UNIVERSITÉ DU QUÉBEC À MONTRÉAL

UNE SÉPARATION COLLOÏDALE AMÉLIORÉE AVEC L'AJOUT DE SURFACTANT POUR LA CARACTÉRISATION ET LA DÉCONTAMINATION DE SÉDIMENTS MULTIPHASÉS

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RÉSUMÉ

Cette étude cible les questions relatives aux systèmes aqueux de fines particules près ou sous le micron qui sont importantes et nombreuses en environnement avec les résidus anthropiques et en particulier avec les matériaux anthropogéniques des sédiments de rivières et des lacs. Le but principal visé était de démontrer l'importance d'utiliser un surfactant comme agent pour améliorer la séparation colloïdale en milieu aqueux. Dans cette technique les surfactants altèrent la charge de surface des particules qui vont dicter le comportement et la destination des phases respectives du système par les floculations ou suspensions.

À cause de leur masse extrêmement petite, l'effet de gravité est atténué et joue un rôle plus voilé avec le temps. Pour des études de caractérisation de tels systèmes, en environnement, où les difficultés tiennent à la présence des fines sous microniques et aux mélanges polyphasés, ces systèmes répondent mal à l'application des méthodes conventionnelles habituellement utilisées de séparation comme la séparation magnétique en milieu sec ou humide, la séparation électroacoustique et la séparation par liqueurs denses.

Les paramètres fondamentaux du potentiel zêta déterminent l'état et les conditions pour une suspension ou pour une floculation. La mobilité des particules solides peut être mesurée par une technique acoustique ESA qui permet de calculer les valeurs du potentiel zêta. Cette détermination implique l'intégration des mesures de la distribution granulométrique, du poids spécifique et les considérations des paramètres chimiques du système soit le pH, la température et la conductivité.

Nos résultats indiquent, comme l'hypothèse originale le supposait, que les minéraux naturels ont la même polarité de surface et des intensités de charges comparables aux composés anthropiques pour une composition chimique et structure atomique similaire. Les résultats confirment également que pour un système polyphasé, le signe de polarité et l'intensité du zêta initial sont la résultante de la sommation des valeurs de zêta des phases constituantes. L'équation suivante se vérifie:

$$\zeta \text{ (zeta) mV pour la system} = \Sigma\zeta_a \text{ X } C_a + \zeta_b \text{ X } C_b + \ldots\ldots.$$

Plusieurs systèmes artificiels ont été étudiés et les données initiales du système mesuré servent de guides pour trouver les conditions qui permettront d'induire la floculation et le fractionnement en systèmes moins polyphasés et plus simples facilitant ainsi une caractérisation. Les essais et la détermination des paramètres influençant la séparation colloïdale par un surfactant ont été mises au point initialement sur un sédiment de lac comprenant des particules de sulfures de 2 à 3 µm. La présence de grains de sulfures dans le sédiment original n'avait pas été détectée par diffraction de rayons X mais suite au fractionnement et a une concentration résultant plus élevée dans les couches fractionnées, des sulfures pouvaient être identifier. Cette technique a d'ailleurs été utilisée pour caractériser le fractionnement en couches dans lesquelles on retrouve une forte variation dans la concentration des phases constituantes incluant les sulfures. Le fractionnement résultant est de qualité suffisante pour que cette technique soit considérée dans une remédiation environnementale, en particulier pour les résidus miniers où le potentiel de d'acidité excède la capacité de neutralisation engendrant une problématique de drainage minier acide (DMA).

Initialement le projet a étudié et caractérisé des mélanges simples de suspension de minéraux suivis d'un ajout progressif des phases du système. pour éventuellement simuler un système naturel contaminé. Une comparaison des similitudes et des différences des systèmes artificiels et naturels sert de base aux conclusions.

Mots clés: Potentiel zêta, minéraux naturels, surfactant, sulfures, décontamination, double couche électrique, séparation colloïdale.

ABSTRACT

This study addresses several questions related to aqueous system with fine micron size solid particles in the environmental field of anthropic residues and anthropogenic materials from river and lakes. The main goal was to finalize the development of a surfactant enhanced hydro separation technique applicable in the realm of the colloid fraction size solids. In this technique the surfactant alters the charge surface of the solids that dictate flocculation and suspension and final destination for some phase. Because of the small mass of the particles, gravity will play a secondary role that is time dependant, a function related to the grain size of the solids involved. These environmental problems are difficult to study because they are complex multiphase systems, which cannot easily simplified for an analysis through conventional separation techniques such as dry or wet magnetic separation, electrostatic separation or by heavy liquid separation.

The fundamental and key parameter is the zeta potential. This parameter is directly related to the surface charge of the particles. The zeta potential can be measured with an acoustic technique ESA that yields a mobility value for the solid from which a zeta potential can be calculated by integrating grain size and specific gravity of the solids. The potential zeta is used to define a suspension or flocculation and therefore predict the final deposition site. The other parameters measured simultaneously with the ESA apparatus are chemical parameters of the liquid that are reflected by the pH, temperature and conductivity values.

This project initiated its investigation by characterizing simple natural mineral slurries and by increasing the number of phases until a complex natural contaminated system was simulated for which similitude and differences could be measured and compared. Our results verified the initial assumption that natural minerals had the same surface polarity and similar intensity values as found with its anthropic equivalent for similar chemistry and structure. The results also established that in a multiple phase system, the initial measured zeta have a value dictated by the overall summation of the individual zeta of the constituent phases. We were able to verify the equation of state:

$$\zeta \text{ (zeta) mV for the system} = \Sigma\zeta_a \text{ X } C_a + \zeta_b \text{ X } C_b + \ldots\ldots.$$

After studying simple mineral systems guidelines were established for promoting suspension, flocculation and fractionation of simple and complex systems. This enhanced surfactant colloid separation was found to induce fractionation in a natural multiphase system for grain size distribution with a median of 2 to 3µm. Sulphides in the untreated sediments were not detectable initially by X-ray diffraction but were detectable in the fractionated layers because of the higher concentration of the sulphides in certain layers. The amount of sulphides fractionated appeared sufficient to qualify this process as a remediation technique for which the neutralization potential of the solid would exceed its potential for acid generation with mining residues. These fractionated solids layers can be submitted to more exhaustive characterization that can includes radiochemical analysis when radiometric lead or other radiometric elements are involved.

Key words: Zeta potential, Natural minerals, Surfactant, Sulphides, Decontamination, Electrical double layer, Colloid separation.

INTRODUCTION

Fine-grained sub-micron size contaminated materials are difficult to characterize, manage, remediate or even evaluate their inherent environmental risk and impact. With sub-micron size particles the charge at the surface of the solids are more important than their mass. Sub-micron systems are only slightly influenced by gravity and their surface charge is the most important parameter in understanding such behaviour as flocculation, suspension and mobility in aqueous system. By definition, such systems are colloid systems because of the size and the associated surface charge of the particles.

A non-treated multiphase system of micron size particles will usually display agglomeration because of the differences in the polarity of the chemical compounds and as a result, the conventional physical separation techniques such as magnetic separation, electrostatic and or conventional flotation cannot be successfully used to fractionate the system. This scenario in environmental problems is generally the rule and such materials are difficult to characterize from a physical and chemical standpoint.

The majority of environmental techniques presently available for treatment and remediation of solid residues are mainly applicable to coarse grain materials. The procedures usually consist in a simple washing with a pre-treatment when required. In other cases residues need to be leached or submitted to a pyrometallurgical process. These classical metallurgical techniques cannot always be successfully applied to finely divided matter because of technical or economical considerations. Unfortunately these micron size systems usually contain the bulk of the contaminants whether organic or inorganic, in part because of the larger specific surface area offered by such a system. Presently, no non-destructive process can fractionate these systems in such a way that the contaminant phases could be isolated and separately managed for a remediation.

The first part of this memoir deals with the study of an artificially made system prepared to approximate multiphase contaminated systems often found with lake sediments. It was anticipated that in order to elucidate the fundamentals for a technique applicable to natural complex system, a study of simpler system was necessary.

More specifically the second part of this memoir would like to establish:

- If anthropogenic compounds and their corresponding natural minerals have similar surface characteristics;
- If natural multiphase systems the initially measured bulk zeta potential can be related to the sum of the zeta for the individual phases present multiplied by their individual concentrations;
- If by knowing the zeta of a system and most of the minerals present can it be possible to forecast if such a system can be fractionated for an eventual remediation;
- If with this technique, knowing the mobility of the decanted solid, can a stability factor or a risk assessment be given related to possible environmental changes such as pH, Eh, conductivity, flooding etc.

STATE OF THE ART & PREVIOUS WORKS

Colloid filtration or separation is a technique developed by the ceramic industry and is not presently used in the environmental field. The colloid separation technique was developed for a simple system of one or two solid phases with a liquid for which a suspension or flocculation can fractionate the system into its component parts. This technique is also used in the pigment industry for coating inorganic pigments in order to achieve products with specific surface characteristics.

In previous preliminary studies related to specific environmental problems, successful attempts were made by our laboratory to apply this colloid fractionation technique. For instance, further chemical and radiochemical characterization of the Dankritz residue from uranium production was made possible due to the successful concentration of the alpha emitters (hot particles) from the residues.[1] In addition, preliminary results related to contaminated river sediments indicated that colloid separation had a definite potential for its remediation.[2] Other investigations of electric arc furnace (EAF) dust [3.4.5.6] and red mud from aluminium production,[7] which are fine grain industrial residues, have helped us in our attempts to develop general guidelines for an eventual version of an hydro technique for fractionating micron to sub-micron size material.

In all of these studies, the goal was to induce a separation or fractionation by mixing in a surfactant to the system with the intent to induce charge modification on the surfaces of the different chemical compounds. These charge modification could promote suspension or flocculation of some phases. In other instances, the intensity reduction of the particle surface charge promotes agglomerations through collisions between particles and as they grow bigger they settle out of the suspension.[8] In most cases, this type of behaviour yielded simpler systems for which additional fractionation can theoretically be accomplished for a better and a more complete separation.

In other systems, it was observed that a strong overall negative or positive charge could hide large discrepancies between the intensity values of the charges for the individual compounds making up the system. This situation often resulted in a layering structure in which each layer had the same sign but a different charge intensity corresponding to the associated layered phase composition.[3.4] From these studies it was further noticed that industrially produced (anthropic) compounds, which can have natural mineral equivalent could behave differently because of a different chemistry. This difference can be caused by solid solution (ionic substitution) or other chemical and physical phenomenon.[9.10.11.12.13] In such a case, it is necessary to distinguish between natural primary phases from secondary mineral equivalent or antropic phases in order to ascertain the behaviour differences between the two phases in modeling attempts.

These empirical rules are not fully understood; it is therefore crucial to relate to these behaviours and identify the controlling parameters to understand and gain insight to the phenomena found with more complex systems. It is anticipated that in numerous environmental systems, this fractionation process can isolate contaminants, allow for a better characterization, understanding of transportation process, mobility parameters for the fate of contaminants, and overall risk assessment

The zeta potential of a slurry can be measured by an acoustic measuring technique. The "Electroacoustic sonic amplitude (ESA)," is used to calculate a zeta potential for a single phase or for complex systems in an aqueous phase. With such information, it is now possible, to relate the mobility state for the solids of the system with the ESA signal or the calculated zeta potential for slurry behaviour. In such a system, the zeta potential defines an energy state where suspension or flocculation is better defined. The zeta is a working potential that will dictate for a flocculation or a settling phase the aqueous envelope that will be included with the solid particles. This envelope will include the first tightly adsorbed layer and part of the second diffuse surrounding layer and the amount of the diffuse layer included with the flocculating particle will depend on the value of the zeta potential.[8]

PREVIOUS RESULTS FOR CONTAMINATED SEDIMENTS.

A master thesis [1] dealt with the contaminated sediments of the Böse River and Sussersee (Sweet Lake) from the region of Eisleben in close proximity to the industrial mining complex of Mansfeld. The colloid separation technique was evaluated as a possible remediation of the sediments by fractionating the mineral phases that contained the heavy metals contaminants.

The results indicated that using this procedure, it was possible to substantially reduce the level of heavy metals in the sediments. The concentration of cadmium was reduced by 40%, lead by 60%, and a reduction of 70% for zinc was obtained. Even if the process conditions were not optimized at least the potential for an initial procedure of a method was outlined. At this stage the method offered guidelines but more detailed information was required to optimize, qualify and quantify the procedure and make it applicable to a larger number of environmental problems.

The first part of this study will attempt to establish a model using natural minerals to approximate the Sweet lake sediments and determine the parameters that are required to use surfactant and ESA data and be capable of decontaminating natural environmental problems.

The working hypothesis for most environmental systems is that, the surface chemistry for the mineral constituents of the sediments are equivalent to artificial phases produced by industrial processes. Therefore for modeling, the phases that constitute the system are equivalent to primary natural mineral samples that can be found in mineralogical collections. Anthropic processes should not modified these phases so that their original surface characteristics reflect their chemical composition, crystal structure and original genesis process

A simple natural system will be made in order to evaluated if the following equation can be used to represent the state of the system:

$$\Sigma\xi = \xi 1 \text{ X } C1 + \xi 2 \text{ X } C2 + \xi 3 \text{ X } C3 \ldots\ldots$$

ξ and C stand for zeta potential and concentration (percentage) of the single-phases.

The concentration of the phases or compounds required by the modelling equation will be determined with X-ray diffraction.

The ultimate test will be to compare the natural system to the artificial system of Sweet-Lake sediments representing a complex multiphase system for which anthropic processes could have affected the surface chemistry or other parameters of the system and their behaviour.

The physical characterization was performed at UQAM and the CREUST. The sampling was the responsibility of UFZ.

CHAPTER I

1 CHARACTERIZATION AND OBSERVATIONS OF NATURAL MINERAL SINGLE PHASE SLURRIES

1.1 Introduction

The compounds and/or equivalent minerals identified in previous studied contaminated rivers and lake sediments were studied individually in a slurry state and in simple mixture. The selected equivalent natural mineral used were taken from a mineralogical collection or acquired through an industrial mineral supplier. All powdered samples were characterized and the apparatus and technique used are briefly outlined below.

1.2 X-Ray diffraction

For each compound or mineral equivalent the powdered sample was submitted to a mineralogical identification to confirm the nature of the substance. A cobalt tube was the X-ray diffraction source in the apparatus. With this technique mineral phases present in an amount greater than 1% are detected and identified. As an example a sphalerite sample yielded a diffractogram, which indicated that around 98% was sphalerite with roughly 1% pyrite and 1% galena. The concentrations are evaluated according to the peak heights or intensity. X-ray diffraction was also used to evaluate the results of surfactant fractionation produced by the propose technique. The peak heights were used as a semi quantitative evaluation for the corresponding mineral or compound concentration.

1.3 Scanning electron microscope

The semi quantitative elemental composition of individual grains (mineral phase), their associated morphologies and grain size were established using a Scanning Electron Microscope (SEM) Hitachi S2300. Elemental distribution by mapping images for different chemical elements was also used for a semi quantitative evaluation of the quality of the fractionation yielded by the process. Also extensive use was made of back-scattered images. These images with their variable brightness intensities made it easy for quick sulphides identification with a semi-quantitative concentration in each sample or fractionated slurry.

1.4 Grain size distribution, specific gravity and zeta potential

1.4.1 Grain size distribution

The grain size distribution was determined by means of a neon and helium gas mixture laser-based apparatus (Laser Sizer, CISA100 Galai Instruments Inc.) with a range limit determination capability from 0,5 µm to 600 µm. The histogram of the distribution for particles, surface and volume allows the determination of the number of modes (population concentration size) present in a sample. In this study, the calculation of the zeta was made using the median by volume value obtained with the Galai apparatus.

1.4.2 Specific gravity

Specific gravity of the powdered minerals was determined precisely by means of an Ultrapycnometer using helium gas. The advantage of this method over comparable water–based techniques is that the helium gas will fill all voids and pores while water could have problems with capillary action and gas trapping. In addition with a gas apparatus no lost can occur by solubility lost of solids.

1.4.3 ESA and titration

The surface charge measurements, the titration with acids, bases and surfactants, were made using either an ESA-8000 or the ESA-9800 Zeta Potential Analyzer which makes use of electroacoustics signal (Matec Instrument Companies, Inc.). The Electroacoustic Sonic Amplitude (ESA) signal allows the calculation of the zeta potential for a solid in a water base suspension with a solid concentration between 2 to 5% v/v for a total volume of approximately 250 ml of slurry. The EAS signal indirectly, gives an approximation of the intensity and the polarity sign of the charge at the surface of the solid particles. The zeta potential defines an energy state for the system corresponding to a suspension or flocculation and allows for a more precisely defined state of matter. Simultaneously, other measurements are also made on the slurry including temperature, pH and conductivity.

1.5 Single-phase mineral systems and their characteristics

After considerations regarding river, lake and soil composition, twenty one (21) single mineral phases were selected, prepared for our characterization. These results are presented in tables 1.1 and 1.2. For the preparation, the samples were broken in small chips (≤ 0.5 cm.), crushed in a ball mill using tungsten carbide balls so that the resulting grain size could pass a 38 μm sieve and subsequently most of the samples were submitted to a wet attrition to attain smaller particle size.

For some samples, depending on the availability of the material, two samples were prepared, a non-attrited powder and an attrited sample. For each attrition, 40 grams of solid < 38μm was submitted to a wet attrition using zirconium beads with a diameter of 0.6 to 0.8mm. The attrited slurry had to pass a ≤ 25μm sieve and as a result the residence time in the attritor was a function of the hardness, resistance and the resulting grain size distribution for each mineral sample. This procedure yielded, 19 attrited, 16 non-attrited and one mixed samples (table 1).

Table 1.1
Natural mineral slurries and related characteristics (no attrition of the samples)

Name and description	Density (g/cc)	Diameter (micron)	Zeta (mV)	pH (units)	Conductivity (uS/cm)
Quartz (Ottawa sand)	2.674	10.08	-110.3	6.67	29
Albite	2.769	8.75	-213	8.96	179
Microcline	2.601	9.11	-225.2	9.03	133
Biotite (attrited+non-attrited)	3.097	8.53	-107.3	8.58	154
Bauxite	2.624	7.28	151.9	7.08	26
Calcite	2.884	8.03	169.9	8.27	118
Dolomite	2.934	8.01	125.1	8.59	227
Barite	4.155	8.57	13	7.22	182
Gypsum	2.334	10.8	6.8	.48	1654
Galena	7.078	9.07	-7.3	6.57	230
Sphalerite	4.151	10.62	-20.5	6.68	1662
Pyrite	4.977	8.93	-9.3	3.51	2282
Chalcopyrite	4.233	6.8	-14.2	5.09	1045
Apatite	3.209	11.36	-13.8	6.73	82
Illite	2.673	9.8	-45.6	3.24	398
Montmorillonite	2.568	10	-306	8.89	837
Kaolinite	2.673	11.71	-28.8	4.74	18
Magnetite	4.212	9.05	-85	7.5	79
Hematite	3.879	6.46	-3.40	6.37	47
Manganese oxide(pyrolusite)	4.382	8.58	-9	7.055	107

These data indicate that few minerals have a positive zeta potential and the precise value can be modified by the presence of a contaminant in the form of an associated mineral or by a change in grains size, pH, conductivity and surfactant additions. The results also indicate that the silicates are strongly negative, the oxides and sulphides are moderately negative while the carbonates are strongly positive and sulphates moderately positive. For the clay minerals, montmorillonite is strongly negative and illite and kaolinite displays the same polarity with a more moderately negative zeta.

The intensity value of the zeta potential for attrited samples is substantially lower than non-attrited powders, and this phenomenon is directly related with their smaller grain size and a smaller grain distribution. A smaller grain size for the slurry is translated into a larger surface area; therefore the total charge is distributed among a larger particle population that results in lower values for the zeta. The attrition also affects the pH and the conductivity. The results indicate a slight increase in conductivity for the attrited samples. From this group of samples, kaolinite and hematite attrited samples display an anomalous zeta, showing a decrease in its absolute value coupled with a marked increase in the pH.

Table 1.2

Natural attrited mineral slurries and related characteristics

Name and description	Density g/cc	Attrition time(min.)	Diameter (micron)	Zeta (mV)	pH Units	Cond. uS/cm
Quartz (monomineralic)	2.693	75	2.8	-97.5	6.75	18
Quartz (Ottawa sand)	2.674	55	2.04	-91.3	6.09	24
Plagioclase (calcic)	2.774	60	2.19	-88.9	9.08	192
Albite	2.769	60	2.01	-130	9.52	237
Microcline	2.601	60	1.95	-132.3	10.1	238
Biotite (attrited + non-attrited)	3.097	15	8.53	-107.3	8.58	154
Muscovite	3.051	60	7.29	-131.9	8.44	299
Bauxite	2.624	40	1.95	41	7.36	20
Calcite (non-evaporated)	2.884	60	1.22	50.2	7.96	132
Calcite (evaporated)	2.884	60	0.98	45.4	8.23	141
Dolomite	2.934	60	0.82	22.3	8.79	405
Barite	4.155	20	2.18	10.4	6.84	186
Gypsum	2.334	7	4.31	2.7	7.56	1617
Chalcopyrite	4.233	30	2.76	-10.7	4.57	792
Apatite	3.209	20	1.69	4.4	6.85	62
Kaolinite	2.673	10	2.72	-43.8	5.57	15
Magnetite	4.212	37	3.03	-49.1	8.21	100
Hematite	3.879	25	2.74	-34.3	6.63	72
Manganese oxide (pyrolusite)	4.382	23	2.31	-9.03	6.86	47

1.6 Visual observations of slurries and their corresponding zeta and particle size distribution

Attempts were made to correlate the parameters of the mineral slurry with the behaviour state of the system, i.e. the concentration of the suspension or the thickness of the sediment column. For visual observation, the slurries were allowed to decant in flat bottom glass tubing from which their suspension or decantation could be evaluated and related to the measured zeta of the slurry. The slurries that were allowed to decant for 3 days were defined as a long decantation process in our study.

Figure 1.1 Comparing the attrited and non-attrited mineral slurries, from left to right: a) non-attrited quartz. b) attrited quartz. c) non-attrited bauxite d) attrited bauxite.

