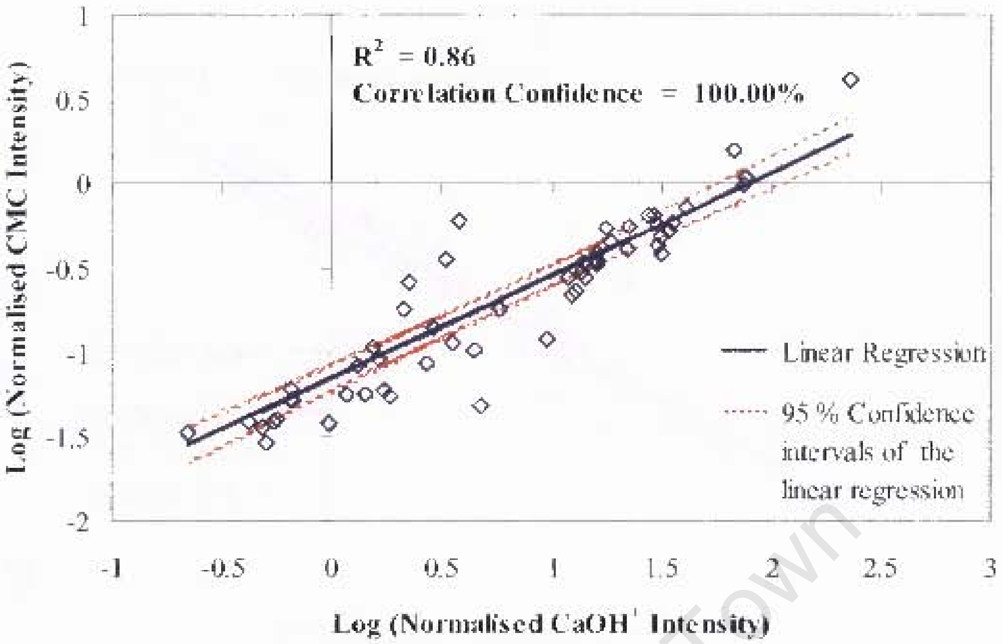


Figure 6.16 – Normalised intensities of CMC molecules shown versus normalised intensities of $CaOH^+$ ions on a log – log scale

However, this relationship does not imply that there exists a solution interaction between the CMC molecules and $CaOH^+$ ions. As was shown in the previous sections, the increase of CMC adsorption can be attributed to both the effect of reduced surface negativity of talc and the increased presence of metal hydroxide species on the surface of talc.

Using similar methods, the interaction between CMC adsorption onto talc and the presence of Ca^{+2} ions can be examined. Previous results have shown that the adsorption density of Ca^{+2} onto the basal planes of talc is negligible; however, these ions may still have an effect on CMC molecules while present in the suspension medium. The results are shown in Figure 6.17. The results show that a statistically significant linear relationship exists between the adsorption of CMC molecules onto the basal planes of talc and the adsorption of Ca^{+2} ions onto the same surface. The R^2 value for the relationship is 0.77 which corresponds to a 100.00% confidence in the linear relationship. The residual plots of the data are shown in Appendix B.