As a general rule we have found that, the smaller the particles size (micron size) the more stable is the associated suspension. Also, if the surface charge of the particles is increased the more stable will be the resulting suspension. The increased surface charge is responsible for an increasing repulsion between the particles and consequently generating a more stable suspension.

In figure 1.1, four suspension samples for quartz and bauxite are compared. For both minerals the grain size and surface charges are adequate to induce a suspension. As anticipated, the attrited samples displayed a more abundant suspension when compared to the non-attrited, which are related to the smaller grain size. Figure 1.2 illustrates slurries of dolomite and calcite in which no suspension can be observed after 3 days. On the other hand, the thickness for the column of sediment is different. For the attrited samples the sediment layer is thicker.

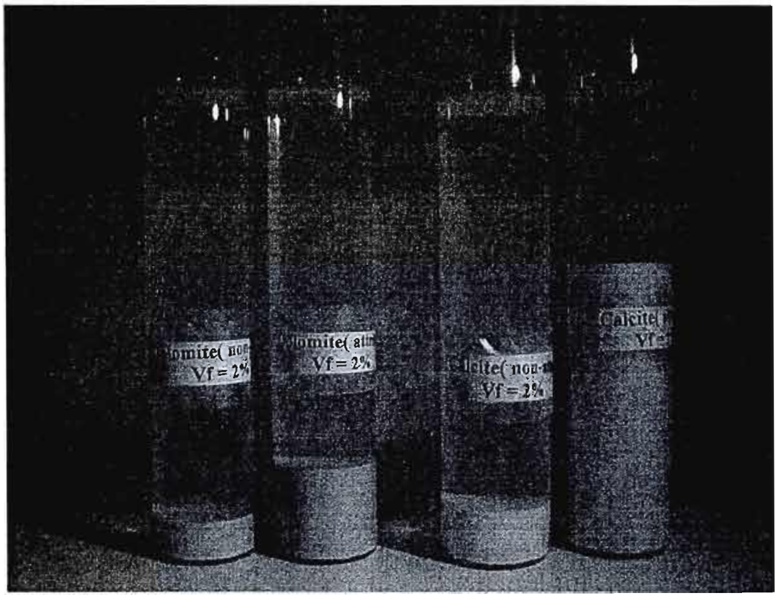


Figure 1.2 Comparing the attrited and non-attrited mineral slurries, from left to right: a) non-attrited dolomite. b) attrited dolomite. c) non-attrited calcite d) attrited calcite.

Industrial processes often generate fine grain solids with their residues and consequently these should be considered in environmental impact risk evaluation. Furthermore, since the suspension represents the finest size fraction and since this size fraction has a greater adsorption capacity of metallic cations, these suspension could carry most of the contaminants. Therefore, considerations related to an increase in the potential mobility are important in an environmental context. For these suspensions, certain parameters will dictate where they will flocculate and stabilize. The suspensions are not reserved to only light elements, suspensions of barium, lead and copper have been found associated with effluents of industrial residues.[2.9.10.11.12.13]

1.7 The role of pH and conductivity on the surface charge of single-phase particles

In the mineral slurries the electrical double layer around particles is the result of preferential adsorption of ions and this double layer is a function of the surface charge of the solid. The most accepted view is that soluble cations are the building blocks of the double layer. Our results indicate that the H^+ and OH^- are just as important as most cations and anions in building the double layer.

It is common practice in the mineral industries to modify the polarity and intensity of the surface charge of a mineral slurry by changing the pH value. For each mineral at the certain pH there is an isoelectric point or a zero point of charge (pzc). Table 1.3 gives the pH for some oxides and silicates at which the isoelectric point is reach. For lower pH or more acidic conditions, the surface charge is positive while for higher pH or more alkaline conditions the surface charge is negative.[14]

Table 1.3

The point zero charge (pzc) of some Oxides and Silicates

Mineral	pzc (pH)
Quartz	1.0- 2.0
Cassiterite	4.5
Rutile	5.8
Hematite	4.8- 6.7
Corundum	9.1
Zircon	5.8
Beryl	3.2
Microcline	1.8

Source: H. L. Shergold, 1987[14]

In the literature, the isoelectric point of mineral slurries and their corresponding pH are given but no information related to conductivity or time of equilibration.

We have established for our samples, the correlation between pH, conductivity and equilibration time through a titration of our minerals slurry. In these measurements, the zeta potential reflects or monitor the changes associated with the surface charges of the solids while the pH and conductivity reflects the changes in the chemistry of the liquid. In some cases, the equilibration required so much time that the ESA titration equipment could not be used. In these cases the titration had to be approximated by adding manually the acid or base followed by measurements at longer regular intervals. A detailed titration study of each selected mineral was beyond the scope of this project, but nevertheless, titration was performed on the following mineral groups:

Quartz being the representative of the silicate family;

Chalcopyrite for the sulphides;

Hematite and magnetite for the oxides;

Calcite and dolomite for the carbonates.

Nitric and sulphuric acids were used for the acid segment of the curve while sodium hydroxide was used as a strong base. Sodium chloride and potassium chloride were used to modify the conductivity of the liquid and its effects on the zeta value.

In each titration experience, 220 ml of the slurry, with a solid concentration by volume of 2 %, has been used while acid, base and salts were gradually added to the slurry. The titration was made in the ESA from which the zeta can be calculated. As the ESA signal is being measured, simultaneous measurement of pH, conductivity and temperature are also recorded.

1.7.1 Titration of quartz with nitric acid

The titration results of the acid segment for quartz were established with nitric acid and the results are presented on figure 1.5. The acid was added with a titration equipment for which the volume increment was set at 0.1 ml with an equilibration time of 1 minute.

By adding acid and lowering the pH, the zeta potential became more positive from an initial value of –40mV to approximately -5mV while the pH changed from 6 to 2 after the addition of 20 ml of 0.1N acid. Initially the pH varied rapidly from 6 to 3 with the addition of the first 2 ml, then the pH value changed slowly from 3 to 2 with an addition of 18ml of acid. For some reason that cannot be explained at this time, the conductivity displayed a linear increment with the acid addition. It is possible that some contaminants present with the quartz would react with the acid. The X-ray diffraction pattern of figure 1.3 and 1.4 does not indicate any evidence of other mineral phases being present as a possible contaminant.

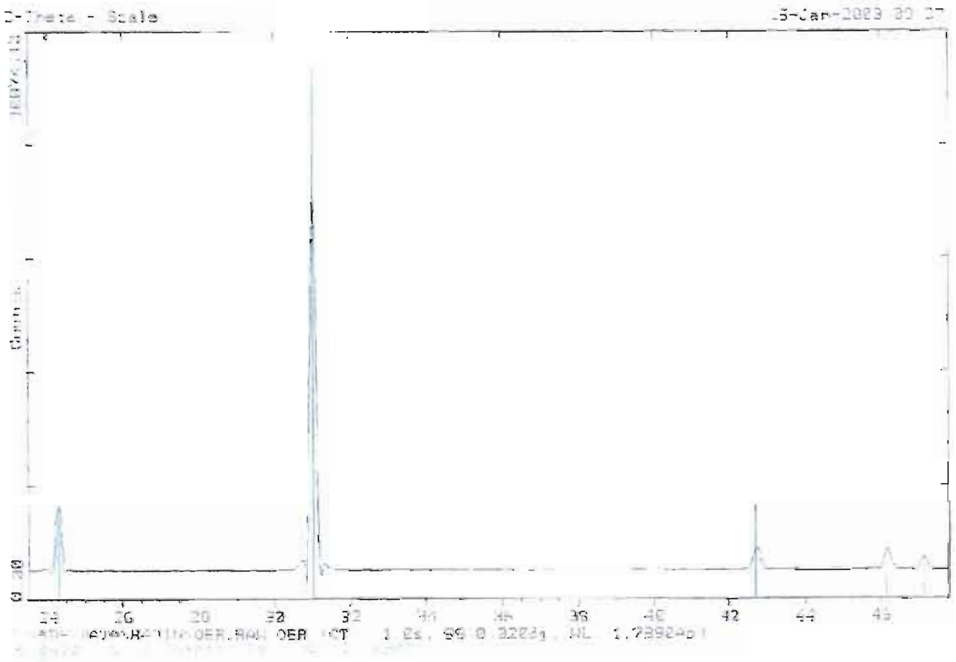


Figure 1.3 Overly XRD patterns of quartz samples.

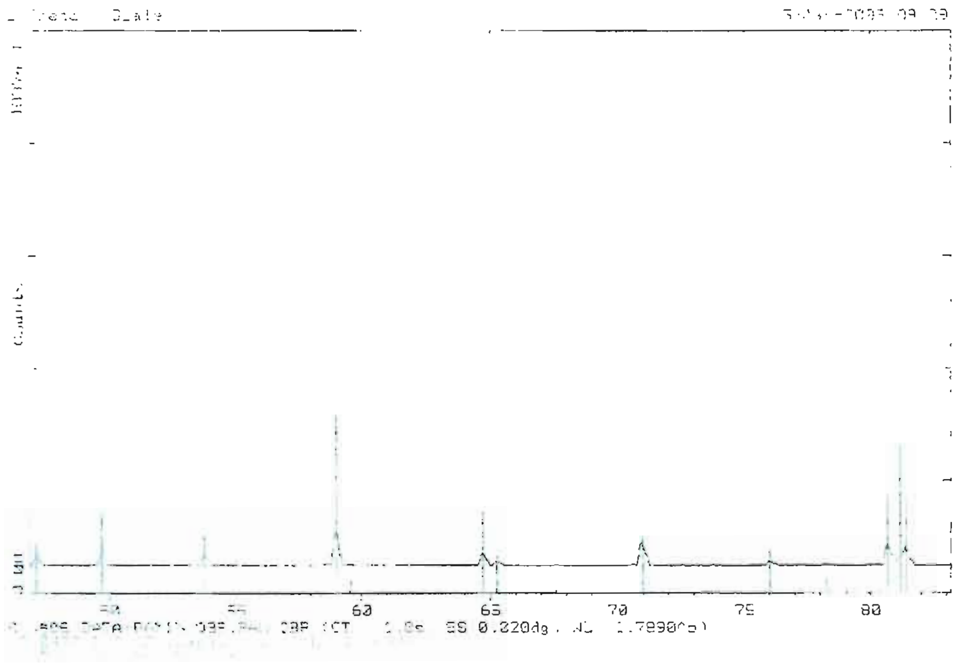


Figure 1.4 Overly XRD patterns of two quartz samples.

An interesting observation was that the quartz slurry did not reach nor crossed the isoelectric point. In an attempt to determine the isoelectric point we increased the equilibration time. In this case, 20 ml of nitric acid was added manually to 220 ml of the attrited quartz slurry in increment of 2ml of 0.1N with an equilibration time of 3 days between each measurement (figure 1.6). The point zero charge was then attained between pH 1 and 2. Clearly equilibration is a major parameter and depending on the mineral and the modifier added to the slurry, a longer equilibration time could be necessary before the double layer structure is in place. This phenomenon is akin to ageing of the system and is a kinetic variable to be considered.

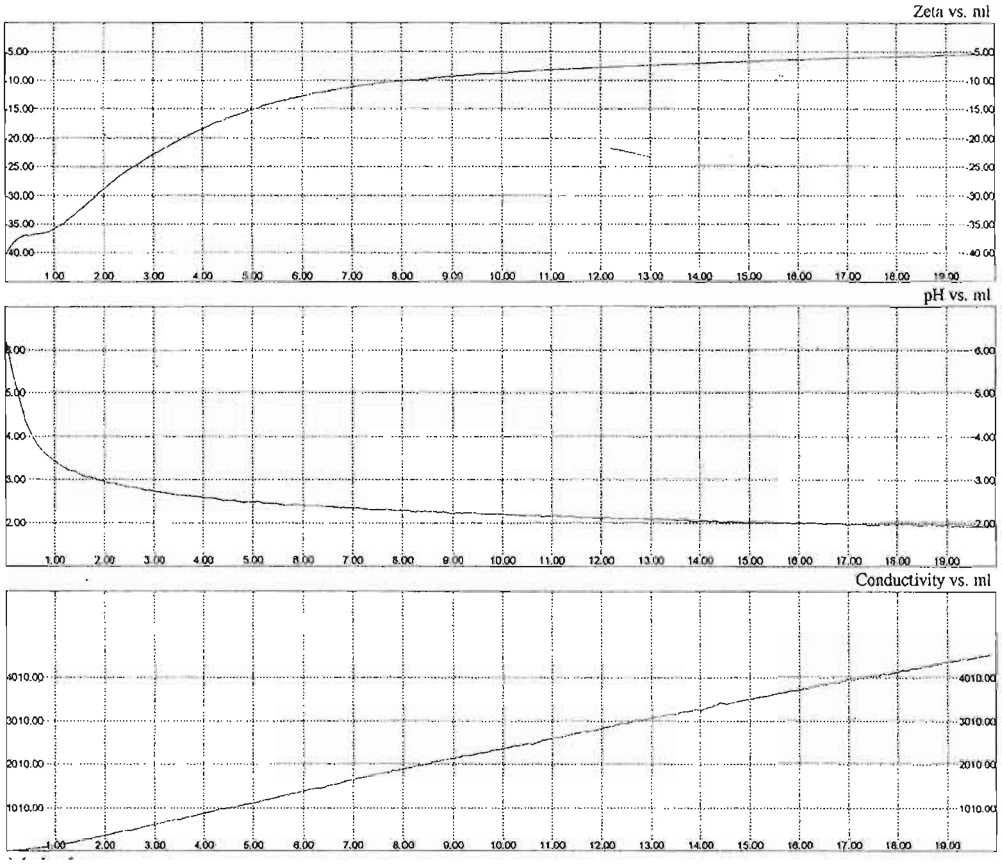


Figure 1.5 Zeta potential, pH and the electrical conductivity of the attrited quartz slurry (2% v/v), versus nitric acid (0.1N) addition by volume.

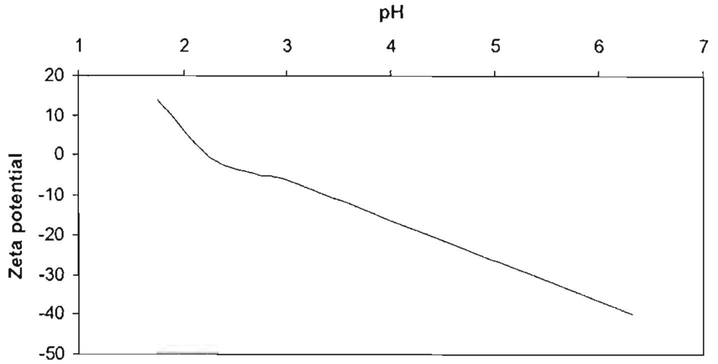


Figure 1.6 Location of the isoelectric point for attrited quartz slurry (2% v/v). Nitric acid was added manually at intervals of 3 days.

1.7.2 Titration of Quartz with sulphuric acid

For the titration a molar concentration of 0,1 sulphuric acid was used with volume increment of 0,1ml with an equilibration time of 60 seconds. The results on figure 7.1 indicate that the zeta maintained negative value between values of 53 and 22 for a corresponding pH variation between 5.8 and 2.2. At the onset of the titration, the pH varied from 5.8 to 3.25 with the addition of only 3,5 ml of diluted acid. This corresponds to a small acid addition for such a large variation of the surface charge. The conductivity increased in a linear fashion between 25 and 3900 μS/cm. Because of the relative and apparent stability of the pH at 2.2, the experiment was ended and the zero point charge was not reached.

Both figures 1.5 and 1.7 have similar titration curves even though the titrations were achieved with different acids. Conductivity in both cases has a linear relationship. The only anomaly was found with nitric acid where decrease in pH corresponds to a larger zeta change.

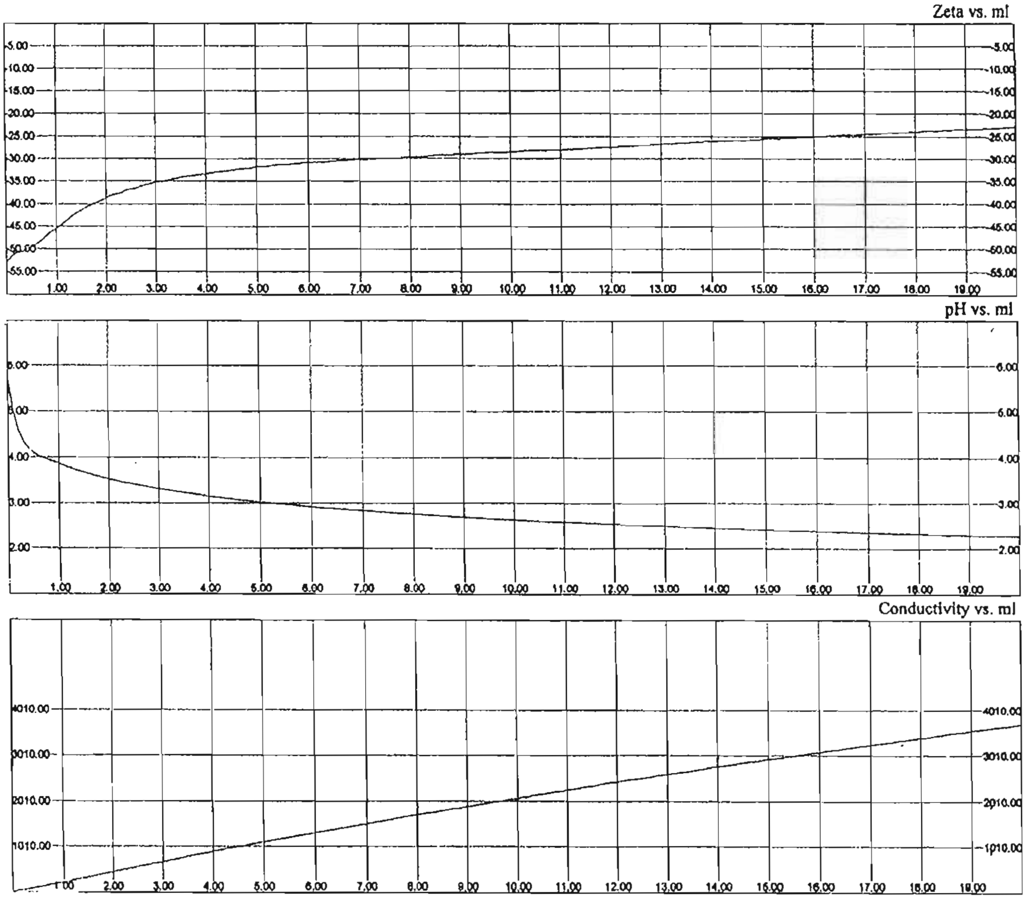


Figure 1.7 Titration of Quartz 2% v/v with sulphuric acid 0.1M. Acid increment of 0.1 ml with an equilibration time of 1 minute.

1.7.3 Titration of Quartz with sodium hydroxide NaOH

Sodium hydroxide was used to attain the alkaline segment of the titration curve. The results of the addition of sodium hydroxide to the quartz are presented in figure 1.8. A solution of 0,5 N was added to the 2%v/v of an attrited quartz by increment of 0,05 ml with an equilibration time of 10 seconds.

The pH changed from 6.5 to 11.2 while the conductivity increased from 0 to 2 500 µS/cm. The zeta variation is more complex, it changed rapidly at first from -100 to -138 mV for a small amount of NaOH and this was followed by a more gradual increase of absolute value of zeta from -138 to -165 corresponding to a maximum increase for a pH of 11. Additional increase of sodium hydroxide resulted in a decrease in negativity from 165 to 132mV. No explanation can be offered at this time for this phenomenon, it is possible that it is related to grain size variation by agglomeration or by the lost of the fines through acid digestion. It is interesting to note that an alkaline solution can be used to increase rapidly the negative charges at the surface of a quartz sample up to a saturation value followed afterward with a reverse effect, which brings about a reduction in the intensity.

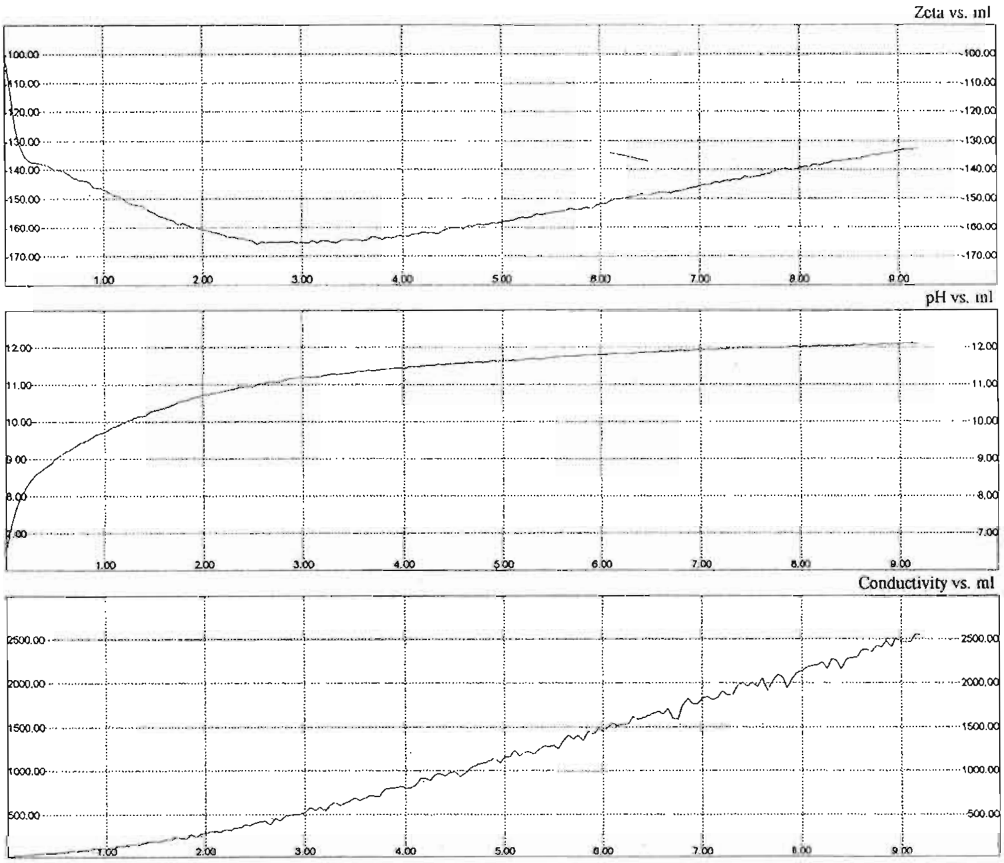


Figure 1.8 Titration of a quartz slurry 2% v/v withsodium hydroxide (0.5N). The volume increment was 0.05 ml with an equilibration time of 10 seconds.