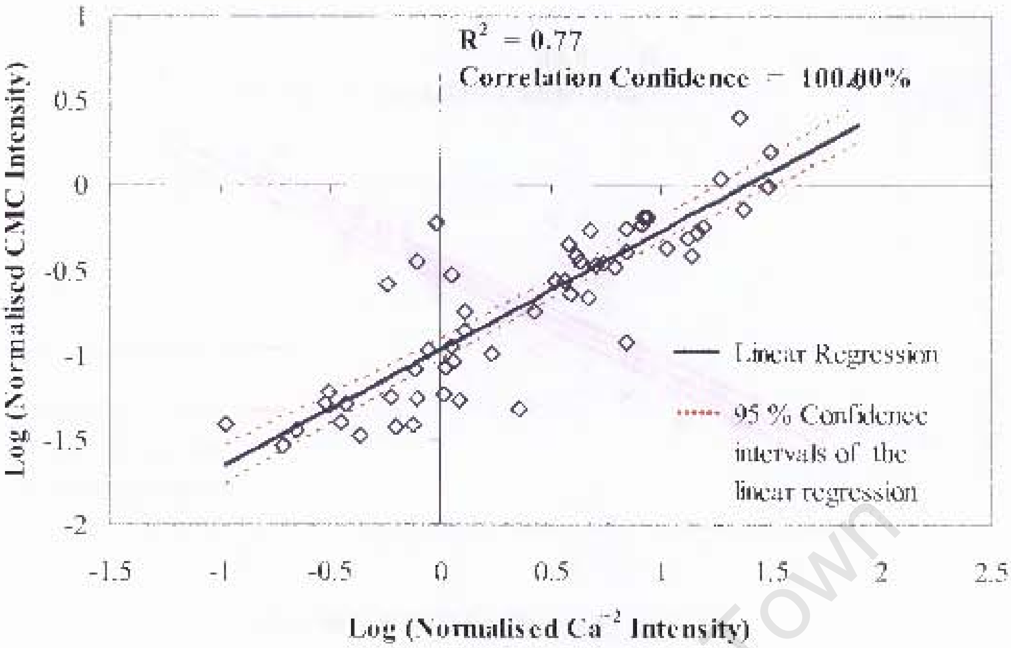


Figure 6.17 – Normalised intensities of CMC molecules shown versus normalised intensities of Ca^{+2} ions on a log – log scale

As mentioned above, the adsorption of Ca^{+2} ions onto the surface of talc in the absence of CMC in solution is negligible. Therefore, the increase in the adsorption of Ca^{+2} ions onto the surface of talc is caused by the presence of CMC in solution rather than vice versa. The adsorption densities of Ca^{+2} ions on the surface of talc basal planes in the presence and absence of CMC in solution, at pH 9 is shown in Figure 6.18.

The results show that in both cases, in the absence and presence of CMC, the normalised intensities of calcium ions on the basal planes of talc are significantly larger than that on the blank reference sample. This indicates that in both cases a significant amount of calcium ions adsorb onto the surface of the talc basal planes. However, in the absence of CMC the adsorption of Ca^{+2} ions is still small enough to be considered negligible, while in the presence of CMC molecules in the suspension medium, the adsorption of calcium onto the basal planes of talc increases by two orders of magnitude.

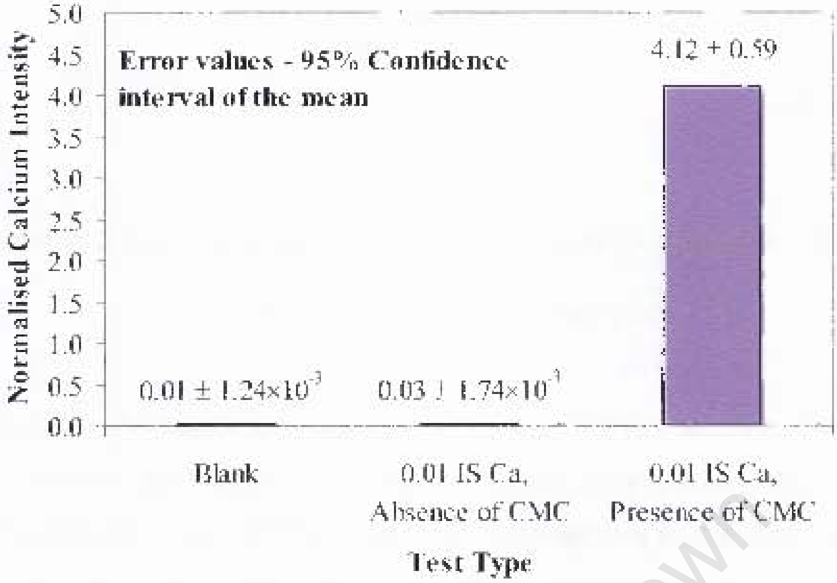


Figure 6.18 - Normalised intensities of calcium ions on the basal planes of talc at the ionic strength of 0.01, pH 9, in the presence and absence of CMC in solution

These results indicate that the relationship between calcium adsorption and CMC adsorption onto basal planes of talc shown in Figure 6.17, is driven by the presence of CMC in the solution medium and therefore represents solution interactions between Ca^{+2} ions and CMC molecules.

The increased adsorption of calcium ions onto the surface of talc is consistent with the findings of Parolis et al (2006), who showed that calcium ions interact with CMC molecules in solution and form gels. Calcium ions are known to have a high affinity for carboxylic acid groups which form part of the CMC molecules. Divalent calcium ions form bonds with the proton deficient oxygen atoms which form part of the carboxylic acid group. This then causes the CMC molecules to coil. The schematic representation of the reaction between the calcium ions and carboxylic acid groups is shown in Figure 6.19. This interaction between polyvalent metal cations and carboxylic groups is similar to that described by Liu and Laskowski (1999), who showed that such interactions take place between CMC and lead ions.

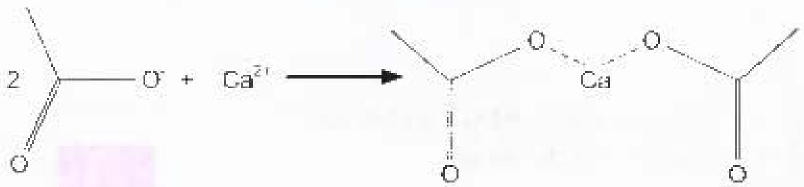


Figure 6.19 Schematic representation of the reaction of Ca^{2+} *ions with the carboxylic acid groups present on the CMC molecules.*

Therefore it is possible that the increase in the adsorption density of calcium ions on the presence of CMC molecules in solution is caused by the chemical reaction which takes place in the solution medium between Ca^{2+} ions and CMC molecules. If such a reaction takes place, then the viscosity of the CMC solution should decrease with the addition of calcium ions. Such results were demonstrated by Parolis (2006).

The calcium ions then adsorb onto the mineral surface as part of the CMC molecular structure. The greater degree of polymer-calcium interaction within the solution medium causes the polymer molecules to become more coiled. The increased coiling then facilitates a denser adsorption of the polymers, which in turn causes the adsorption of calcium cations onto the surface of talc to increase.

Another reason for denser adsorption of CMC molecules onto talc in the presence of calcium rich solutions rather than solutions containing potassium ions, is the increased degree of coiling of CMC molecules due to the solution interaction between CMC molecules and Ca^{-2} ions present in solution.

6.4 SECTION KEY FINDINGS

From the results presented in this chapter, the following key findings can be identified:

- The combination of ToF-SIMS images with low resolution SEM images have shown that the basal planes of talc particles can be successfully isolated for surface specific analysis.

However, it was found that talc edges could not be isolated for measurement, due to a large degree of obstruction by the particle basal planes during the sample preparation process.

- The adsorption of calcium ions on the basal planes of talc was found to take place mainly in the form of $CaOH^+$ ions. These findings contradict those of Fuerstenau (1988), who postulated that metal hydroxide species do not interact with the talc basal planes.

  This finding reinforces the importance of surface specific measurements in the study of the adsorption of ionic species on the surface of minerals.

- Surface specific ToF-SIMS measurements also showed that potassium ions adsorb onto the basal planes of talc. The adsorption of these ions was found to be less dense than that of $CaOH^+$ ions at the same solution ionic strength.

- The surface potential of talc particles (as indicated by apparent zeta potential measurements), at a constant pH of 9, was found to decrease as a function of increasing ionic strength of solutions for both calcium and potassium ions. However the presence of calcium nitrate solution was found to reduce the surface potential of talc to a significantly larger degree than in the presence of potassium nitrate solution at the same ionic strength.