1.7.4 Titration of quartz with the salts (NaCl and KCl)

An attempt was made to evaluate the effect of a high conductivity for a liquid on the zeta potential by using solutions of sodium chloride or potassium chloride. The titration was performed by adding a salt solution of 10% w/w with increment of 0,025 ml with an equilibrium time of 60 seconds. It was found that the zeta varied from -105 to -18mV. Initially the pH changed from 5.7 to 5 and stabilized by slowly reaching a minimum value of 4,75. The conductivity of the slurry increased in a linear fashion to extreme value that would have exceeded 10 000 µS/cm corresponding to the saturation for the ESA electrode (figure 1.9). During our experiment the abundance of the counter-ions (Na^+ and K^+) in the water base slurry increase and that is accompanied by a reduction in pH, which in turns can possibly indicate a desorption of H^+ from the electrical double layers.

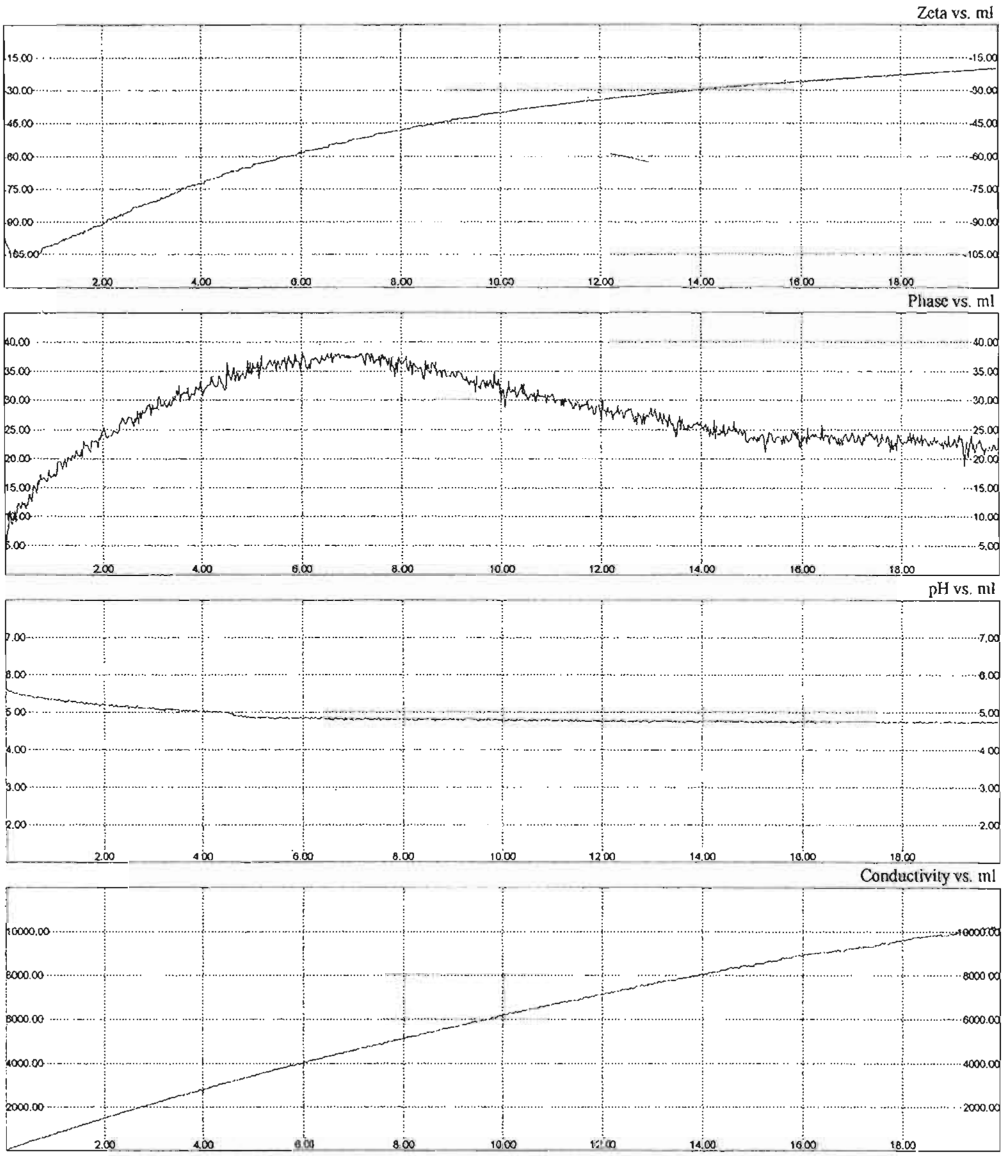


Figure 1.9 A salt titration for quartz slurry (2% v/v), with NaCl (10%w/w), Volume increment of 0.025 ml and equilibration time of 60 seconds.

This increase in free protons in the liquid and its effect on the system has been explained by a model proposed by Karlsson et.all, (2001), who studied the effect of alkali-metals and alkali-earth metal chlorides solutions on quartz and their corresponding surface characteristics.

[...] Alkali and alkaline-earth metals affect the Brønsted properties of the surface by forming outer-sphere complexes that shield surface charges from one another. In this model the background electrolytes indirectly affect dissolution rates through the ability of solutes to influence the adsorption/desorption of inner-sphere protons, promoting the development of surface charge. Because the efficiency of this shielding of the charges is largely controlled by the charge and distance of the counterions to the surface, the hypothesis predict that more charge accumulates on silica surface that is suspended in an electrolyte solution containing weakly hydrated counterions than one that contains larger more strongly hydrated counterions.[16]

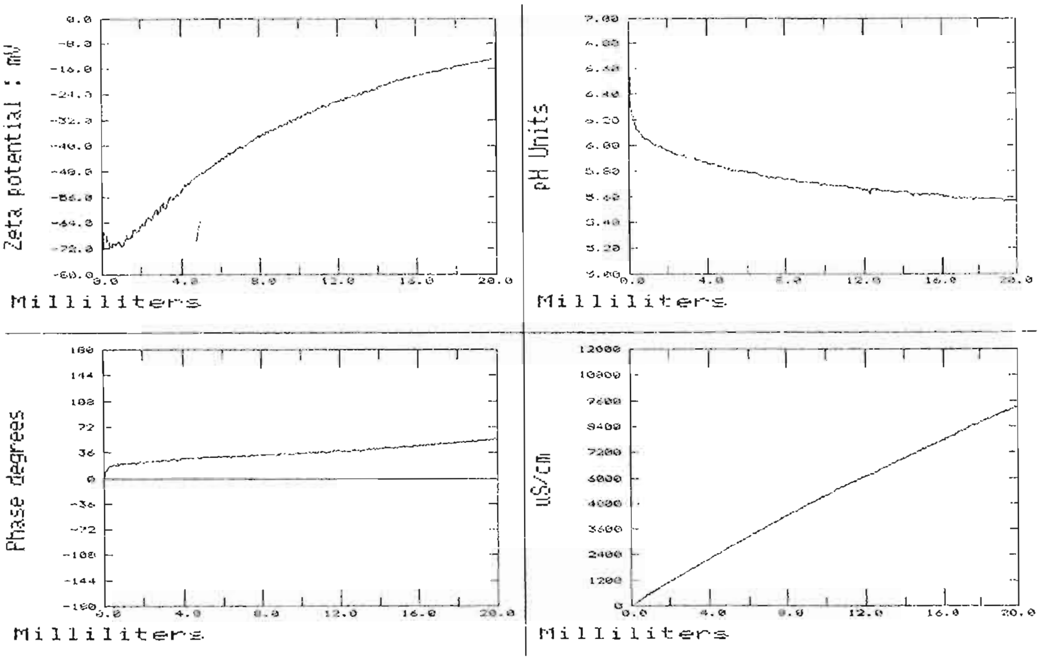


Figure 1.10 Salt titration of the quartz slurry (2% v/v), with KCl (10%w/w). Volume increment was 0.025 ml and the equilibration time of 60 seconds.

Similar results were obtained using potassium chloride as the titration salt and the results are presented in figure 1.10. These results clearly indicate a direct relationship between zeta and the conductivity related to the Brønsted property. It is possible that this effect at high conductivity is more important than the pH and the proton effect.

1.7.5 Titration of calcite using nitric acid

The acidification of calcite slurry with nitric acid indicates a decrease in the zeta potential from near +60 to +40 mV corresponding to a decrease in pH from about 7,8 to near 6,5, while the conductivity increases markedly, the results are shown on figure 1.11. It is postulated that at the surface of the carbonate, the calcium, CO and Co_2 have been dissociated and Ca is lixiviated in the liquid. The relative high abundance of Ca^{2+} could be one of the major reasons for reducing the positive charge of the calcite particles by consuming the acidity H^+ of the acid or the free proton at the inner layer.

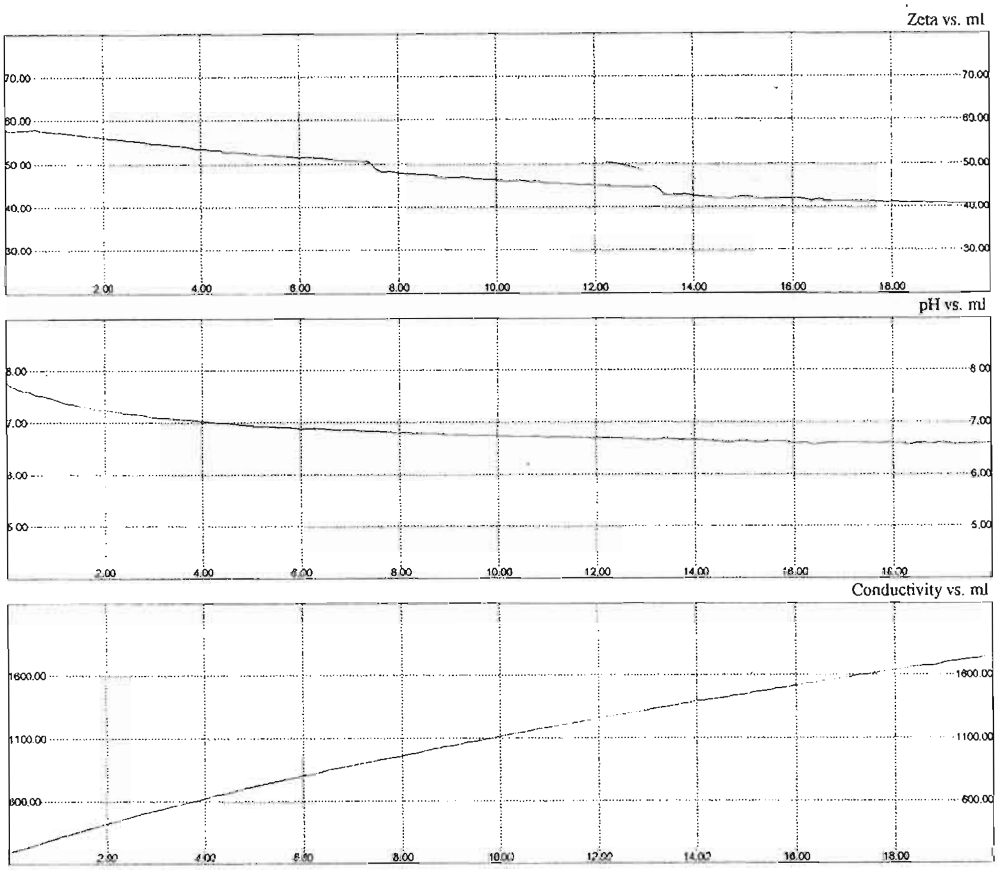


Figure 1.11 Titration of an attrited calcite slurry 2% v/v with nitric acid (0.1N). Volume increment of 0.15 ml for an equilibration time of 60 seconds.

It is known that Ca^{2+} is capable of inducing a large negative charge at the silica surface and perhaps similar mechanism could play a crucial role with the calcite slurry as well.[16] Perhaps the same mechanism has neutralized a part of the positive charge of the calcite particles.for larger amounts of acid in the slurry the zeta remains constant and the conductivity keeps on rising.

1.7.6 Titration of attrited calcite with sulphuric acid

Similar results have been obtained for the titration with sulphuric. The results of figure 1.12 show that the addition of sulphuric acid into the slurry, did not lower the pH below 7, but increased the dissolved surface groups accompanied by a decrease in the zeta potential.

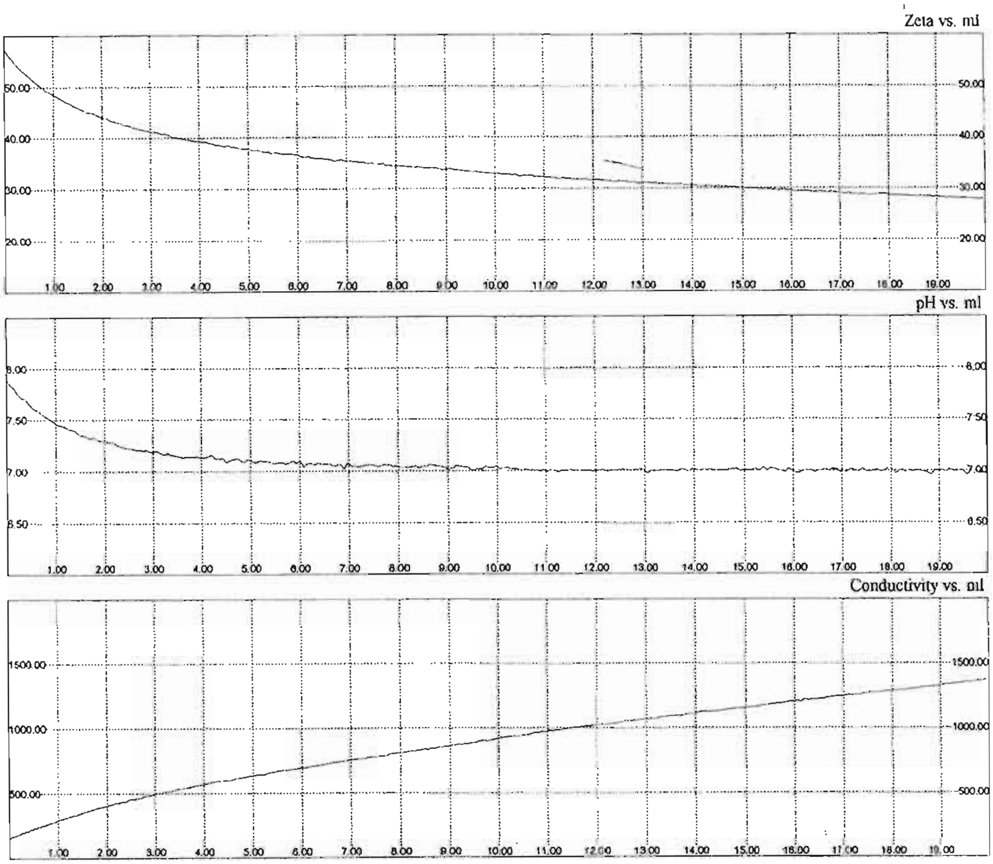


Figure 1.12 Titration of an attrited calcite slurry 2% v/v with sulphuric acid (0,1M). Volume increment of 0.075 ml for an equilibration time of 180 seconds.

1.7.7 Titration of attrited calcite with sodium hydroxide

Figure 1.13 presents the titration of calcite slurry with NaOH. With the addition of the first 2 ml in the slurry the pH increased rapidly and as a consequence it would appear that the excess hydroxyls reduced the zeta potential. After reaching a pH of 11.7, the zeta potential remained stable. But the conductivity increased by a large amount. This increase is probably associated with the dissociation of the surface chemical groups.

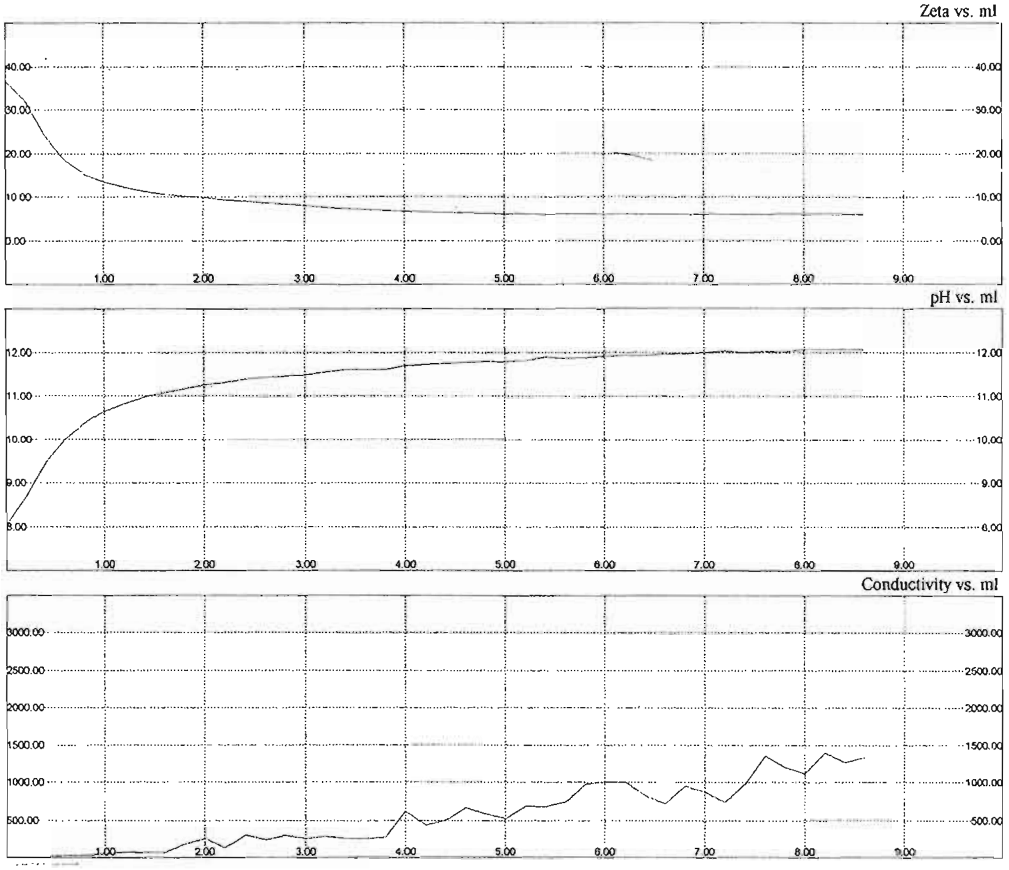


Figure 1.13 Titration of an attrited calcite slurry 2% v/v with sodium hydroxide (0.5N). Volume increment of 0.2 ml for an equilibration time of 10 seconds.

1.7.8 Titration of attrited dolomite with NaCl

The titration results of dolomite with a salt solution of sodium chloride are presented in figure 1.14. The graphs clearly indicate that while the pH increased slightly the zeta potential decreased by as much as +38 mV corresponding to a linear increase in conductivity from a few hundreds to near 12 000 μS/cm

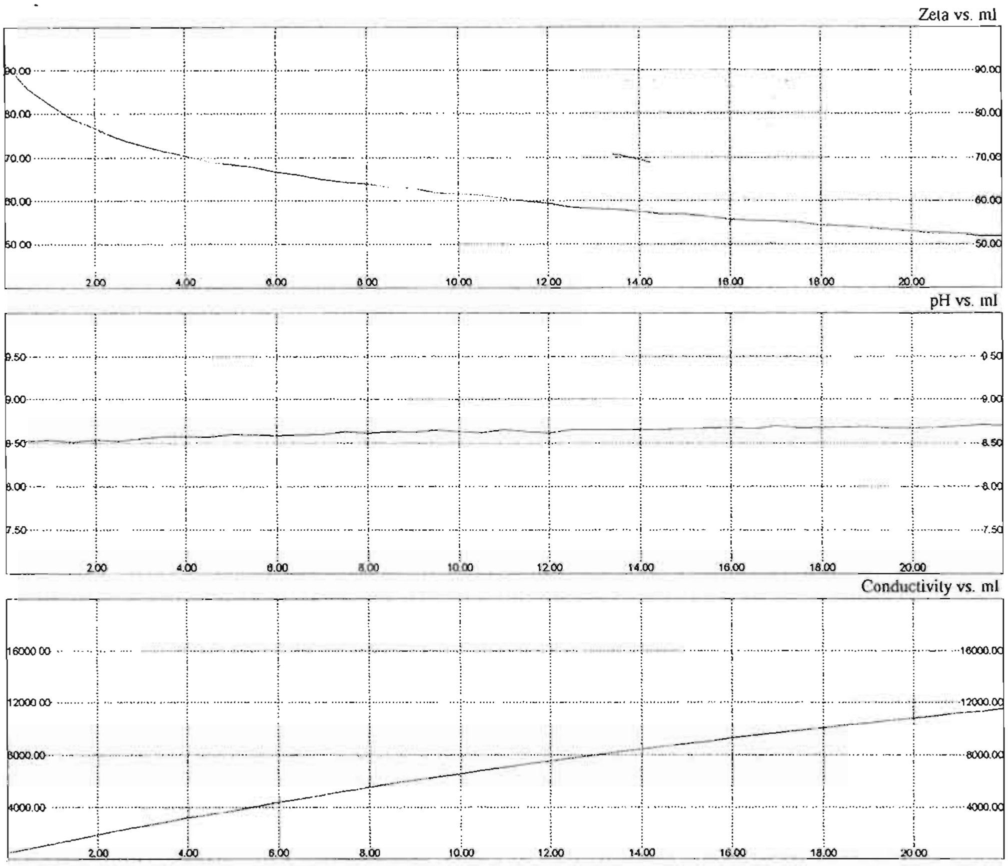


Figure 1.14 Titration of an attrited dolomite slurry 2% v/v with NaCl solution (10% w/w). Volume increment of 0.5 ml for an equilibration time of 30 seconds.

A possible explanation would be that the abundance of Cl^- counter-ions releases the OH^- from the electrical double layers that results in a slight rise in pH's value. The same argument proposed by Karlsson's model could explain the association between the surface charge reduction and a corresponding increase in the electrical conductivity.[16]

1.7.9 Titration of hematite slurry with nitric acid

For this titration of non-attrited hematite slurry, the procedure was modified. The initial pH was rendered alkaline by adding a sufficient NaOH so that the initial pH was 10.4. This major pH modification did not brought about an equivalent change in the electrical conductivity, The results are presented in figure 1.15, the zeta changed from –140 mV to +135mV and for a pH of 6.2 the slurry system was at the isoelectric point or the point at which a polarity change will occur.

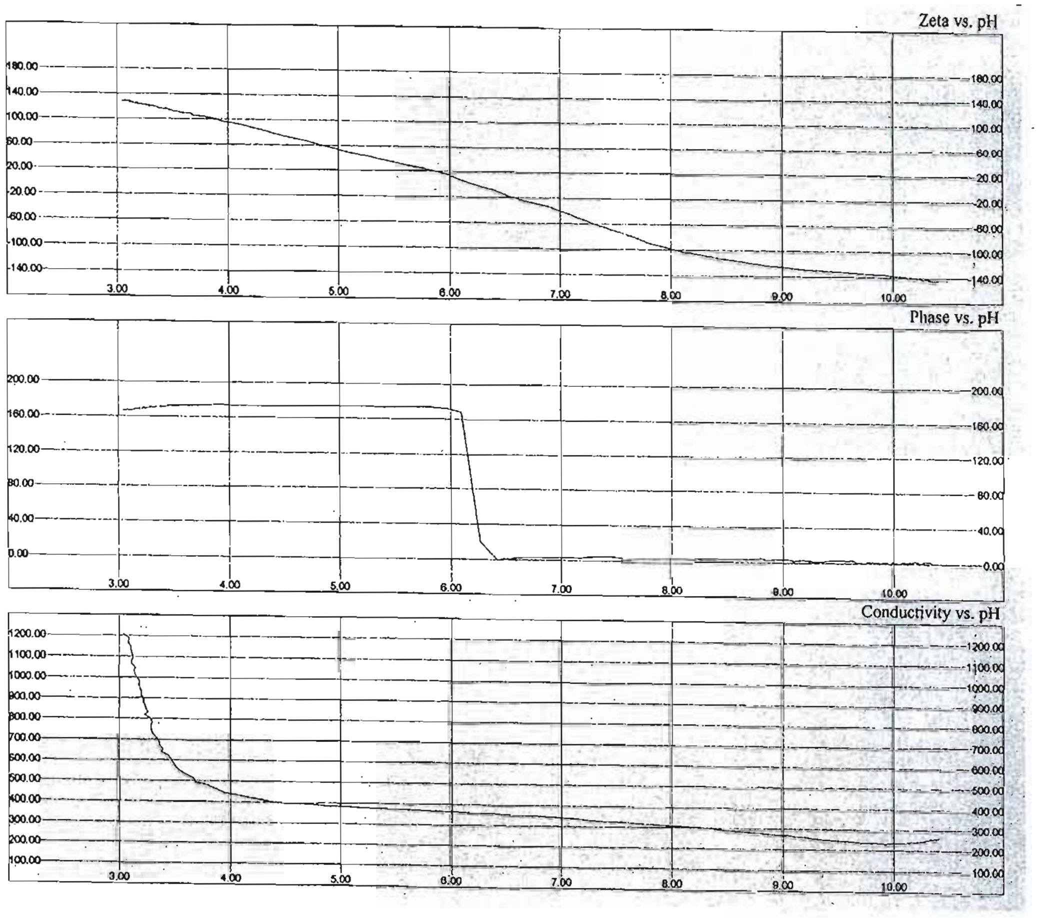


Figure 1.15 Titration of hematite slurry 2% v/v with HNO3 (0.5N). Initially the pH was raised to 10.4 by adding sodium hydroxide (0.5N).

The conductivity of the slurry displays an increase for a pH under 3.5. A possible explanation could be associated with the increase in free proton concentration in the liquid promoted by a counterions rearrangement within the electrical double layers. The inner-sphere adsorbed more OH^-, which would tend to lower the pH. But at pH lower than 4, hematite surface groups are dissociated and in turn this increases the conductivity of the liquid.

1.7.10 Titration of hematite with a salt solution of NaCl

In figure 1.16 the titration results of the 2% v/v hematite slurry with a salt solution of NaCl with a concentration of 10% w/w are presented. Initially the value for the zeta potential was –10mV corresponding to a pH of 6,45, the system reached the isoelectric point at a pH of 6,3. This change occurred with a low conductivity. At higher salt concentration the value for zeta gradually changed from 0 to around +25 mV with a corresponding pH between 6,15 and 6, while the conductivity increased linearly.

Again, the possible explanation appears to be related to the abundance of Na^+ and its adsorption by the double layers with a simultaneous release of H^+ from inner core electrical double layer responsible for the slight decrease in pH.

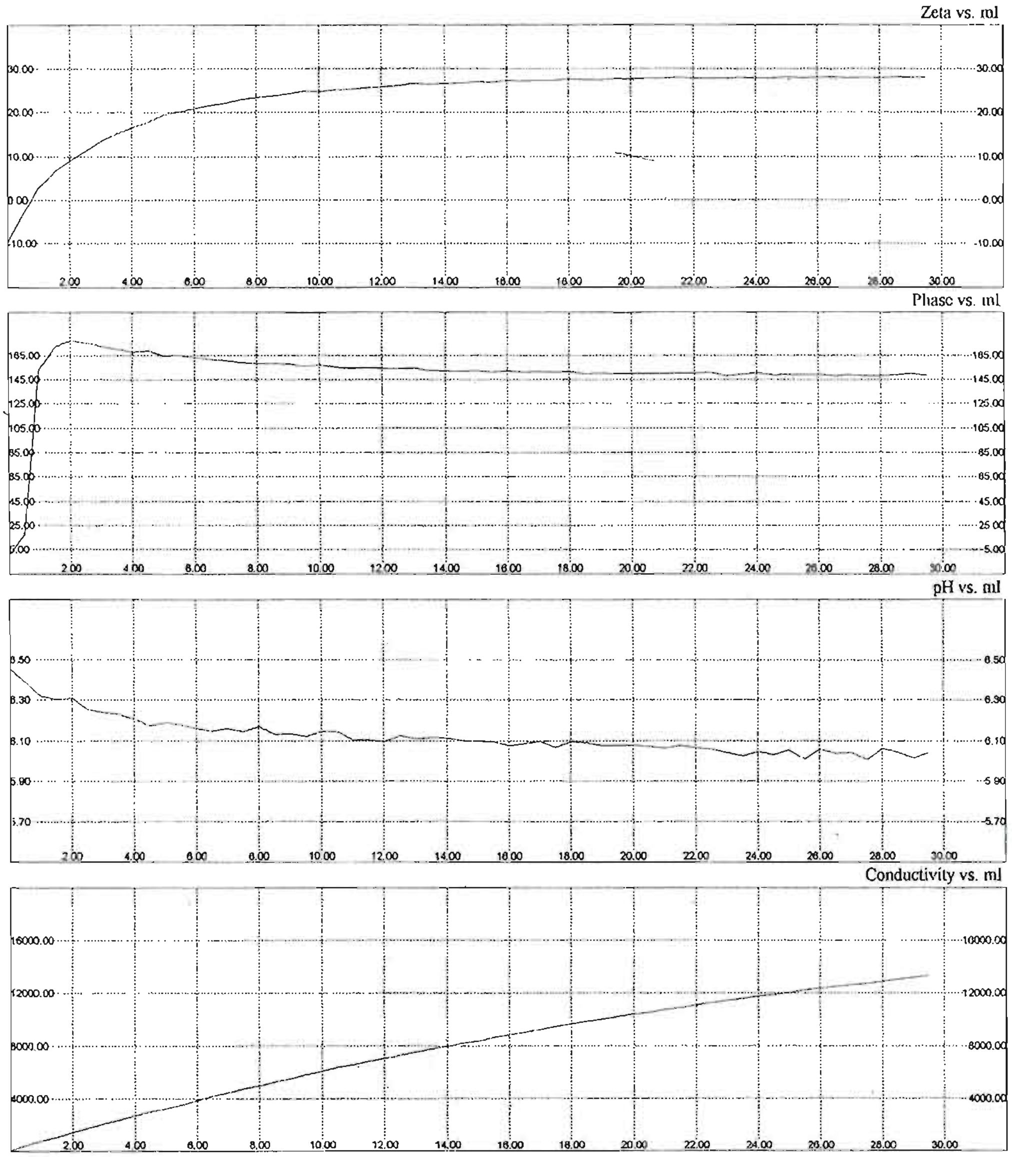


Figure 1.16 Titration of hematite slurry 2% v/v with a solution of 10 % w/w of NaCl . Volume increment of 0.5 ml with an equilibration time of 30 seconds.

1.7.11 Titration of magnetite with nitric acid and sodium hydroxide

The initial pH of the slurry was slightly alkaline at a pH of 8,5. The nitric acid (0.5N) was then gradually added to the magnetite slurry reducing its pH value from 8.5 to 2.5 (figure 1.17). With the acid addition the value for the zeta changed from

– 82 mV to +32 mV with a pH of 2.5. The zero point charge was attained at a pH of 3,3 with a relatively low conductivity of less than 2000 µS/cm.

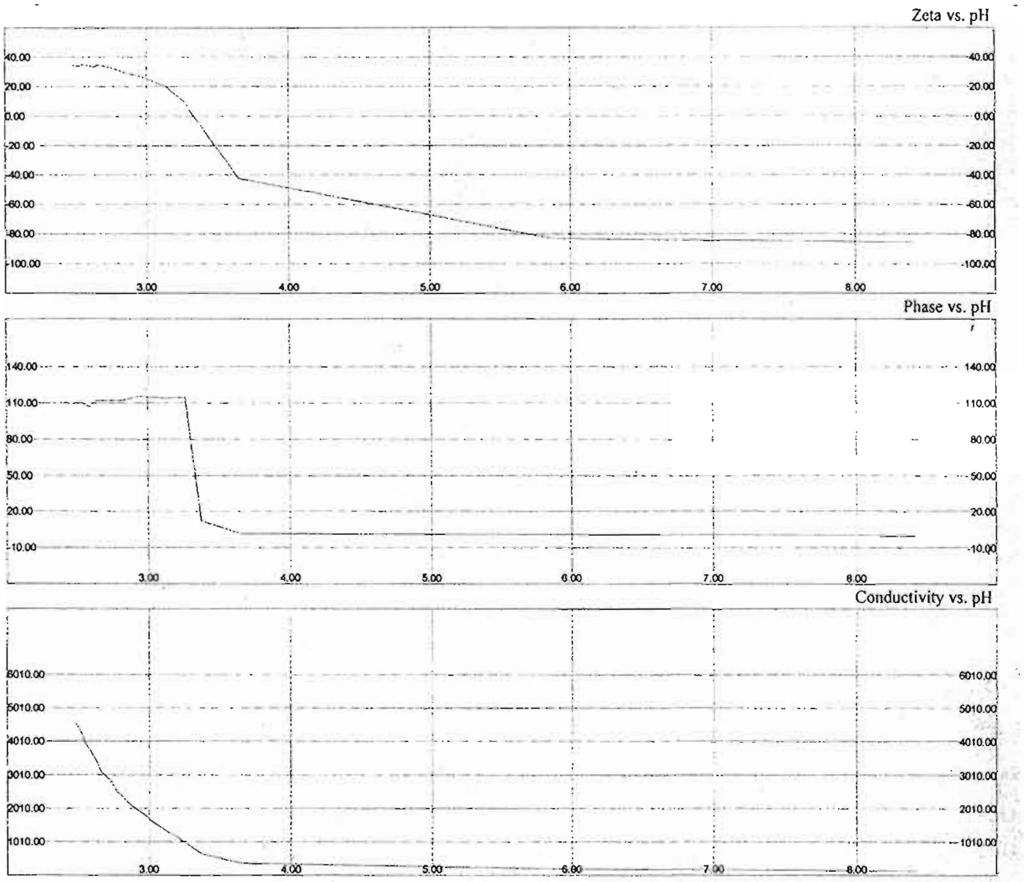


Figure 1.17 Titration of magnetite 2% v/v with nitric acid 0.5 N. For each pH step of 0.05 (unit) an equilibration time of 15 second was applied.

Without removing the sample from the titration cell the pH of the acidified sample was gradually increased by addition of NaOH 0.5N, (figure 1.18) and at a pH of 5.9.

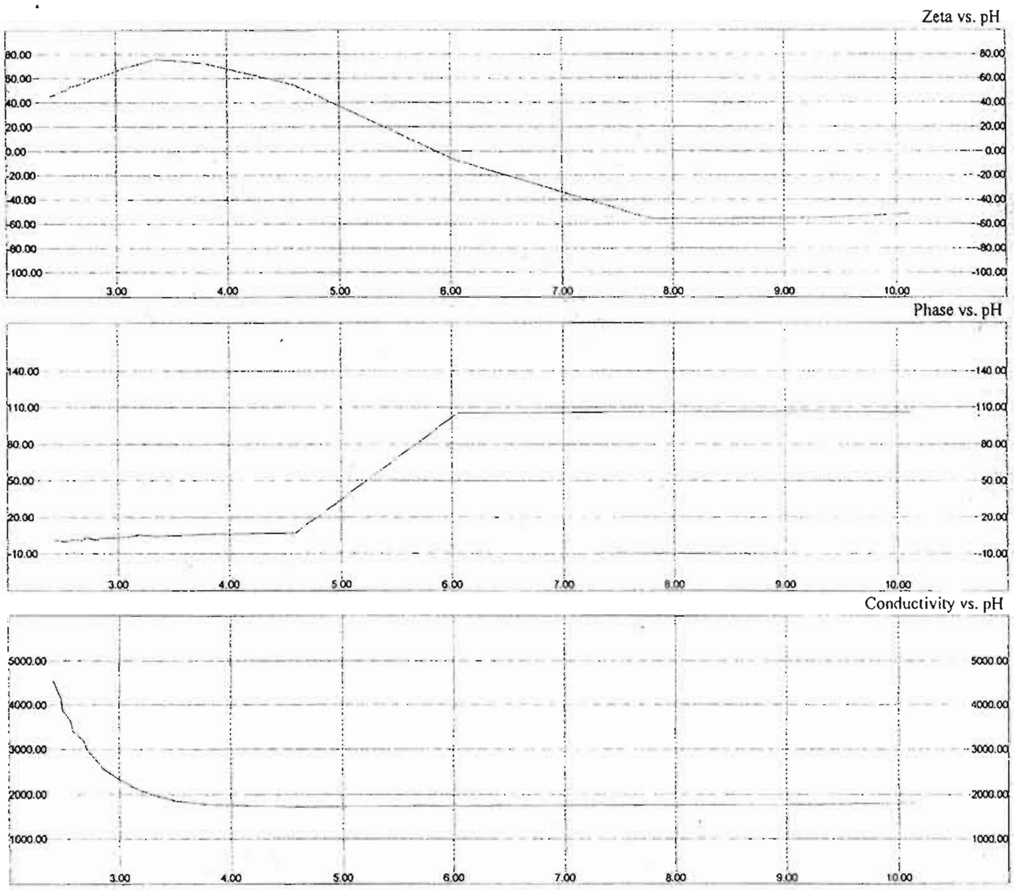


Figure 1.18 Titration of magnetite slurry of 2 % v/v with sodium hydroxide 0.5 N. For each pH step of 0.05 (unit) an equilibration time of 15 second was applied, initially the ph of the slurry was made acid by the addition of nitric acid.

By comparing the last two figures, the results indicate the importance of the role played by the types of co-ions and counter-ions. Despite the fact that in both experiments the same slurry has been used, two different values for the point zero charge have been obtained. For the titration with HNO_3, pzc was achieved at a pH 3.3 where the electrical conductivity was close to 750 uS/cm, but by introducing NaOH into the same sample the pzc is reached at pH 5.9, where the conductivity was almost 1800uS/cm because of the presence of Na in solution. The abundance of ions, coming from acid, base and particles surface groups can result in a major shift for the pzc value.

The results presented above clearly indicate that the associated isoelectric points for minerals are meaningful if the ions and the conductivity for the liquid fraction are specified.

1.7.12 Titration of the magnetite slurry with a solution of NaCl

In order to investigate the effect of Na+ and Cl^- ions on the surface charge of magnetite particles, a solution of (10%w/w) NaCl was used to titrate the slurry at a concentration of (2%v/v). A total amount of 19 ml of the salt solution was added to the slurry and this raised the conductivity of the liquid from 100 uS/cm to 10500 uS/cm and the zeta potential from -86 mV to –30 mV (figure 1.19). The high concentration of Na+ counterion in saline supernatant solution resulted in desorption of H+ from the electrical double layers around the particles. The excess of the free proton's concentration in the supernatant could explain the slight decrease of the pH. As discussed previously, reducing the pH increases the zeta potential, which enhance the effect of electrical conductivity.

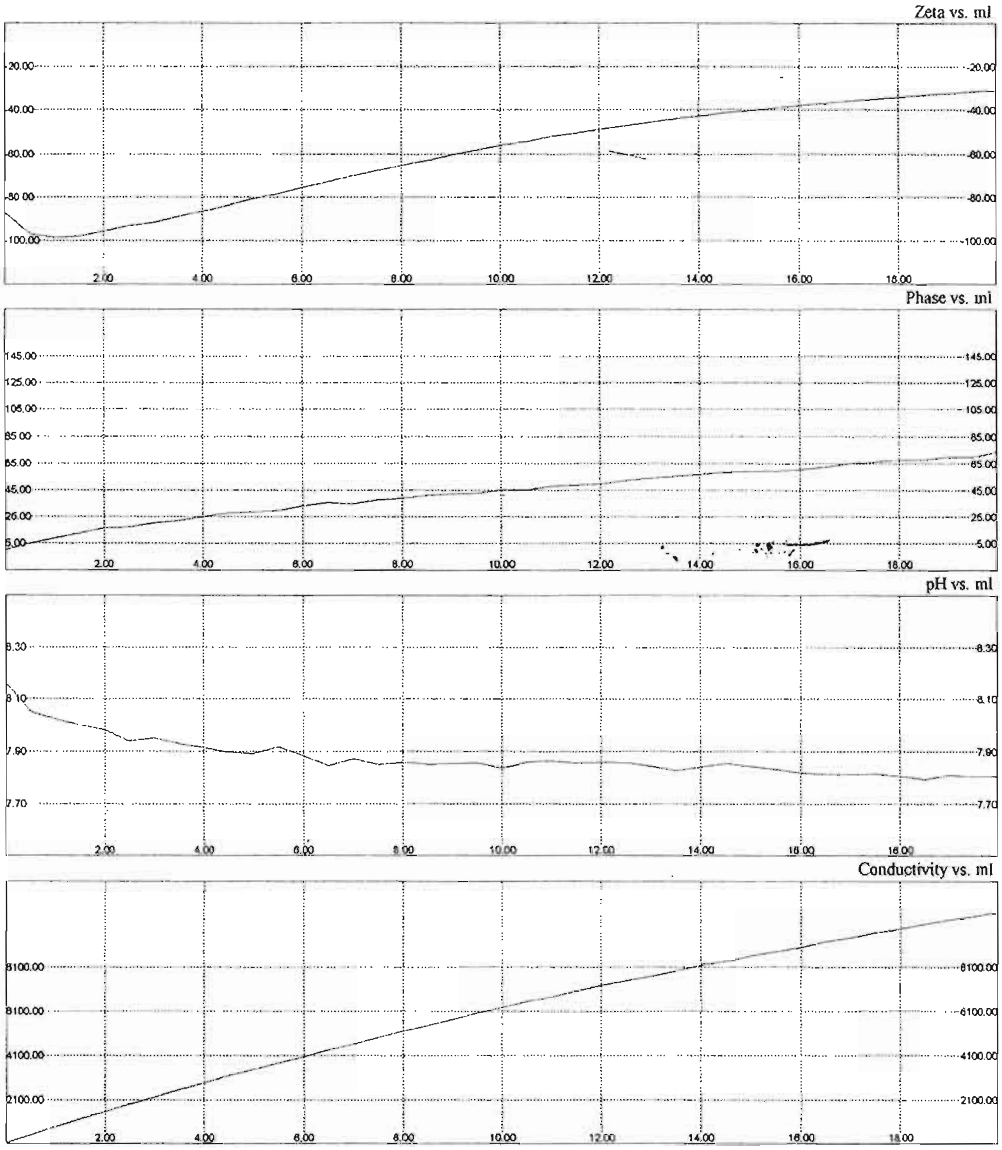


Figure 1.19 Titration of slurry of magnetite 2% v/v with a 10% w/w solution of NaCl. Volume increment of 0.5 ml and an equilibration time of 30 seconds.

For all values of conductivity and pH, the value of the zeta potential changes from a minimum of –99mV to –35 mV. The conductivity varies in the same order of magnitude as the zeta, while the pH initially is slightly lowered and then remained relatively constant throughout the titration process.

1.7.13 Titration of chalcopyrite slurry

The mining industry relies on the negative charge at the surface of the sulphides and a flotation cell was developed for mineral concentrators using a bubble foaming surfactant exhibiting a positive charge that will capture the negative sulphides and concentrate them at the surface. If slurry of chalcopyrite is prepared with neutral water, the initial zeta will have a value of –14 mV. By increasing the acidity to a pH of 2 the zeta potential will decreases slightly to –22mV. For more aggressive acidic pH the zeta increases to +18 mV in a linear fashion at a pH value of 0.7. The isoelectric point or zero charge is attained around a pH of 1 (figure 1.20). During the acidification the slow and slight initial decrease in zeta could be associated with the ion groups lixiviated from the surface of the grains and/or to the lack of equilibrium of the electrical double-layers. The following major increase of the zeta value is related to the H^+ adsorption by the electrical double-layer.