- The adsorption of CMC onto the basal planes of talc (as indicated by ToF-SIMS measurements) was found to take place to a greater extent in the presence of calcium nitrate in solution than that of potassium nitrate at the same ionic strength.

- The increased degree of CMC adsorption was shown to increase with reduced surface potential of the talc particles, as indicated by apparent zeta potential measurements.

- No correlation was found between the degree of adsorption of CMC molecules onto the basal planes of talc and the adsorption of potassium ions. This result indicates that no chemical interaction takes place between CMC molecules and potassium ions in the solution medium.

- A strong correlation was found between the adsorption of CMC molecules onto the basal planes of talc and the adsorption of $CaOH^+$ ions. This dependence was attributed to the decrease in the negative surface potential of talc particles as a result of $CaOH^-$ adsorption, leading to a greater electrostatic adsorption of anionic CMC molecules. The correlation was further attributed to the increase in CMC adsorption onto the talc surface a result of an acid/base interaction with the calcium hydroxide groups present on the surface of talc.

- A strong correlation was found between the adsorption of CMC molecules onto the basal planes of talc and the adsorption of Ca^{+2} ions. This correlation was attributed to the solution interaction between the divalent calcium ions and the anionic carboxylic acid group present on the CMC molecules, causing these molecules to coil. The increased amount of Ca^{+2} ions adsorbed on the basal planes of talc as a function of CMC adsorption is attributed to the calcium ions being adsorbed on the surface of talc as part of the CMC molecule itself.

6.5 REFERENCES

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7 Summary and Conclusions

7.1 SUMMARISED DISCUSSION OF THE RESULTS

The overall objective of this study was to investigate the surface properties and structure of New York talc, and its effect on the adsorption mechanisms of different types of polymeric depressants in the presence of calcium and potassium ions in solution.

In order to fulfil the objective of the study, a number of experimental tests were performed on New York talc under a series of solution conditions, which were described and discussed in detail in the previous chapters. This section presents a summary of the key findings of this thesis and presents a critical discussion of these findings in the context of the available literature. An alternative model for the surface charge distribution of New York talc is also proposed.

7.1.1 Talc surface charge distribution

The basal planes of talc are widely thought to be completely neutral, while the edges of talc are thought to undergo a change from positive to negative at a pH ≈ 2.5. These assertions are generally based on zeta potential measurements of talc suspensions, which yield an isoelectric point of talc at pH ≈ 2.5.

However, the rheological and potentiomteric titration measurements of New York talc have shown that the behaviour of talc is inconsistent with the currently accepted surface charge distribution of talc.

The point of net zero charge determined by titration was found to differ significantly from the electrophoretic isoelectric point, because unlike electrophoretic measurement, titration measurements are not biased by the complex hydrodynamics of plate-like suspensions.

Furthermore, the yield stress peak of talc suspensions did not coincide with neither the point of net zero charge nor the isoelectric point. Such behaviour is consistent with that of anisotropic minerals that carry a different electrical charge on multiple particle planes.

On the basis of these findings, an alternative surface charge distribution of talc was proposed where the basal planes of talc carry a permanent negative charge due to random substitution of silicon ions in the tetrahedral layers of talc with aluminium ions of a lesser charge. The edges of talc were proposed to change from positive to negative at a pH below the point of net zero charge, as illustrated in Figure 7.1.