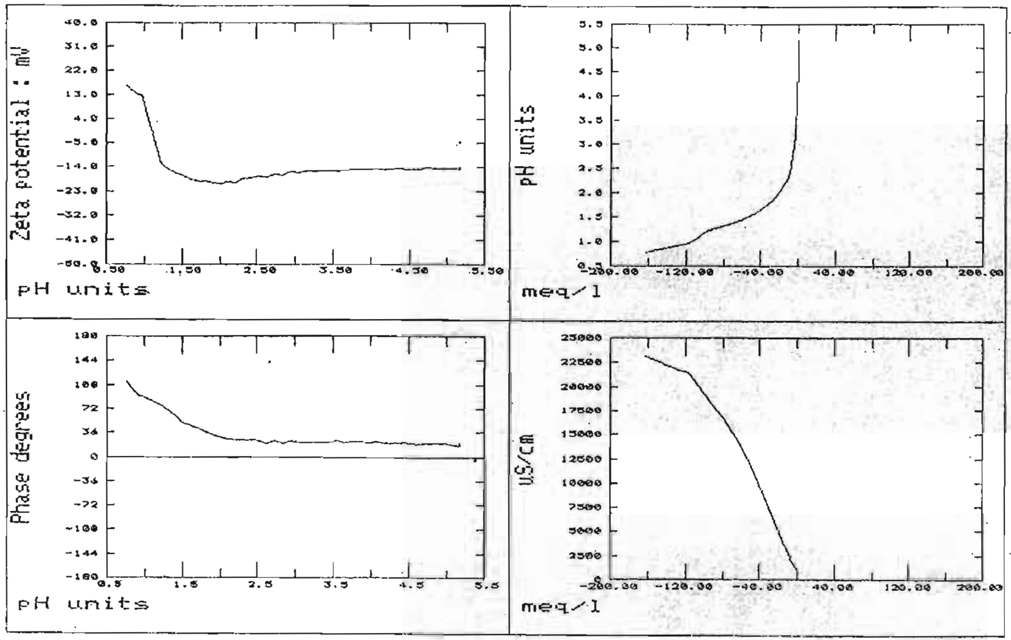


Figure 1.20 Titration of a chalcopyrite slurry 2% v/v with nitric acid (0.5N) at increment pH step of 0.05 for an equilibration time of 15 seconds.

1.7.14 Titration of chalcopyrite with a solution of NaCl

Chalcopyrite slurry was also used to study the effect of salt solution on its surface characteristics. It was further assumed that chalcopyrite would be a suitable representative of the sulphides family from which extrapolation could be made for the other sulphide species. The salt solution used was prepared with NaCl at a 10% w/w concentration. By increasing the electrical conductivity of the chalcopyrite slurry from 1000 uS/cm to 5000 uS/cm, surface charge became more negative with a zeta value change from -22 mV to -34mV.

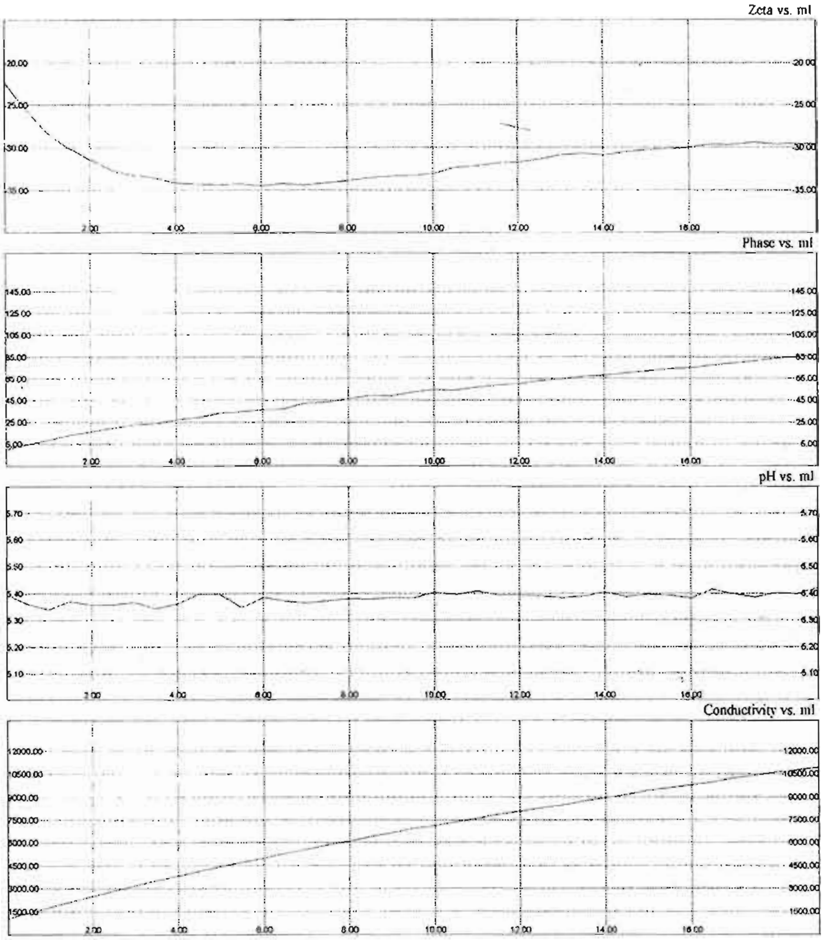


Figure 1.21 Titration of slurry of chalcopyrite (2% v/v), with a solution of 10% w/w of NaCl. The volume increment of the salt solution was 0.5 ml and equilibration time of 30 seconds.

Further increase in conductivity up to 10 000 uS/cm is illustrated in figure 1.21 which shows a minimum surface charge at -34 mV with a final zeta increasing slightly to -29 mV. The curve monitoring the ph variation is constant and stable at 5.40. This is indicative of the minor roles of H^+ and OH^- ions' for the ions exchange process in sulphides. Indeed considering the high conductivity of the original chalcopyrite's slurry, the adsorption preference of the inserted ions (Cl^- and Na^+) and initial co-ions and counterions by the electrical double layers played the dominant role in modifying the surface charge.

1.8 Discussion

In our mineral slurry preparation, attrition of the mineral phase resulted in a finer particle size distribution. In turn, this divides the electrical zeta potential on to a larger number of smaller particles, which results in a smaller intensity value for the zeta potential. Grinding or breaking up the larger particles with resulting increase in the total area, divides the initial surface-charge among a larger number of finer particles. This lost in charge is compensated by their mass lost which results in an increase in their dispersion capability giving the system a higher mobility and more stable suspension since the finer particles are more sensitive to charge repulsion.

Our results indicate that the pH is one of the most important parameters and tools for surface charge variations. For a large number of mineral systems, pH alone could force the zeta to a zero value or at its isoelectric point. On the other hand, each acid or base produces characteristic anions and cations and they also react differently with the mineral surface groups. All these released ions have specific roles in modifying the sign and magnitude of the surface charge of minerals. It is therefore important, to specify the acid and base used and the corresponding conductivity when determining the isoelectric point of a system.

Our results clearly highlight the interactions of equilibration time required by a system after modifying or changing the main parameters. As an example, for quartz slurry an equilibration time of three days was determined with the addition of nitric acid. Initially, after 1 minute even though a pH of 2 was attained, the polarity remained negative and with time the change of polarity was observed at a pH of 2.2. Longer equilibration time allowed the electrical double layer to adjust itself with the new conditions and adsorbed more H^+ and consequently became more positively charged and eventually crossed the isoelectric point.

For alkaline pH, published studies on quartz slurries found that by increasing the pH, the surface charge of quartz particles becomes more negative. This information is in agreement with our titration results for quartz with sodium hydroxide, but the intensity value becomes unpredictable after a pH 11. It seems as if at high pH the electrical double layers are saturated and the charge become less negative related somehow to the larger concentration of ions in the liquid resulting in a saturation level for the system. On the other hand at higher pH the probability for the dissociation of the surface group for the finer quartz particles is increased which in turns can induce instability in the electrical double layer.

During the titration of calcite slurry with nitric acid, a similar decrease in the surface charge was observed under acidic conditions. The dissociation of the surface group of the calcite particles and the resulting introduction of Ca2+ in liquid resulted in more negative surface charge.

The majority of our tests, on silicate, carbonate, oxide and sulphides (apart from the above-mentioned exceptions) indicated that a lowering of the pH and the adsorption of H^+ by the electrical double layers result in a more positive surface charge in the slurries. On the other hand alkaline condition results in a high abundance of adsorbed OH^- by the electrical double layer of the particles and a more negative surface-charge is obtained.

The introduction of salts solutions into the mineral slurries increases the effect of the ions availability in the liquid beside the H^+ and OH^- ions. Addition of NaCl and KCl into distilled water has no effect on the pH, but our experiments on the natural mineral slurries point to the possibility of a pH modification.

In dolomite slurry desorption of Ca^{2+} and its substitution from the electrical double layers by Na+, increase the abundance of the free Ca^{2+} in the liquid and result in a more negative charge on the solid.

The above-mentioned cations competition and the preferential adsorption in the electrical double layer explain the variation of the pH during the titration with salt solutions. In studied with silicates and oxide minerals the increasing concentration of the Na^+ or K^+ in the electrical double-layers and desorption of H^+, provided enough free protons to decrease the pH. On the contrary in carbonate slurries adsorption of the Cl^- counterions and desorption of OH^- resulted in a slight rise in pH. In other instances, the adsorption of newly added ions by the double layers can directly modify the surface-charge without having any effect on the pH, for example the titration of chalcopyrite slurry indicated that all surface charge variations occurred at a constant pH.

CHAPTER II

2 EVALUATION OF SLURRY MIXTURES OF SINGLE-PHASE MINERAL SLURRIES

2.1 Introduction

This section analyses the mixtures made up of previously characterized single-phase slurries. These experiments wanted to verify if the zeta potential of a mixture was a simple summation of the zeta potential for the individual mineral phase multiplied by their concentration in the mixture. We also needed to determine if the separation of the mineral phases mixture could be made. If successfully the parameters under which the fractionation is accomplished would be noted and the quality of the separated fractions be evaluated. If the fractionation is not possible, the decanted column of the mixtures would be examined to evaluate its homogeneity and finally our last goal is to evaluate stability and mobility potentials for decanted solids. In nature, a selected river sediment can be studied and a stability assessment can be arrived at. For environmental considerations and forecasting, if a mobility potential could be determined for a sediment under new conditions like turbidity current or flooding conditions, this would help in assessing risk factors to the area covered by the decanted sediment.

2.2 Mixed phases

2.2.1 Mixing of quartz and calcite

The first mixture consisted of quartz and calcite because both displayed opposite zeta potential polarity values, even though they had similar specific gravity, and median grain size by volume. In addition, their slurry had similar pH and conductivity values. Twenty mixtures were prepared with different concentrations and they were characterized for grain size, pH and zeta potential. The results are presented in table 2.1 and figure 2.1.

These results support the initial hypothesis of this study in which the bulk zeta potential of the system is equal to the summation of individual mineral single-phase zeta multiplied by their respective concentration in the mixture. In other words, the zeta for a complex natural system could represent a summation of the zeta for each mineral phase adjusted to their concentration level in the system, if anthropic phases present in the system have zeta potentials similar to their mineral equivalent.

Table 2.1

Zeta potential, pH and the electrical conductivity of the mixed quartz and calcite slurries for different concentrations

Wt % of Qz In slurry	Wt % of Cal. In slurry	Size (micron)	Zeta (mV)	PH (unit)
0.0	100.0	9.05	122.0	8.5
9.7	90.3	9.20	111.5	8.4
17.7	82.3	8.39	96.5	8.3
24.4	75.6	9.18	90.4	8.3
30.1	69.9	8.95	84.9	8.2
31.9	68.1	9.56	82.2	8.0
35.0	65.0	8.23	77.4	8.2
36.8	63.2	9.80	76.3	8.0
43.5	56.5	8.39	59.7	8.2
51.9	48.1	8.14	38.4	8.5
63.3	36.7	8.48	25.3	8.2
66.0	34.0	8.65	5.5	8.0
71.3	28.7	8.77	-6.5	8.1
72.9	27.1	8.20	-2.6	8.2
78.2	21.8	9.08	-16.7	8.3
84.4	15.6	9.52	-42.0	8.5
91.5	8.5	9.89	-65.4	8.7
100.0	0.0	8.37	-82.3	8.5

The data of table 2.1 defines a linear relationship between zeta and the concentration of the mixtures. Using the experimental values for quartz and calcite in the equation of state we can see a close correlation between the calculated values and the measured values. According to the data table 2.1 the isoelectric point should be attained for 68% quartz and 32% calcite. These results are very close to the values of 60% quartz and 40% calcite yielded by the equation ℵ.

Equation ℵ: **ξ bulk = ξc x C of calcite + ξq x C of quartz**

The small differences between the calculated and experimental concentrations for the isoelectric point could be the result of slight variation in pH and grain size distribution for the slurries (table 5). The strong opposite surface charges exhibited by these two phases can induce agglomerations in the mixture, which in turn will resist dispersion even after sonication. These agglomerations will modify the larger size fraction of the slurry.

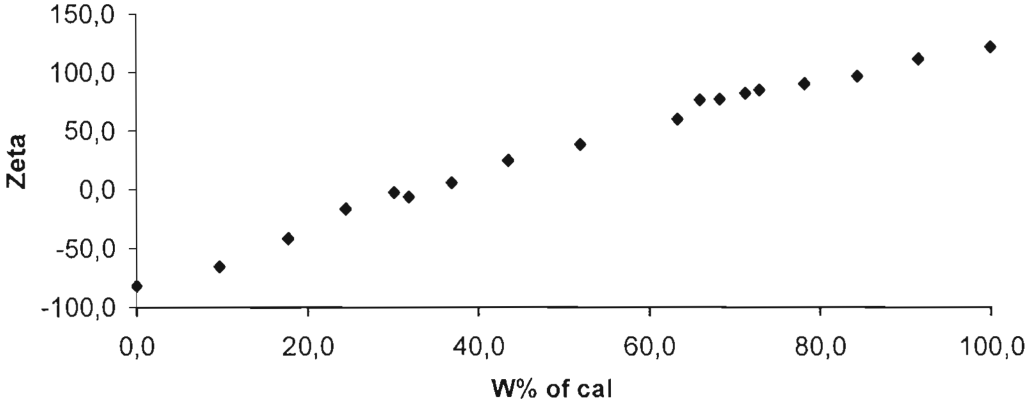
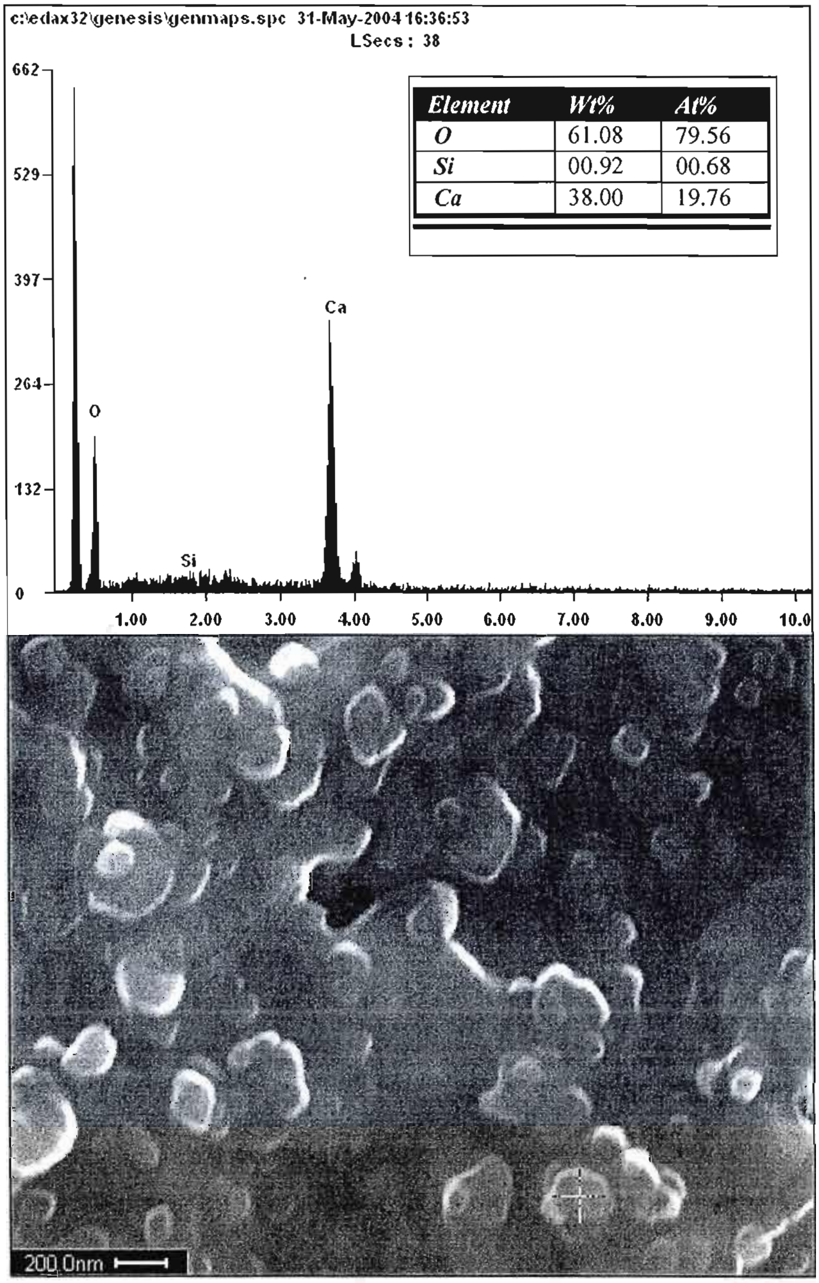


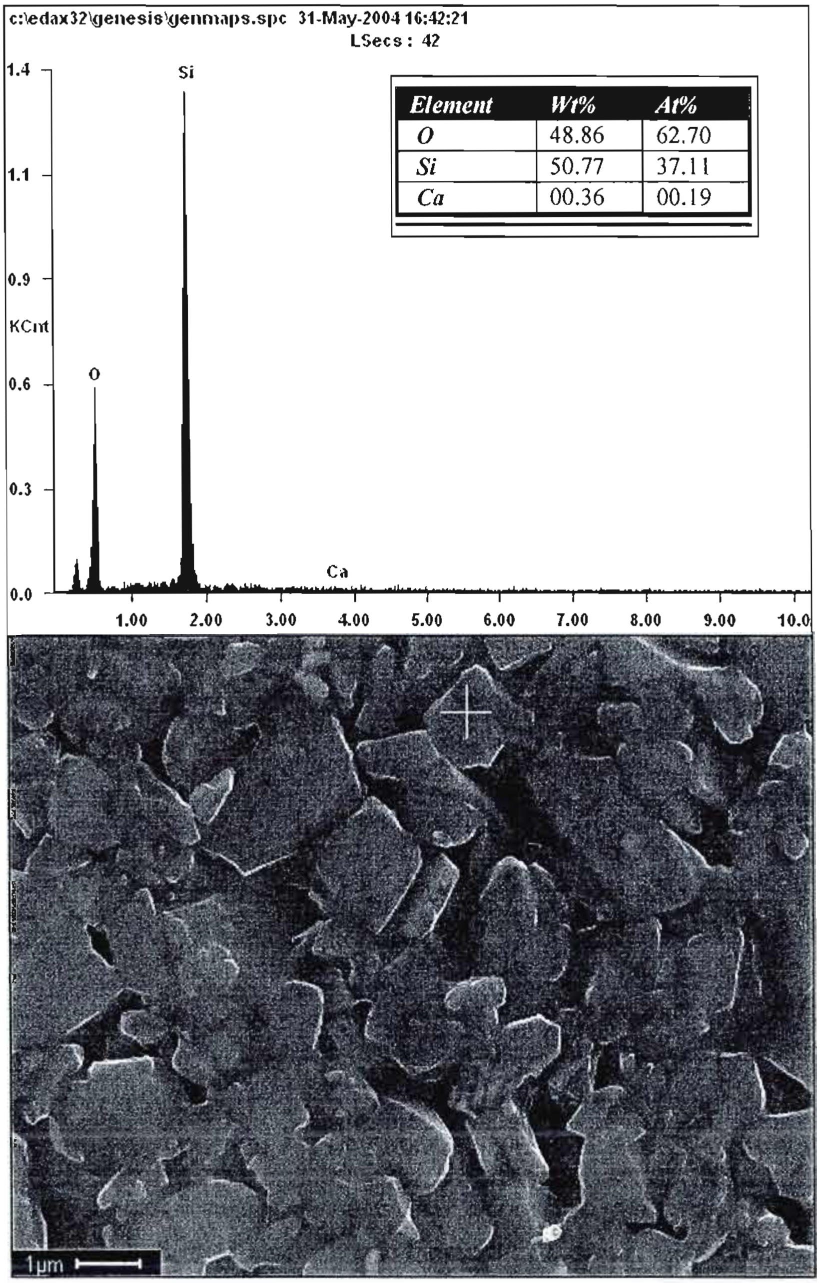
Figure 2.1 The Zeta potential versus concentration of calcite in mixture with quartz.

Because of the high intensities of both phases with opposite polarity we anticipate a strong attraction and a strong adsorption or cohesion bonds at the interface of both minerals. The figures 2.2 to 2.4 are scanning electronic microscope (SEM) surface images, which compare slurries of calcite and quartz alone and as a mixture. For the mixture an attempt was made with a surfactant as a dispersing agent, the surfactant used was anionic, known under the commercial name saratan a sodium salt naphthalene sulfonate polymerized with formaldehyde ($(C_{10}\,H_5SO_3Na\text{-}CH_2\text{-})_n$)



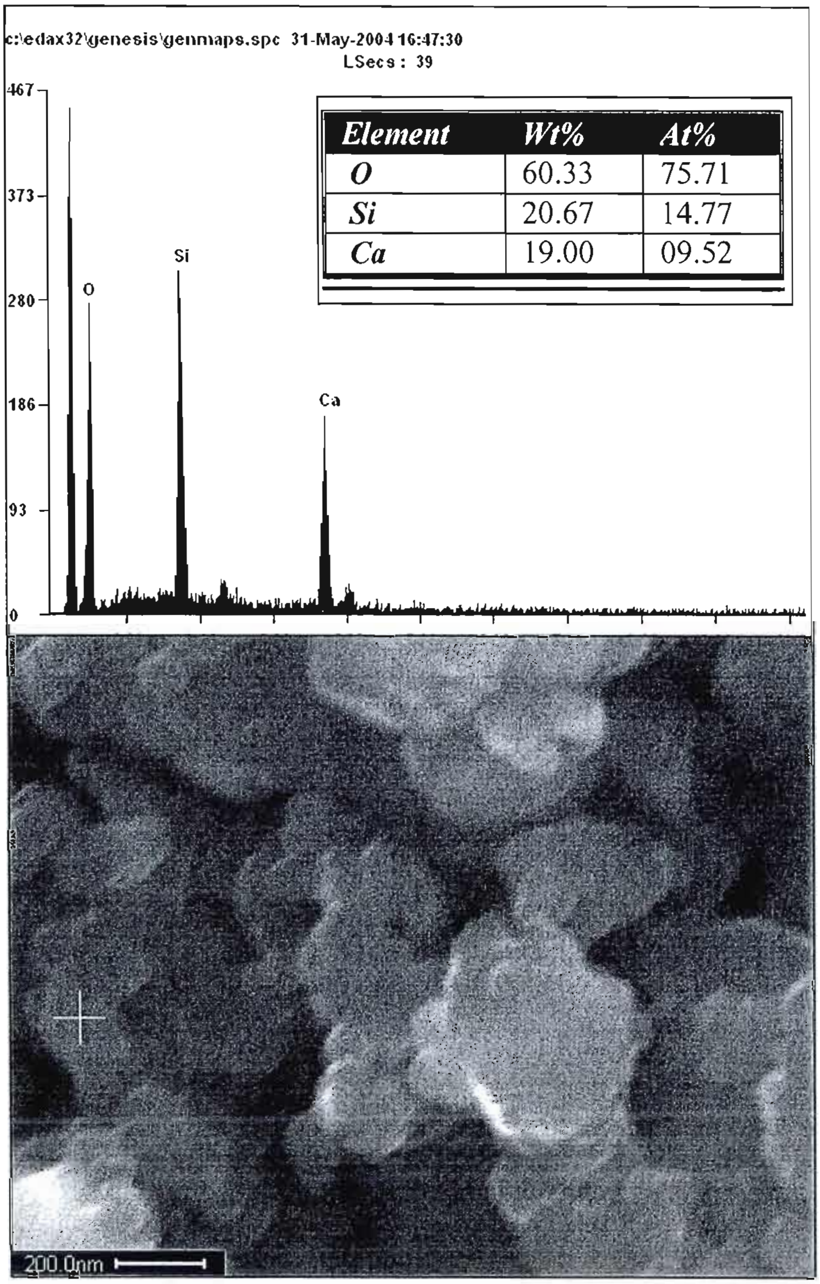
Element	*Wt%*	*At%*
O	61.08	79.56
Si	00.92	00.68
Ca	38.00	19.76

Figure 2.2 The SEM photo and chemical analysis of attrited calcite sample.



Element	*Wt%*	*At%*
O	48.86	62.70
Si	50.77	37.11
Ca	00.36	00.19

Figure 2.3 The SEM photo and chemical analysis of attrited quartz sample.



Element	Wt%	At%
O	60.33	75.71
Si	20.67	14.77
Ca	19.00	09.52

Figure 2.4 The SEM photo and chemical analysis of the mixture of 40% of attrited calcite and 60% of a quartz samples with the addition of Saratan as a dispersant.

2.2.2 Separation and stability of quartz and calcite mixtures

A mixture of quartz and calcite slurry is so strongly bonded that no suspension can be produced with the addition of a dispersant even after sonication. The sample under investigation corresponded to a mixture of 60% quartz and 40% of calcite. The SEM analysis reveals surfaces of quartz coated with the fine fraction of calcite, while the coarser fraction of calcite is coated with the finer fraction of quartz (figure 2.4). The resulting agglomerated solid is stable and would possibly withstand parameter variations that could normally impart mobility to a decanted solid.

2.2.3 Mixing silicate phases

Figure 2.5 illustrates the mixing characteristics for tectosilicates of microcline, albite and quartz while figure 2.6 shows the results from mixing different phyllosilicates including clays.

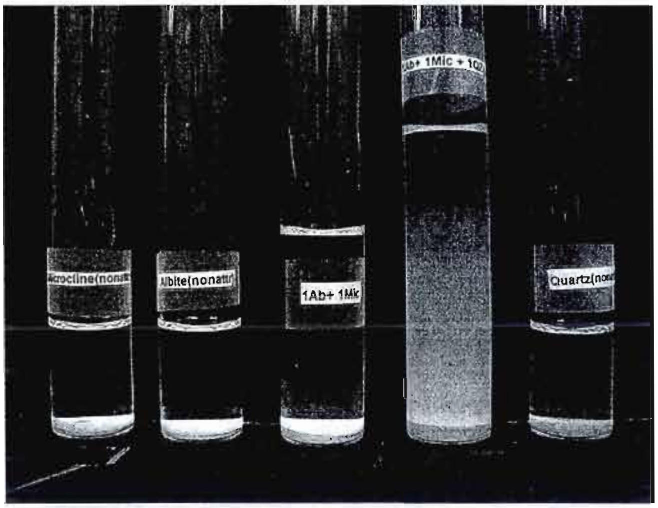


Figure 2.5 Tectosilicates and their mixtures, from left to right: a)Mic non-attr. b)Ab non-attr. c)1Ab non-attr.+1Mic non-attr. d)1Ab non-attr.+1Mic non-attr.+1 Qz non-attr. e)Qz non-attr.

The tectosilicates mixtures after a decantation time of 26 days display a weak suspension for quartz alone and a mixture of albite and microcline but for the mixture of feldspars (albite - microcline) and quartz a strong suspension is observed. This strong and stable suspension of quartz, albite and microcline reflects the increase in the repulsion forces between the fine particles because of the strong negative zeta of the constituent phases (figure 2.5).

The figure 2.6 represents mixtures of different phyllosilicates, which show different behaviour and variation in their column heights for decanted solids after a period of 24 hours. Unlike the tectosilicates, the phylosilicates all have negative phases, but these repulsion forces are not capable in dispersing the solid particles or inducing strong suspensions. The sum of the muscovite, illite and biotite yields a much tighter packed sediment arrangement.

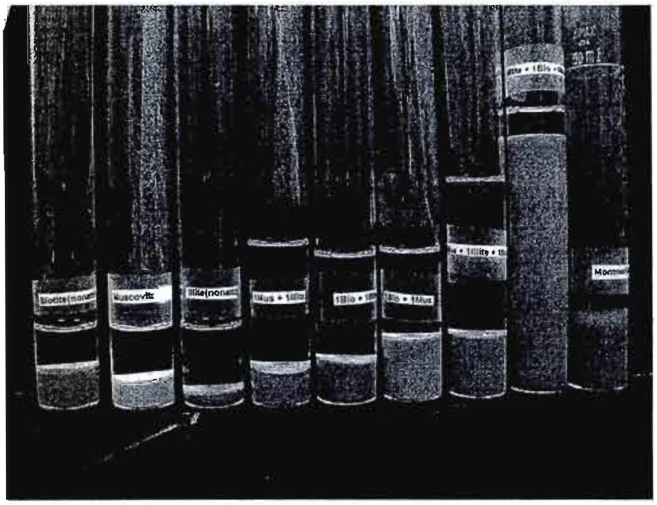


Figure 2.6 Phylosilicates and their mixtures, from left to right: a)Bt non-attr.b)Mus attr. c)Ill non-attr. d)1Mus attr.+1Ill non-attr. e)1Bt non-attr.+ 1Ill non-attr. f) 1Bt non-attr.+ 1Mus attr. g)1Mus attr.+1Ill non-attr.+1Bt non-attr. h) 1Mus attr.+1Ill non-attr.+1Bt non-attr.+1Mont non-attr. i) Mont non-attr.

Also from the illustrated data if montmorillonite is added to the previous mixtures the heights of the sediment increases markedly. For the mixtures of illite, muscovite and biotite the measured zeta is comparable to the calculated zeta (table 2.2) but the absence of suspension could be related to the sheet like structure where point charges are located on edges and are not evenly distributed.

This can result in a less efficient repulsion system with no suspension and with a closer packed sediment arrangement. With montmorillonite the surface charge is so high that the equation is not applicable and the absolute value for the zeta of the system is greater than the calculated zeta value.

2.2.4 Mixing carbonate phases

Mixing equal amounts of the non-attrited calcite and dolomite slurries are shown in figure 2.7. The higher amount of the suspended material after 20 days of decantation time confirms the stronger repulsion forces between sub-micron size particles in mixture for the two strongly positive charged mineral phases.

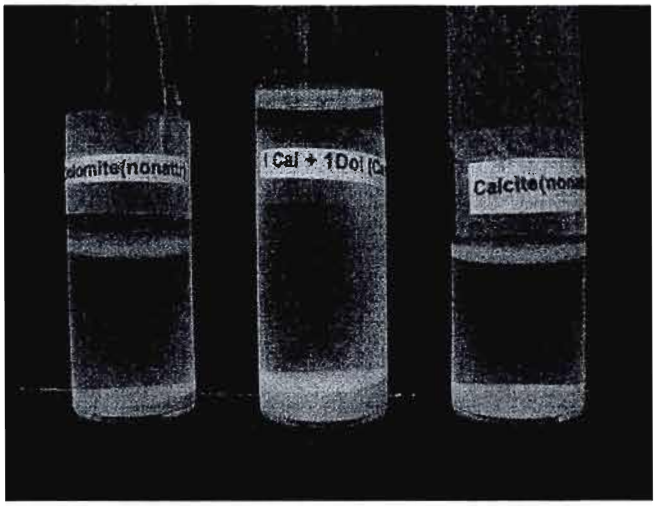


Figure 2.7 Carbonates and their mixture, from left to right: a)Dol non-attr. b)1Cal non-attr.+1Dol non-attr. c)Cal non-attr.

2.2.5 Mixing sulphide phases

The sulphides mixtures after a decantation time of 16 days show no suspension. The weak negative surface charge of the sulphide particles and their associated high density, result in a complete decantation with no suspension. The repulsion force cannot induce a strong suspension (figure 2.8).

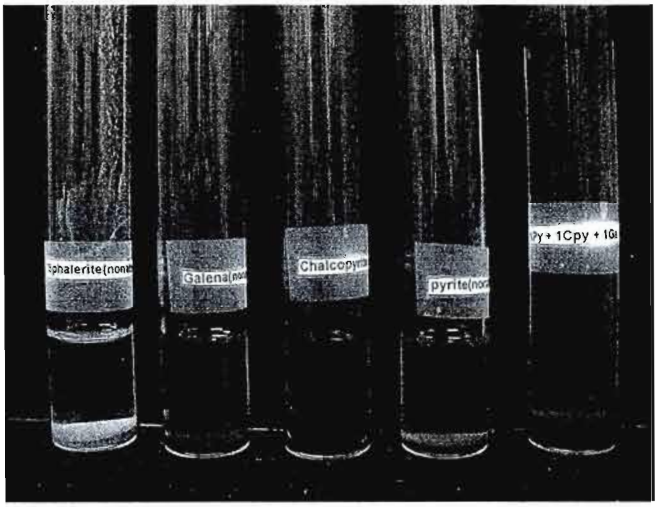


Figure 2.8 Sulphides and their mixture, from left to right: a)Sph non-attr. b)Ga non-attr. c)Cpy non-attr. d)Py non-attr. e)1Sph non-attr.+1Ga non-attr.+1Cpy nonattr.+1Py non-attr.

2.2.6 Mixing of two, three and four mineral phases

Following experiments is being done to verify if the equation ℵ is still applicable for more complex systems and if the measured zeta of such a system is the result of a summation function. For these experiments, other single-phase mineral slurries of silicates, carbonates, oxides and sulphides were characterized and eventually mixed to form more complex systems. The results are presented in table 2.2 for their grain-size distribution, pH and the visual observations of the slurries are presented in figures 2.5 to 2.11.

Figure 2.9 shows samples of attrited calcite, dolomite, quartz with zeta potentials of +83mV, +73mV and –84mV; also present are mixtures of calcite-quartz, and dolomite-quartz after a decantation time of one month. In each case the single-phase slurries display a more stable suspension compared to their mixture. The mixture of calcite and quartz with the zeta potential of +2mV, displays the highest decanted column compared to the mixture of dolomite and quartz with a zeta potential of –7mV, which corresponds to the individual decanted column of the calcite before mixing.

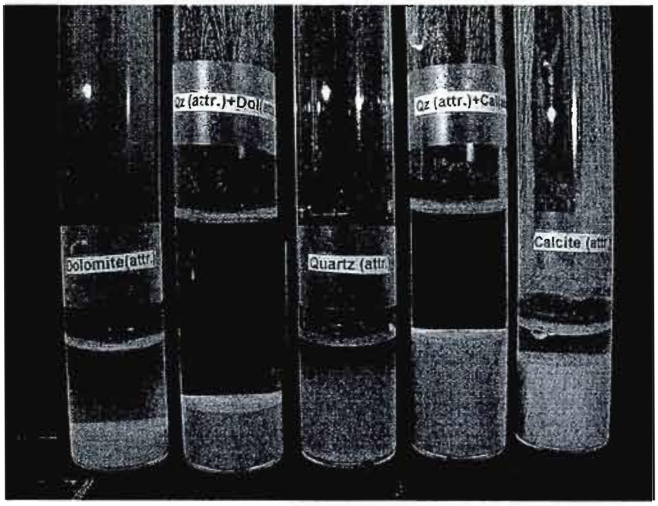


Figure 2.9 Mixture of attrited carbonate slurries and attrited quartz, from left to right: a) Dol b) 1Dol + 1Qz c) Qz d) 1Qz + 1Cal e) Cal.

Table 2.2

Complex and single-phase mineral systems and their characteristics calculated and measured a week after mixing

1st phase					2nd phase					3rd phase					4th phase					Mixture of phases			
Name	Size Mic.	pH	w%	Zeta mV	Name	Size Mic.	pH	w%	Zeta mV	Name	Size Mic.	pH	w%	Zeta mV	Name	Size Mic.	pH	w%	Zeta mV	Size Mic.	pH	C. zeta (mV)	M. zeta (mV)
Qz	11.11	8.2	50	-145	Cal	9.17	8.1	50	153											9.14	7.8	4	11
Qz	11.11	8.2	50	-145	Mont	9.47	8.1	50	-255											9.41	8.4	-200	-201
Cal	9.17	8.1	50	153	Mont	9.47	8.1	50	-255											8.22	8.6	-51	-220
Qz	11.11	8.2	33	-145	Cal	9.17	8.1	33	153	Mont	9.47	8.1	33	-255						9.92	8.3	-82	-197
Dol	8.27	8.4	50	106	Mont	9.47	8.1	50	-255											7.91	8.9	-75	-225
Dol	8.27	8.4	67	106	Mont	9.47	8.1	33	-255											7.53	8.9	-14	-206
Dol	8.27	8.4	75	106	Mont	9.47	8.1	25	-255											6.79	8.8	16	-173
Ab	8.64	8	50	-213	Mic	9.19	7.8	50	-246											8.17	7.9	-230	-201
Ab	8.64	8	33	-213	Mic	9.19	7.8	33	-246	Qz	8.47	6.7	33	-171						8.83	7.9	-210	-210
Bt	8.64	8.2	50	-128	Mus	9.21	8.1	50	-210											8.58	8	-169	-148
Bt	8.64	8.2	50	-128	Ill	8.55	6.8	50	-120											7.95	7.6	-124	-120
Bt	8.64	8.2	50	-128	Mus	9.21	8.1	50	-210											9.54	7.4	-169	-163
Bt	8.64	8.2	33	-128	Mus	9.21	8.1	33	-210	Ill	8.55	6.8	33	-120						9.84	7.7	-153	-158
Bt	8.64	8.2	25	-128	Mus	9.21	8.1	25	-210	Ill	8.55	6.8	25	-120	Mont	9.47	8.1	25	-255	10.07	8.1	-178	-228
Cal	9.17	8.1	50	153	Dol	8.27	8.4	50	106											11.65	8.5	130	130
Py	9.71	5.6	25	-5.8	Cpy	7.01	3.5	25	-14	Ga	8.84	6.6	25	-7	Sph	9.61	7.1	25	-27	10.27	6.7	-13.45	-14
Qz	2.89	6.8	50	-84	Cal	3.09	7.9	50	83											4.3	7.9	-0.5	2
Qz	2.89	6.8	50	-84	Dol	5.01	8.6	50	73											3.73	8.5	-5.5	-7

Ab : albite Bt : biotite Cal : calcite Cpy : chalcopyrite Dol : dolomite Ga : galena Ill : illite Mic: microcline Mus : muscovite
Py : pyrite Qz : quartz Sph : sphalerite Mont : montmorillonite Mic. :Micron

C.Zeta : Calculated Zeta(based on the equation) M.Zeta : Measured Zeta

Figure 2,10 illustrates the mixtures of microcline with different amounts of dolomite after 12 days of decantation. Considering the individual zeta potentials of dolomite and microcline, which are +125mV and –225mV, it was anticipated that, a mixture of two parts dolomite with one part microcline, would result in complete agglomeration with no suspension. Experimentally it was observed that this mixture did yield a small suspension and the smallest amount of suspension was obtained for equal amounts of dolomite and microcline. Obviously just mixing one part of the dolomite has satisfied the surface charges and adding more dolomite has increased the amount of the suspension resulting in repulsion from the non-neutralized particles.

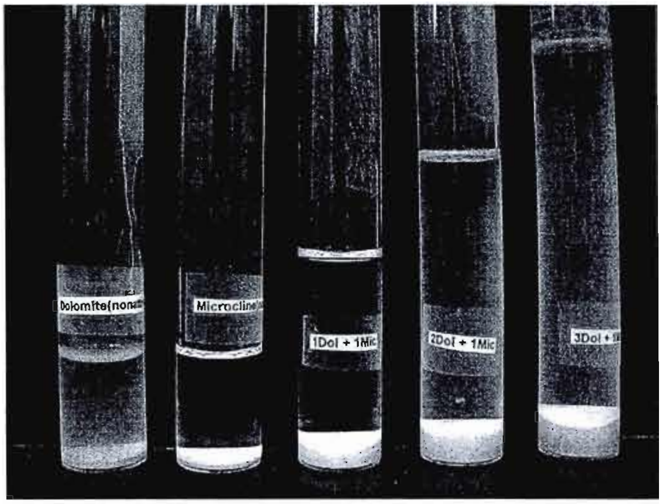


Figure 2.10 Mixtures of the various ratios of the non-attrited dolomite slurry with non-attrited microcline's slurry, from left to right: a) Dol b) Mic c) 1Dol + 1Mic d) 2Dol + 1Mic e) 3Dol + 1Mic.

Figure 2.11 illustrates the results of mixing carbonate with montmorillonite slurry after 20 days of decantation. Initially the zeta potentials of calcite and montmorillonite are +153mV and –255mV respectively. It was also anticipated that by mixing two parts of calcite and one part of montmorillonite would result in a complete agglomeration and no suspension. But as shown by figure 2.11 even by introducing three parts of calcite for one part montmorillonite did not resulted to a complete agglomeration. Again the addition of montmorillonite behave in a non-conventional way, the calculated values are not in agreement with the measured zeta (table 2.2).

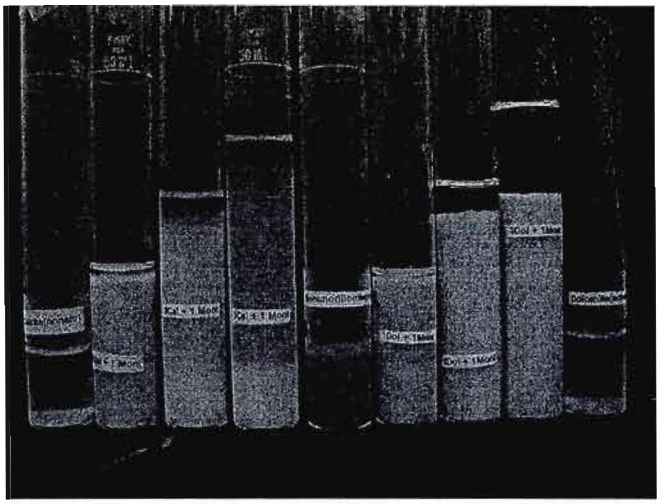


Figure 2.11 Mixtures of various ratios of non-attrited calcite and dolomite slurries with the montmorillonite slurry, from left to right: a) Cal b)1Cal+1Mont c)2Cal+1Mont d)3Cal+1Mont e)Mont f)1Dol+1Mont g)2Dol+1Mont h)3Dol+1Mont i) Dol.

The measured surface-charges of the different mixtures of dolomite with montmorillonite could be found in table 2.2. Adding one part of dolomite into the similar amount of montmorillonite slurry had no effect on overall surface charge and its zeta potential stayed stable at –255mV, where the calculated amount based on equation ℵ was expected to be –75mV. Even with adding three parts of dolomite to one part of montmorillonite the measured zeta potential of mixture was not at the isoelectric point. Instead the measured zeta was –173mV instead of the calculated value of +16mV.

An added observation which is an interesting point is the presence of dolomite the system displays a sharp decantation surface above which a clear liquid stand out above the solid and the addition of additional amount of dolomite did not reduce the height of the decantation column.

2.3 Ageing, sample preparation and storage

In slurries, leaching of the solid particles, re-crystallization of the soluble elements as well as agglomeration of particles can take place with time, and they will all modify the solid surface characteristics. With time variation in the particles electrical double layers have an important effect on the net surface charge of the slurries. Often, for economical considerations, products are being dried and stored since it minimizes space and transportation expenses Even though ageing has been known for a long time in mineral processing industry we conducted experiments to better understand the equilibration time related with our mixtures of mineral phases. An ageing test is illustrated in figure 2.12 where montmorillonite and attrited quartz with volume fraction of 1% have been left for one year without any disturbance. In these one-year-old samples the decantation column has been greatly reduced leaving a weak suspension while a strong suspension is associated for recently prepared samples (figures 1.1, 2.6 and 2.9).