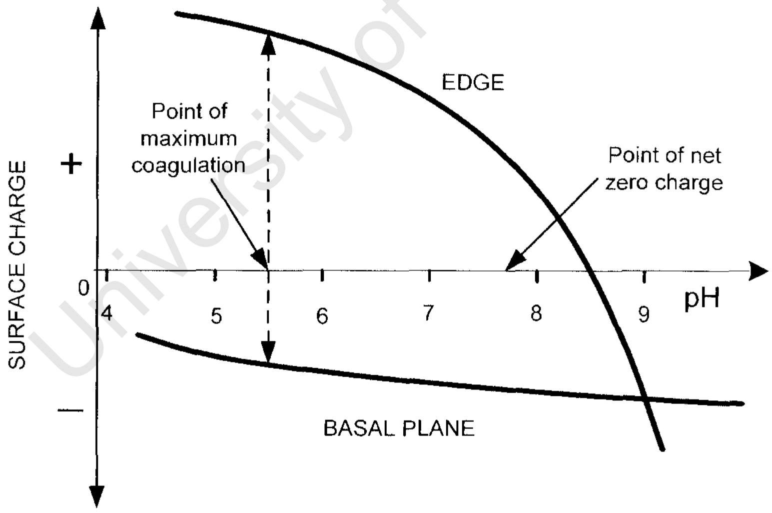

Figure 7.1 – Proposed charge distribution on the surface of talc

A microprobe analysis of New York talc confirmed the presence of aluminium ions on the talc surface in sufficient quantities to cause significant shifts in the electrical charge of the talc basal planes. The presence of the negative charge on the basal planes of talc was further confirmed by cationic adsorption on the basal plane surface. Positively charged potassium ions (which adsorb onto mineral surfaces by means of electrostatic attraction) were shown to adsorb onto the basal planes of talc.

The proposed surface charge distribution of talc was further confirmed by the rheological behaviour of talc suspensions in the presence of both anionic and non-ionic polymeric depressants. At high dosages of guar gum, the yield stress peak of talc suspensions began to approach the point of net zero charge of New York talc, due to the "masking" of the charge on the talc basal planes by the neutral guar gum molecules. The adsorption of guar gum therefore brought talc particles closer to the state of isotropy, where the only electrical charge having an effect on the rheological behaviour is that of talc edges. This showed that the change from positive to negative on the edge surfaces occurs at a high pH.

The proposal for an alternative surface charge distribution of talc was further reinforced by the rheological behaviour of talc in the presence of anionic CMC. The addition of CMC was show to have an effect on the rheological behaviour of talc at pH values below pH $\approx$ 8, which approximates the net point of zero charge of talc determined by titration. Since CMC molecules are anionic, these results indicate that the adsorption of CMC takes place mainly in the pH region where talc particles carry a positive charge.

The alternative distribution of surface charge of talc particles was verified by means of a number of independent experimental techniques, such as potentiomteric titration, rheological measurement both in the presence and absence of anionic and non ionic polymers, electronic microprobe measurements and ToF-SIMS measurements of ions adsorption.

The exact magnitude of the electrical charge on the basal planes and edges of talc remains unknown. Similarly, the exact point of zero charge of the talc edges remains unknown due to problems arising from sample preparation techniques.

7.1.2 Effect of talc surface charge on polymer adsorption

The adsorption characteristics of polymeric depressants onto talc have been intensively studied by a number of researchers. The investigations were mainly carried out with the use of bulk solution adsorption techniques.

In order to investigate the adsorption mechanisms of polymeric depressants onto talc as a function of talc surface charge, this study employed a relatively novel method, whereby the behaviour of talc suspension in the presence of polymer under various conditions was studied using rheological measurements. This approach was successful as it indicated that the differences in the inter-particle interactions of talc as a function of polymer dosage and type, hence relating the changes in the surface charge distribution of talc as a function of polymer adsorption.

The adsorption of non-ionic guar gum onto talc was found to be independent of the surface charge of talc particles. This finding is in agreement with the premise that guar gum adsorption takes place by means of hydrogen and hydrophobic bonding and is therefore independent of surface charge. The results also showed that the adsorption of guar gum takes place mostly on the basal planes of talc, due to its effect on the rheological behaviour of talc suspensions. This finding is in agreement with researchers such as Steenberg and Harris, who found similar trends (Steenberg & Harris, 1984).

The adsorption of CMC was found to be strongly affected by the surface charge distribution of talc, as it occurred mainly in the pH region below the measured point of net zero charge of talc. In other words, the adsorption of CMC mainly took place in the pH region where the talc surface exhibits a net positive charge. These results are consistent with the premise that electrostatic attraction plays an important role in the adsorption of CMC onto talc and are in agreement with the findings of other researchers (Morris *et al.*, 2002; Wang & Somasundaran, 2005).