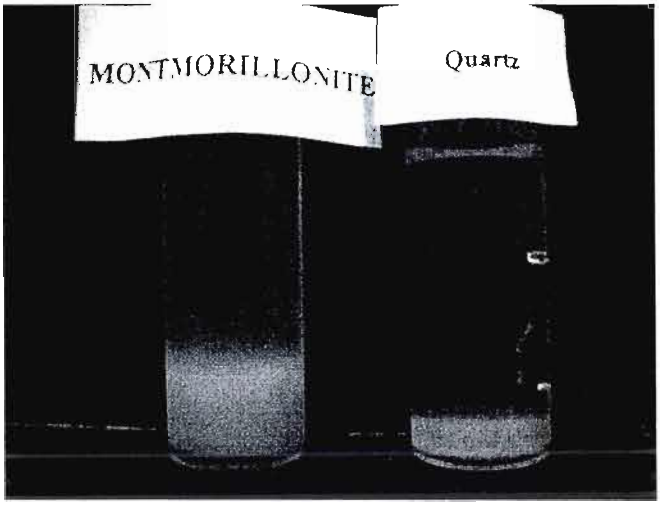


Figure 2.12 Non-attrited montmorillonite (left) and attrited quartz (right) slurries after one year without any disturbance.

The physical characteristics of size, pH, conductivity and surface charge for recently prepared quartz slurries are compared with two other samples, prepared a year ago stored dried and wet, in table 2.3. The results indicate that during the storage period, the surface charges of the both dry and wet stored samples where reduced. The stored wet samples show an agglomeration with time corresponding to the zeta reduction; in addition, the wet sample shows an increase in pH and conductivity. On the other hand by drying the sample we are able to preserve the initial pH and conductivity (table 2.3).

In mixing the mineral single-phase slurries, an equilibration time is required to attain a stable zeta potential value. If additional time is given, it is possible that ions resulting from further dissociation of the surface groups could occur and the finer particles could be adsorbed by a larger opposite charged particles.

Table 2.3
Comparison between recently prepared quartz slurry and two quartz slurries made from samples stored wet and dry for one year

Name	Size (micron)	pH	Zeta potential(mV)	Conductivity (us/cm)
Quartz non-attrited, recently prepared	8.47	6.65	-171	33
Quartz non-attr stored as a slurry	11.11	8.17	-145	126
Quartz non-attr stored dry	11.09	6.13	-143	35

For the one-year-old sample the minimizing of the absolute value of the zeta potential and induced change of the conductivity and pH are consequences introduced by this prolonged equilibration or ageing of the slurries (tables 2.3 and 2.4). This can mean that industrial residues discharge have probably not been equilibrated with the liquid and are ageing in decantation ponds or in lake bottom as sediments.

Our results indicate that montmorillonite mixtures have the most unstable zeta potentials. In order to obtain more accurate zeta potential values we attempted to determine the shortest equilibration time for montmorillonite mixtures. From the data of table 2.3, it requires at least 7 days to obtain an acceptable equilibration between mixed phases, and have a reliable net surface-charge value.

Table 2.4
Surface-charge measurements, different equilibration time, for mixtures of single mineral phases

		Time between mixing and measurement	Size	pH	Zeta (mV)	Conductivity (us/cm)
First mixture	1Qz + 1Mont	60 minutes	10.9	8.23	-241	720
	1Qz + 1 Mont	20 hours	10.9	8.20	-225	699
	1Qz + 1Mont	3 days	10.9	8.01	-196	801
Second mixture	1Qz + 1Mont	2 days	10.3	8.80	-227	684
	1Qz + 1Mont	9 days	9.6	8.62	-207	703
	1Qz+ 1Cal + 1Mont	24 hours	10.8	8.47	-220	658
First mixture	1Qz+ 1Cal + 1Mont	2 days	10.8	8.44	-214	645
	1Qz+ 1Cal + 1Mont	5 days	10.1	8.42	-199	681
	1Qz+ 1Cal + 1Mont	14 days	10.1	8.38	-197	710
Second mixture	1Qz+ 1Cal + 1Mont	2 days	9.9	8.95	-217	608
	1Qz+ 1Cal + 1Mont	9 days	9.9	8.34	-196	904

2.4 Discussion

Simple mixing of quartz and calcite with opposite polarities and high charge intensities satisfied our equation of state for the system. The measured zeta for the mixture was equal to the summation of the individual zeta potentials multiplied by their concentration. This equation was also satisfied for other mixtures of silicates and sulphides. For these simpler system using single-phase mineral zeta potentials it is possible to give the concentrations for each phase so that the isoelectric point will be attained (pzc).

Anomalies were noticed when montmorillonite was added to the mixture. The global charge in the mixture was found to be more negative than the calculated zeta.

Montmorillonite has a very strong negative charge and as a result the zeta for the entire system is much more negative. It appears as if montmorillonite monopolizes or covers up the positive charges of the system so that no contribution is coming from these positive charges. Even by adding a large amount of the positive surface-charge phases, for the equilibration time used the zeta potential of the mixture is not reduced as anticipated In addition it is possible that in more complex slurries, montmorillonite particles can coat certain phases more than other. This coating can isolate or shield the particles from the rest of the slurry and lower the resulting zeta. This coating property of montmorillonite could be related to its morphology, structure and composition. In other words, the montmorillonite clay, well known for its high adsorption capacity, is extremely efficient in increasing and dictating the negative sign of the system acting like a dispersing agent using strong repulsive negative surface charge which increases the overall mobility of a system with the possible formation of a suspension.

Other mineral phases were also found to reduce the height of the decanted column and stabilize the solid or reduce its mobility. Our results suggest that when the charges display large differences then the smallest phase or fraction coats the other phase resulting in the stabilization of the solids. For the case of calcite and quartz slurry, even surfactant treatment and sonication were not able to break the strong interface bonds between the positive charged calcite and negative charged quartz particles, which is confirms by the mobility and the high stability of the agglomerates.

Suspension that appears equilibrated and stable within the time frame of the laboratory displays ageing after longer period of time. Our samples after one year still displays a suspension, the zeta has been reduced with a corresponding increase in pH and conductivity. The possibility of surface charge modification over a long period means that equilibration time is important in modeling systems and predicting its behaviour. This also means that attenuation is at work and mobile systems will be stabilized with time. Indirectly by deduction from trial runs to determine the effect of pH and conductivity it was found that flooding could modify the pH and conductivity of the liquid and consequently modify the mobility factor for the system.

CHAPTER III

3 THE SURFACE-CHARGE AND THE CONTROLLING VARIABLES IN MULTI-PHASE SYSTEMS

3.1 Introduction

The ultimate goal of this study was to apply our finding on single and simple mixtures to a natural complex system and evaluate if the system can be fractionated into simpler modes. In addition, we had to verify if the general guidelines established for the simple systems are still applicable to natural multiphase system. Because of previous work done by our group on river and lake sediments, the lake sediments from the Sussersee (Sweet Lake) of the Mansfeld industrial region (see appendix) were selected. The Sussersee lake is the collecting basin for all-important copper processing area, which means that anthropic phases are expected.

Relying on our data from single and simple mineral slurries we attempted to approximate the composition of the sediment with our mineral mixture and evaluate and calculate the resulting zeta potential for both the laboratory multiphase system and the Sweet-lake system. The mineral concentrations were determined by X-ray powder diffraction and modal analysis. This sediment is considered as contaminated and represented a complex mixture natural and anthropic compounds produced from pyrometallurgical ore processing in which primary and secondary mineral phases have also been identified.

3.2 Zeta of the natural system versus the zeta of artificially prepared system

The bold comparison of the calculated zeta of the Sweet lake sediment using the mineral concentration given by X-ray diffraction and using the zeta of the mineral slurries yielded a zeta of –118 mV, compared to measured values from – 53 mV to – 108 mV for natural zeta of the system. Considering the presence of organic matter and the finer grain size distribution of the Sweet-lake sediments, the correspondence between the two values is not so different.

3.2.1 Sample preparation

The sediment samples were received from Germany in their original slurry form in polyethylene containers. Two mixtures were prepared with the same concentration in mineral equivalent but with slightly larger grain size distribution. The first mixture was made from dried mineral powders and the second one was made from the wet stored single-phases (figure 4.1 and tables 3.1 and 3.2).

Table 3.1

Percentages of the minerals in Sweet Lake sediment and its equivalent artificial mixture with calculated zeta potential

	Percentage of minerals in Sweet-Lake sediment	*Calculated zeta for Sweet-Lake sediment (mV)	Minerals' measured zeta potential at mixing time (mV)	Percentage of the minerals in mixture	*Calculated zeta for mixture (mV)
Quartz	63.13	-91.54	-145	63.39	-91.92
Calcite	13.80	21.11	153	12.84	19.65
Albite	12.59	-26.82	-213	12.21	-26
Microcline	5.14	-12.64	-246	5.3	-13.04
Muscovite	2.77	-5.82	-210	2.44	-5.12
Clinochlore (biotite)	1.60	-2.05	-128	1.38	-1.77
Pyrite	1.16	-0.07	-5.8	0.63	-0.04
Chalcopyrite	Very low		-14.2	0.6	-0.09
Sphalerite	Very low		-27	0.6	-0.16
Galena	Very low		-7.3	0.6	-0.04
SUM	100.19	-117.82		100	-118.53

*Calculated zeta= percentage of mineral × mineral's measured zeta / 100

The variation in calculated and measured surface charge of our artificial mixtures could be related to differences in the particles size distribution, pH and conductivity of the mixtures with the individual single-phases. The specific gravity of the Sweet-Lake's sediments, is lower than all its containing minerals (tables 1.1, 3.1

and 3.2). The lower specific gravity is caused by the presence of organic matter in the sediments. In addition, the Sussersee sediments have been strongly influenced by high conductivity and ageing phenomena.

Table 3.2
Comparison between the calculated and measured zeta in Sweet Lake sediment and its equivalent artificial mixtures

	Size (um)	PH (unit)	Density g/cc	Electrical conductivity (us/cm)	Calculated zeta potential (mV)	Measured zeta potential (mV)
Wet stored Sweet-Lake (Sussersee) sediment	13.8	7.0	2.53	1225	-118	-53
Wet stored single-phase mineral mixture	10.8	7.7	2.76	392	-119	-82
Dry stored single-phase mineral mixture	11.3	7.6	2.76	442	-119	-108

Nevertheless, the relatively close correlation between the calculated value and the measured value for the zeta potential of the system would tend to support the hypothesis by which anthropic phase will generally display equivalent zeta as would a natural mineral, as long as both have similar chemical composition and that both are crystalline substances. If this is verified, then the initial zeta of a multiphase system can readily be evaluated by knowing the modal mineralogical composition and the zeta for the equivalent mineralogical individual phases.

3.2.2 The effects of sample preparation on the measured parameters

Table 3.3 presents the results of an experiment that was designed to evaluate the effects caused by sample preparation such as drying, using the original water for sample dilution or deionised water, electrical conductivity fluctuations, grain size variations, pH and zeta.

Samples were prepared using Sweet Lake original water and/or deionised water for dilution of the slurry to attain the fixed volume fraction. The samples were then allowed to equilibrate for 5 days before characterizing the slurry for the usual parameters (table 3.3 and figure 3.1). The reduction in electrical conductivity resulting from using deionised water for the dilution of the slurry increases the absolute value of the particles surface-charge or the zeta potential.

Table 3.3

Effects of water dilution on zeta potential, pH, conductivity and the particle-size of Sweet-Lake samples

	Dilution water	PH a day after agitation (unit)	Zeta 5 days after agitation (mV)	PH 5 days after agitation (unit)	Electrical Conductivity5 days after agitation (us/cm)	Grain size measured by laser (micron)
ND. SW	SW. W	7.34	-25.7	7.66	1799	12.94
ND. SW	DIS, W	7.52	-62.1	7.69	362	12.01
D.SW @150°C	DIS. W	7,66	-32.2	7.73	332	13.77
D.SW @45°C	DIS. W	7.70	-31.1	7.44	508	11.53

SW. = Sweet-Lake's (Sussersee) sample

SW. W= Sweet-Lake's (Sussersee) sample's pore water

DIS.W = Distilled water D.= Dried ND. = Non-dried

Other variations are noticeable for instance with the grain size distribution while the pH remained relatively constant. The smaller grain size for the non-dried sample indicates a better or easier suspension formation related to possible higher repulsion of the particles and less agglomerations when the samples are not dried. The samples in figure 3.1 and 3.2 illustrate the effect of the different preparation on the suspension. These effects are in agreement with the results obtained and presented in earlier sections related to surface charge and the inter-dependence of pH, conductivity and salt content (figures 1.9 and 1.10).

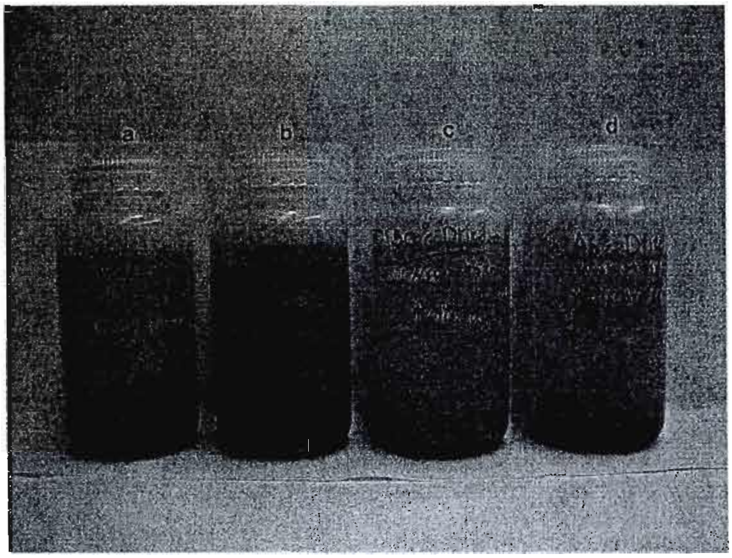


Figure 3.1 Samples for the investigation of the effects on surface charge, drying, pH and conductivity of Sweet-Lake's sediment. (a) Non-dried Sweet-Lake sample, diluted with the Sweet-Lake sediment's pore water; (b) Non-dried Sweet-Lake sample, diluted with distilled water; (c) Sweet-Lake sample, dried at 150 ˚C and diluted with distilled water; (d) Sweet-Lake sample, dried at 45°C and diluted with distilled water. Albeit the same volume fraction for all samples (2 %) the thikness of precipitated sediments and amount of the stablesuspension dramatically vary, which represent the variation in grain size and zeta potential.

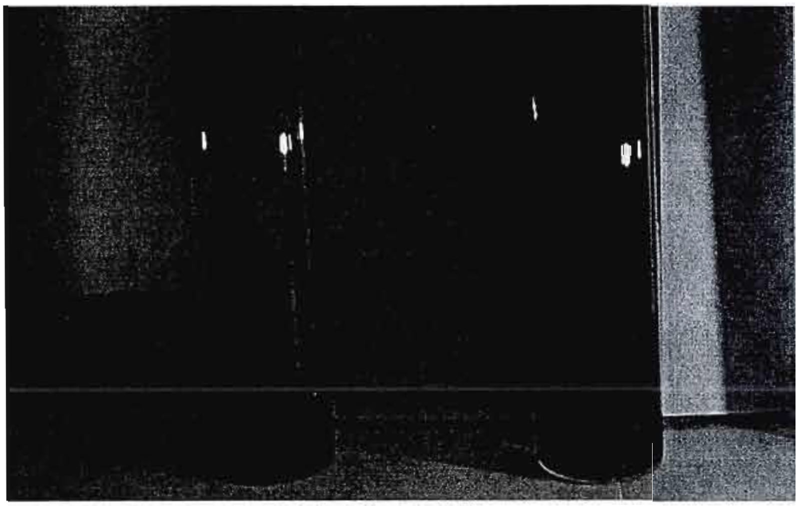


Figure 3.2 Sweet-Lake samples, decantation of 24 hours (both samples were submitted to ultrasounds for 20 seconds): (left) diluted with the Sweet-Lake pore water; no evidence of suspension (right) diluted with distilled water, a strong and stable suspension is evident.

Since drying the sample drastically modifies the zeta potential values, in the following considerations we have attempted to list possible hypothesis to explain this effect:

- Elimination of the nano-size particles fraction because of the irreversible adsorption on the coarser particles;
- Producing some small amount of evaporates more resistant to leaching or dissolution (low Ksp); that contribute to the lower electrical conductivity of the slurry;
- Reduction in the amount of the microorganisms and organic matter with the drying process.

3.3 Flocculation of a suspension or stabilizing a solid by adding a mineral phase with a strong opposite sign

The flocculation of a suspension by mixing a mineral phase with the opposite charged slurries as presented in chapter II could offer an alternative to organic surfactants.

The Sweet-Lake's sediments were mixed with different proportions of carbonate slurries to evaluate their potential effects as a flocculating and stabilizing agent. Five samples of sediments with attrited dolomite and non-attrited calcite and dolomite slurries were mixed, agitated and sonicated with the sediment. The grain-size, pH, surface charge, conductivity and density measurements of the resulting samples are presented in table 3.4. The slurries were also left undisturbed to observe their macroscopic behaviour, which are illustrated on figures 3.3 and 3.4. Figure 3.2 illustrates the strong and stable suspension for a Sweet Lake's slurry if distilled water was used for the dilution step. By adding one part of the non-attrited calcite slurry into the two parts of Sweet-Lake's slurry, surface charge was expected to become less negative, but because of the increase for the pH the surface charge of the mixture became more negative. The same phenomenon was observed by mixing the dolomite phase. Figure 3.3 demonstrates the effect of the added carbonate phases immediately after sonication.

Table 3.4

Physical characteristics of carbonates and their mixtures with Sweet-Lake sediments

Slurries and their proportion in mixtures	Volume fraction	Size (um)	PH (unit)	Zeta (mV)	T (°C)	Cond. (us/cm)	Density (g/cc)
Sweet-Lake's sediment	2%	13.8	7.02	-53	24	1223	2.53
Calcite (non-attrited)	2%	9.2	8.10	153	23	111	2.77
Dolomite (non-attrited)	2%	8.3	8.40	106	22	317	2.93
Dolomite (attrited)	2%	5.7	8.54	83	22	498	2.93
2Sweet-Lake+1Calcite (*n.attr.)	2%	11.6	7.42	-56	24	944	2.61
2Sweet-Lake+1Dolomite (n.attr.)	2%	11.0	7.49	-52	24	1027	2.665
2Sweet-Lake+1Dolomite (attr.)	2%	12.3	7.73	-27	24	1065	2.665
1Sweet-Lake+1Dolomite (attr.)	2%	11.9	7.64	19	24	950	2.73

*n.attr. : non-attrited

The suspensions decant rapidly for the samples with the non-attrited dolomite and calcite. Figure 3.4 shows the same samples after a decantation time of 5 hours. The best results are obtained with attrited dolomite even if it requires a longer decantation time all the solid decants leaving a clear liquid.

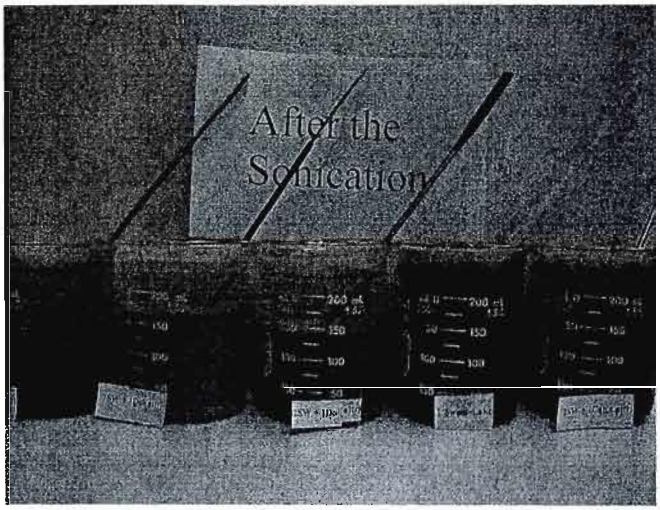


Figure 3.3 Sweet Lake sediment + carbonates, few minutes after providing the sonication; from left to right: a) 2Sweet Lake + 1 non-attrited dolomite; b) 1Sweet Lake + 1attrited dolomite; c) 2Sweet Lake + 1attrited dolomite; d) 1Sweet Lake; e) 2Sweet Lake +1 non-attrited calcite.

In mixtures of Sweet-Lake with calcite an increase in the pH of slurry increased the net negative charge, which is in agreement with our previous results on the effect of the pH on surface charge of the single-phase minerals.

It appears that the grain size influences the flocculation process, larger the particles the faster is the decantation. But in the long term, finer particles are more efficient in reducing the negativity of the surface-charge and precipitating the suspended particles. Also depending on amount added, an equilibration period should have respected, but this variable was not studied precisely.