In order to verify that the differences in polymer adsorption onto talc as a function of pH took place as a result of changing talc surface charge distribution and not as a result of changes in polymer conformation, intrinsic viscosity tests were performed on both CMC and guar gum polymers as a function of pH.

The results showed that in the case of both anionic and non-ionic polymers, no significant conformational changes occurred in the pH range tested. These results verified that the differences in rheological behaviour of talc as a function of pH and polymer addition arise from the differences in talc surface charge distribution, and not polymer conformation.

7.1.3 Effect of calcium and potassium ions on the surface charge of talc and polymer adsorption

The effect that the adsorption of monovalent potassium ions and divalent calcium ions have on the surface charge distribution of talc and consequently its effect on the adsorption characteristics of anionic polymeric depressants were studied using surface specific ToF-SIMS measurements.

An attempt was made at the measurement of the relative adsorption densities of both cations and polymers as a function of particle morphology, i.e. specific measurements on the basal planes and edges of talc respectively. This was done by means of a combination of ToF-SIMS measurements with low resolution SEM images.

The results showed that this technique could be successfully used to isolate the basal planes of talc particles and therefore obtain measurements of relative ion and polymer adsorption specifically on the basal planes of talc. However, it was found that talc edges could not be isolated for measurement, due to a large degree of obstruction by the particle basal planes during the sample preparation process.

The adsorption of calcium ions on the basal planes of talc was found to take place mainly in the form of $CaOH^+$ ions. While some Ca^{+2} ions did adsorb on the surface, their adsorption density was negligible compared to that of the hydroxide ions. These findings contradict the findings of Fuerstenau (Fuerstenau *et al.*, 1988) who deduced that hydroxide ions do not interact with the basal planes of talc, on the basis that the adsorption of ions did not affect the floatability of talc.

This finding, coupled with the finding that talc basal planes carry a negative charge, suggest that the floatability of talc particle may not be influenced by the surface charge of talc basal planes, nor the degree of adsorption of metal hydroxide species. This finding highlights the importance of surface specific measurements when studying the effect of solution chemistry on the surface properties of minerals.

The adsorption of potassium ions on the basal planes of talc was also found to take place, but to a lesser extent than that of calcium hydroxide ions. These results were in agreement with the apparent zeta potential measurements which showed that the negative surface potential of talc was reduced to a greater degree in the presence of calcium ions in solution than in the presence of potassium ions.

The adsorption density of CMC molecules on the basal planes of talc was also studied using ToF-SIMS measurements. It was found that CMC molecules adsorb more densely onto talc basal planes in the presence of calcium ions in solution than in the presence of potassium ions. These findings were in good agreement with the findings of other researchers (Parolis *et al.*, 2004; Khraisheh *et al.*, 2005).

The findings confirm that electrostatic attraction plays an important role in the adsorption characteristics of CMC onto talc. The results are in agreement with the rheological measurements of talc suspension in the presence of CMC, which showed that the suspension yield stress was only affected by the presence of CMC in solution in the pH region where the net charge of talc particles was positive.

The findings are also in agreement with the premise that CMC adsorbs onto talc by means of an acid/base interaction with metal hydroxide species on the surface of talc, since CMC adsorption density correlated with an increased amount of adsorption of calcium hydroxide ions on the surface of talc.

A further factor in the increased adsorption of CMC molecules in the presence of calcium ions in solution was the solution interaction between polymer molecules and calcium ions. This was also tested using ToF-SIMS measurements, where correlations were drawn between the adsorption of CMC ions and other ions present in solution.

It was found that no correlation exists between the amount of potassium ions adsorbed on the surface of talc and that of CMC molecules. There was a strong correlation found between the adsorption of CMC molecules and that of calcium hydroxide ions in solution. This correlation was attributed to the influence of calcium hydroxide ions on the surface of talc, which promotes CMC adsorption.

A strong correlation was also found between the adsorption of CMC molecules and the adsorption of Ca^{-2} ions onto the surface of talc. Since the absorption of talc in the absence of CMC in solution was found to be negligible, the increase in Ca^{+2} ions adsorption was attributed to the chemical interaction with CMC molecules in solution, whereby Ca^{-2} ions react with carboxylic groups of the CMC molecules, causing the polymer to coil. The coiling then causes a denser adsorption of CMC molecules onto talc.

The increase in the adsorption density of CMC molecules in the presence of calcium ions in solution over that in the presence of potassium ions in solution can be explained in terms of the following three factors:

- The reduced negative surface potential of talc due to denser adsorption of calcium hydroxide ions, causing a reduction in the electrostatic repulsion between the surface of talc basal planes and anionic CMC molecules.

- The presence of metal hydroxide ions on the basal planes of talc due to the adsorption of calcium hydroxide ions, allowing CMC adsorption by means of an acid/base interaction between CMC molecules and the calcium hydroxide species on the basal plane surface.

- The chemical interactions of CMC molecules with Ca^{-2} ions in the solution medium, causing an increased amount of coiling of the CMC molecules. This increased amount of coiling then promotes denser special adsorption of CMC molecules on the basal planes of talc.

7.2 CONCLUSIONS

From all the data presented in this thesis the following conclusions can be drawn:

- The basal planes of talc carry a negative charge due to a natural substitution of silicon ions with aluminium ions of a lesser charge in the tetrahedral layers of talc. However, the exact magnitude of the negative charge is not known.

- The edges of talc undergo a charge from positive to negative at a pH below the point of net zero charge of talc, mainly pH 7.7 ± 0.45. The exact point of the zero charge of the talc edges is still unknown.

- The adsorption of guar gum onto talc takes place by means of hydrogen/hydrophobic bonding and is independent of the surface charge of the mineral particles.

- The adsorption of guar gum takes place primarily on the basal planes of talc.

- The adsorption of CMC onto talc is likely to take place largely by means of electrostatic attraction and acid/base interaction with metal hydroxide species present on the talc surface, and is therefore highly dependent on the surface charge of the mineral and the degree of adsorption of metal hydroxide species onto its surface.

- The adsorption of CMC molecules onto talc is further promoted by the chemical interaction between the polymer and Ca^{+2} ions in the solution medium which causes an increased amount of polymer coiling, thus promoting denser adsorption.

- The adsorption of calcium ions on the basal planes of talc takes place primarily in the form of $CaOH^+$ ions. Since the floatability of talc particles was shown to remain unchanged in the presence of metal hydroxide ion species (Fuerstenau *et al.*, 1988), the floatability of talc may not be a function of surface charge of the talc basal planes nor the degree of adsorption of metal hydroxide ion species on the basal planes of talc.

7.3 RECOMMENDATIONS FOR FUTURE WORK

In light of the findings of this thesis, the following recommendations can be made:

The study of New York talc should be continued by repeating the ToF-SIMS measurements on the edges of talc. The samples should be prepared by means of manual cleavage of talc particles, in order to eliminate the problem of obstruction of the edges of talc by the basal planes.

The work presented in this thesis should be extended to include talc samples from different deposits, with variation in factors such as morphology (e.g. Scotia talc, South Africa) and composition (e.g. talc formed by secondary formation by altercation of other silicates, e.g. talc found in the Bushveld complex). Similarly, the work should be extended to include other silicateous minerals (such as pyroxene and feldspar) that occur in PGM bearing ore deposits.

In future studies, the ToF-SIMS measurements should be calibrated in order to obtain a quantitative measurement of CMC adsorption on the surface of minerals.

The effect whereby an increased dosage of CMC from 200 g/ton to 400 g/ton causes an increase in yield stress of talc suspensions as opposed to a decrease should be examined further.

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