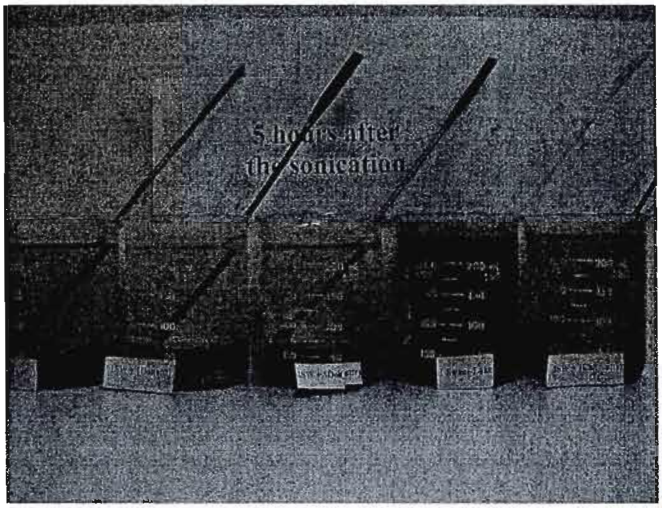
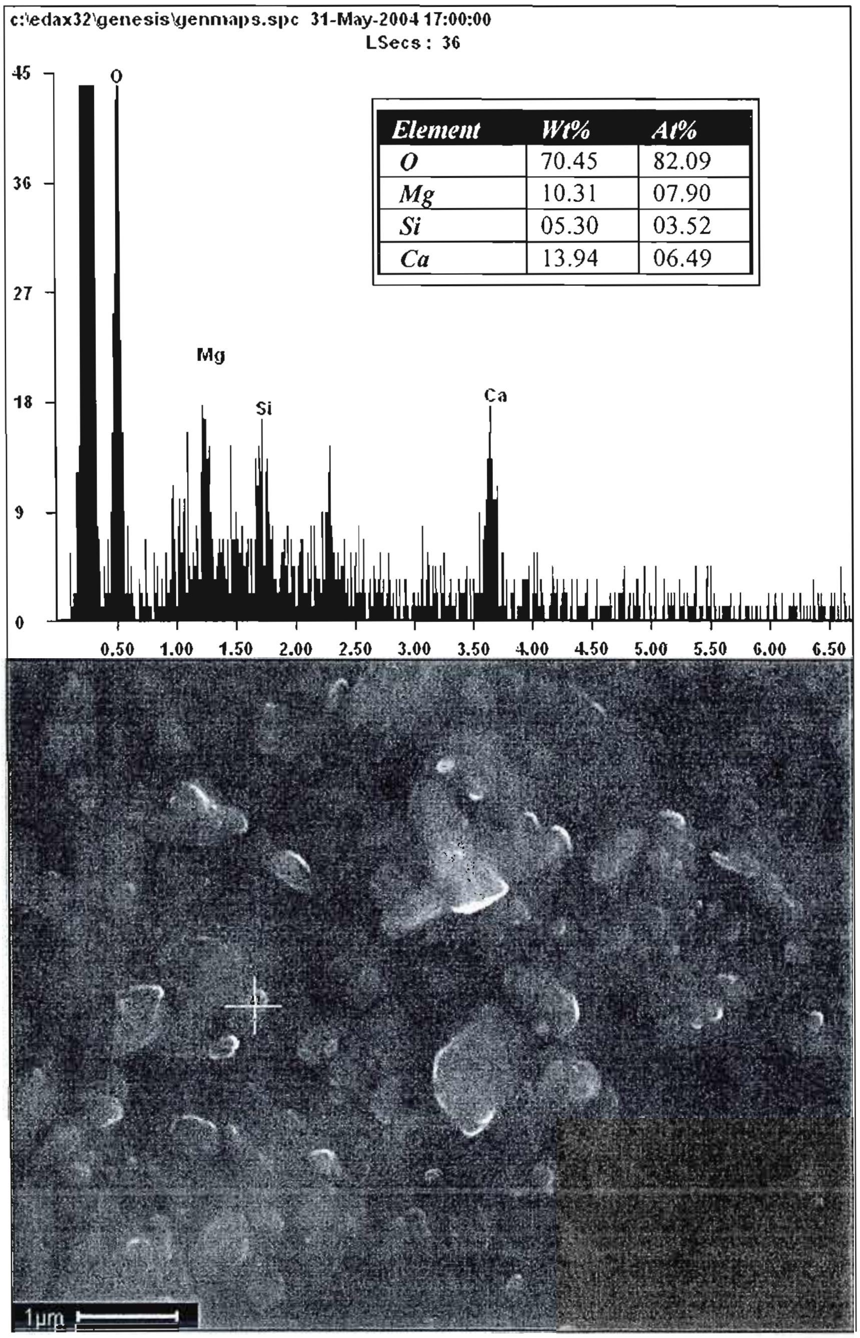


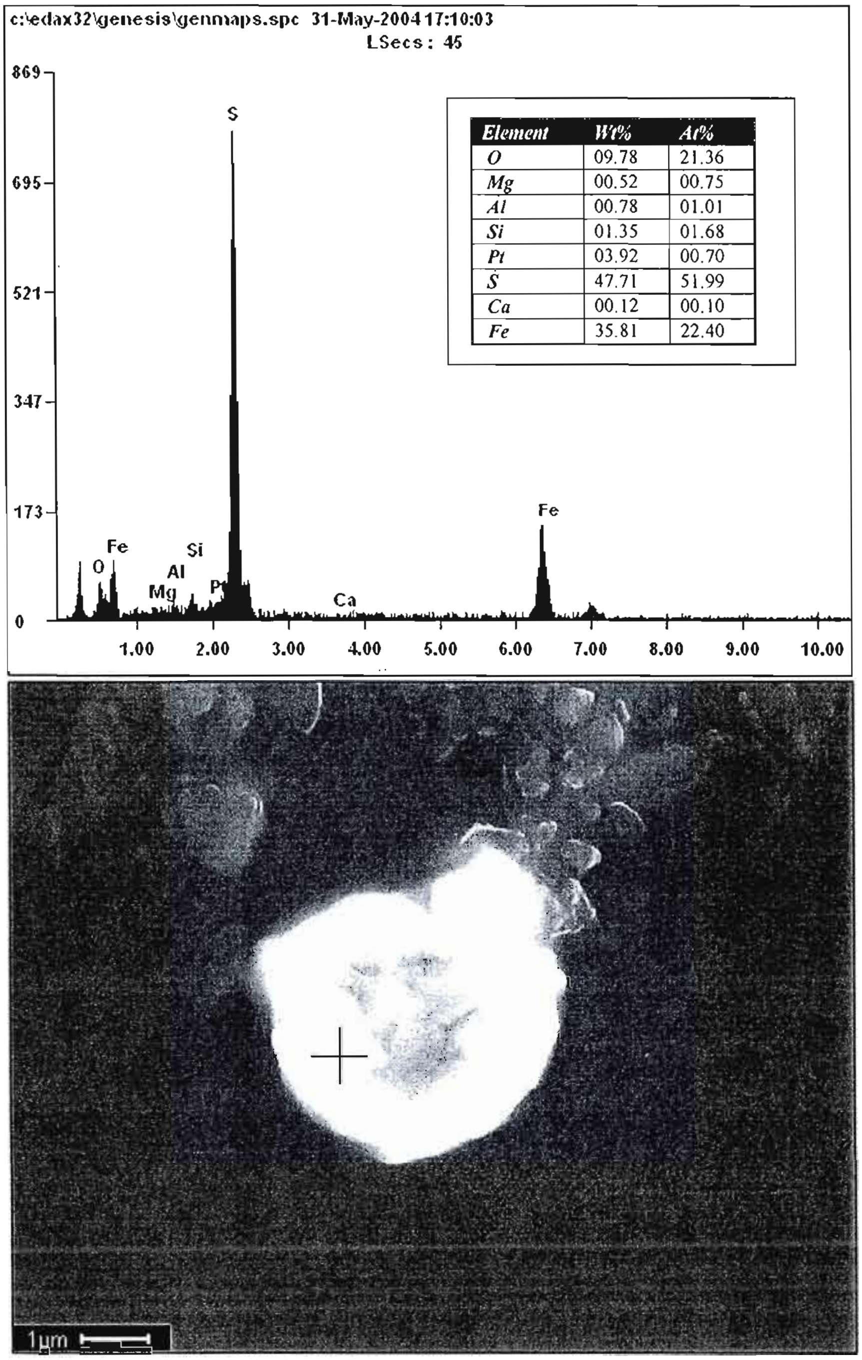
Figure 3.4 Sweet-Lake sediment + carbonates, 5 hours after sonication; from left to right: a) 2Sweet-Lake + 1 non-attrited dolomite; b) 1Sweet-Lake + 1attrited dolomite; c) 2Sweet-Lake + 1attrited dolomite; d)1Sweet-Lake; e) 2Sweet-Lake +1 non-attrited calcite

Mixing of one part attrited dolomite with two parts of Sweet Lake sediments reduced the intensity of the negative sign from –53 to –27 while mixing equal amounts of attrited dolomite and Sweet-Lake sediments reversed the polarity with a potential of +19 mV. The reduction in the charge intensity for the zeta is negligible if, one part of non-attrited dolomite is mixed with two parts of Sweet-Lake sediments. The surfaces of the decanted solids after the adsorption of the attrited dolomite phase were studied with the scanning electron microscope (SEM) and the results are illustrated on figure 3.5 where a silicate grain is coated with fine dolomite particles. On figure 3.6 sulphides are presented in the same sample with traces of dolomite.



Element	*Wt%*	*At%*
O	70.45	82.09
Mg	10.31	07.90
Si	05.30	03.52
Ca	13.94	06.49

Figure 3.5 A silicate particle of the Sweet-Lake sediment that adsorbed the dolomite particles.



Element	*Wt%*	*At%*
O	09.78	21.36
Mg	00.52	00.75
Al	00.78	01.01
Si	01.35	01.68
Pt	03.92	00.70
S	47.71	51.99
Ca	00.12	00.10
Fe	35.81	22.40

Figure 3.6 A sulphide particle of Sweet-Lake sediment that adsorbed dolomite particles.

The semi quantitative chemical analyses indicate that by mixing one part attrited dolomite with two parts Sweet-Lake sediments the dolomitic carbonate is completely adsorbed at the surface and shield the sediment acting as a buffer barrier against pH change. On the other hand having a negative surface-charge (with a pH over 7) the sub micron size silicates, sulphides and some oxide particles will be adsorbed by dolomite and consequently the suspension will become stabilized. Moreover, by using or adding carbonates to the Sweet-Lake sediments the pH increases (table 3.4) which prevents the undesired acidification and lixiviation of the contaminants.

3.4 Discussion

By mixing slurries of equivalent natural minerals, it was possible to approximate the calculated and measured zeta for natural wet Sweet Lake slurry diluted with distilled water The differences in value are related to a higher content of organic matter (residues from vegetation), a smaller grain size distribution and a higher conductivity associated with the natural sediment system. The conductivity of the pore water for the sediments can alter the surface charge of the solid, the zeta and mobility factor. This relation is important for an environmental impact study of certain contaminated sites where mobility or dispersion of the solid and contaminants are a concern. For instance, the results clearly indicate the crucial role of flooding in natural environments. In rainy seasons, flooding, not only brings a stronger agitation and disturbance of the sediment, but also a new volume of water is added, which will dilute both the water originally in equilibrium with the sediments and the dissolved ions. The reduction in conductivity of the system, increase the mobility potential of the solid by increasing its zeta and as a result this should increase the amount of suspension As a consequence, the micron-size sediments and contaminants can be transported as a suspension and can be dispersed over large areas.

Our results also indicated that fine grain mineral with an opposite polarity can be used to flocculate a suspension, reduce the measured zeta and therefore reduce the mobility risk factor. The results have also pointed out that carbonate minerals would have advantages over organic surfactants. The anthropogenic compound is natural, more stable and more resistant than the organic to weathering alterations. This addition would also provide a buffer to an acidity increase of the contaminated site. It is anticipated that if the intensity difference is high and the grain size distribution is small enough between the phases of the system, the added carbonate stabilizer will be adsorbed on the sediment with such an attraction force that only a major influx in the acidity or other chemical reactions could leach out the coating. This process and procedure could find applications with the management of acid mine residues for which the smaller sulphide fractions will most likely be the first to oxidize and generate the potential acidity and lower the pH. By stabilizing the fines with a carbonate, this will lower their mobility potential and the resulted coating would give the system an added protection with this buffering potential.

CHAPTER IV

4 FRACTIONATION OF A NATURAL SYSTEM WITH A POSSIBLE DECONTAMINATION

4.1 Introduction

This chapter presents the results of fractionation attempts for an artificially prepared system and for a natural system of the Sussersee lake sediments. This will be followed by comparison between parameters and results from both model and natural system studies. A list of parameters to be tested by selecting the most important variables influencing the process that can bring about the fractionation of a contaminated sediment into simpler systems will be presented.

Sulphides, considered as eventual contaminants, were added to the mineral equivalent mixture so that the quality of the fractionation and the efficiency for the recovery could be evaluated.

Initially, when artificially prepared systems were mixed without any surfactant the solids would decant without any apparent fractionation evidences. Figure 4.1 illustrates homogenous decanted solids in which particles of different phases containing opposite polarities and intensities of charge have simply agglomerated together without any differentiation. On the other hand, previously presented results have indicated that suspensions in simple systems are possible and can be generated by increasing the surface charge on the particles which results in greater repulsions with the formation of a suspension. An anionic surfactant was selected because of the polarity of the initial zeta representing the entire natural sediment system. This surfactant addition will increase the negative surface-charge of many major mineral phases and as a result the overall negativity for the natural system will increase. In addition, from the preliminary results of Lortie,[15] the anionic surfactant called saratan was found to yield the best results for Sweet Lake based on viscosity modifications generated and the corresponding quantity of surfactant used.

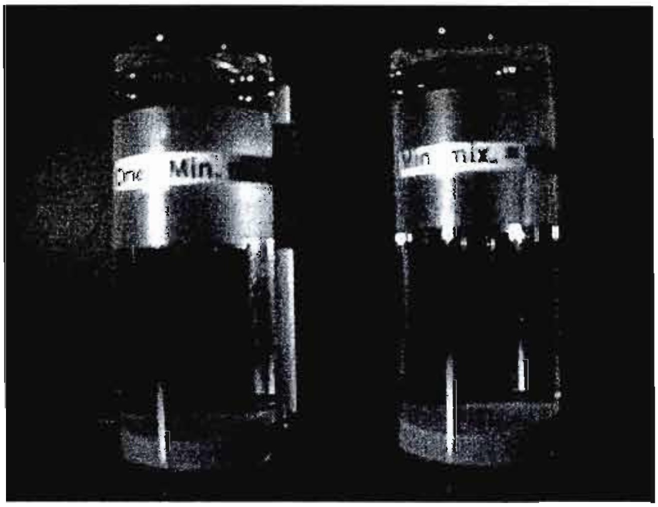


Figure 4.1 The artificial mixtures approximating the composition of Sweet Lake sediments: (left) mixture of a dry-stored single-phase sample (right) mixture of a wet-stored single-phase sample.

4.1.1 Titration with saratan in water

Figure 4.2 displays a linear relationship for the variations in the conductivity of water with various concentration of saratan (1% w/w). The conductivity increase is associated to the sodium of the saratan dissolving in the liquid. The pH was not affected by the surfactant and the zeta is not measurable since no solids are present in suspension.

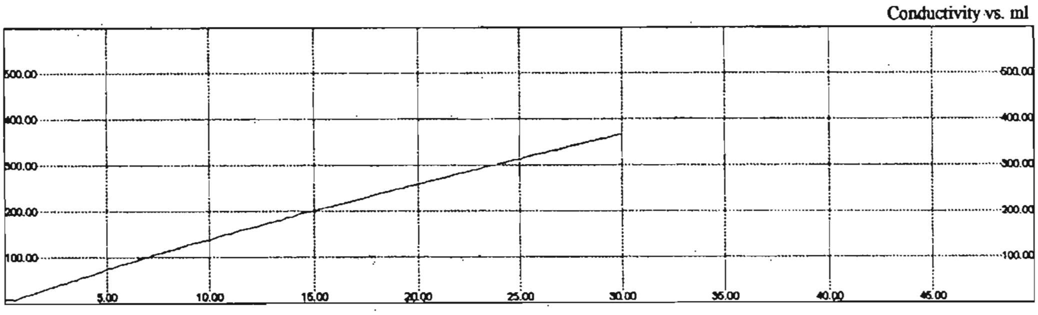


Figure 4.2 Correlation between the concentration of saratan and conductivity of the liquid. Saratan (C= 1%) was added to 220 ml of distilled water, the addition with increment set at 0.25 ml/5sec.

4.1.2 Titration of an artificial slurry mixture with saratan

As anticipated, with the proper agitation and surfactant, a suspension was induced for the equivalent mineral composition of Sussersee sediments. And it was further anticipated that the suspension of all negatively charged phases would decant as a direct function of their mass and inversely proportional to their charge intensity. Therefore, sulphides due to their higher specific gravity and inherent moderately negative charge will decant early on.

Using an ESA 9800 apparatus (Matec Applied Sciences) equipped with an automatic titration device a saratan solution of 1%w/w was added as the titration agent. The results presented in Table 4.1 and figure 4.3 indicates the change in surface charge for the solid particles, the pH and conductivity monitored during the titration experiment. The zeta showed an immediate increase (absolute value) corresponding to a relatively constant pH and a linear increase in conductivity. The initial zeta curve displays a steep slope for the addition of small amounts of surfactant. Further additions of surfactant modify very slowly the zeta and are represented by a very different slope on the curve. In all probability the point at which the slope changes for the zeta curve represents the initial saturation of charges for the double layers. This point could indicate the optimum quantity of surfactant required for the maximum charge modifications and the maximum repulsions attainable by an equivalent mixture of mineral slurry.

Table 4.1
Physical characteristic of dry and wet-stored mineral slurry mixtures, before and after adding the saratan surfactant

Description	Size (micron)	PH (unit)	Zeta (mV)	Electrical conductivity (us/cm)
Wet stored –mineral mixture (with Sweet-Lake's mineral composition)	10.84	7.69	-82	392
Wet stored mineral mixture (with Sweet-Lake's mineral composition) + 2.27% w/w saratan	10.84	7.83	-171	641
Dry stored mineral mixture (with Sweet-Lake's mineral composition)	11.25	7.64	-108	442
Dry stored mineral mixture (with Sweet-Lake's mineral composition) + 2.27% w/w saratan	11.25	7.75	-145	704

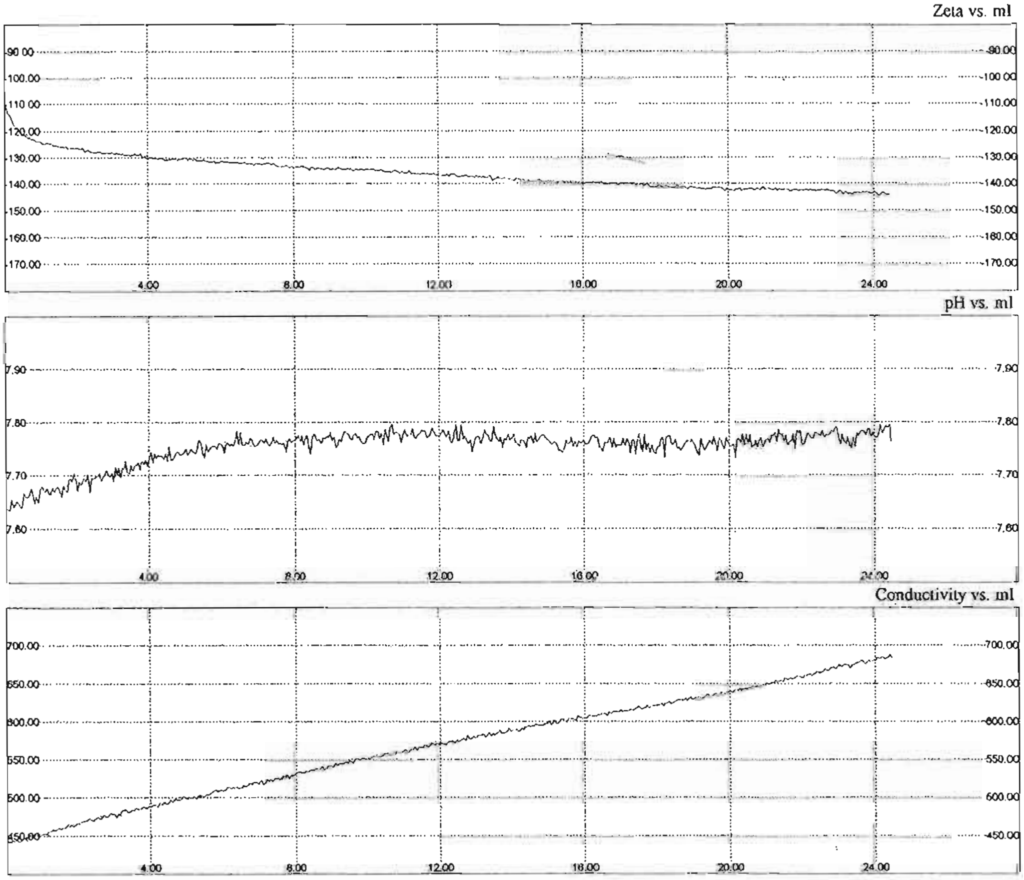


Figure 4.3 Titration results for dry-stored minerals in a modal composition approximating the Sweet lake sediment. The solution of saratan (1%w/w) was added at a rate of 0.05ml/90sec to 220 ml slurry with a volume fraction of 2% solids.

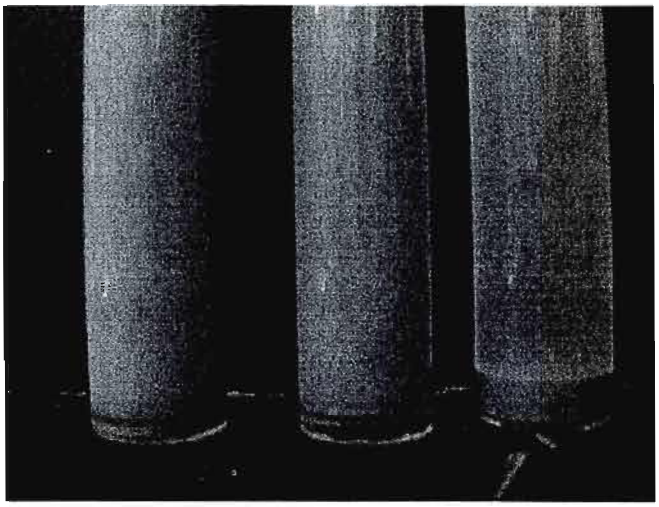


Figure 4.4 Visual comparison of dried and wet-stored mineral slurries with and without saratan. From left to right: a) dried-stored mineral mixture with 2.27%w/w saratan after a 4 hours decantation period. , b) wet-stored mineral mixture with 2.27%w/w saratan after a 4 hours decantation period. c) dried-stored mineral mixture without saratan.

The slurries with the addition of surfactant display more pronounced suspensions and a smaller decanted column of solids.

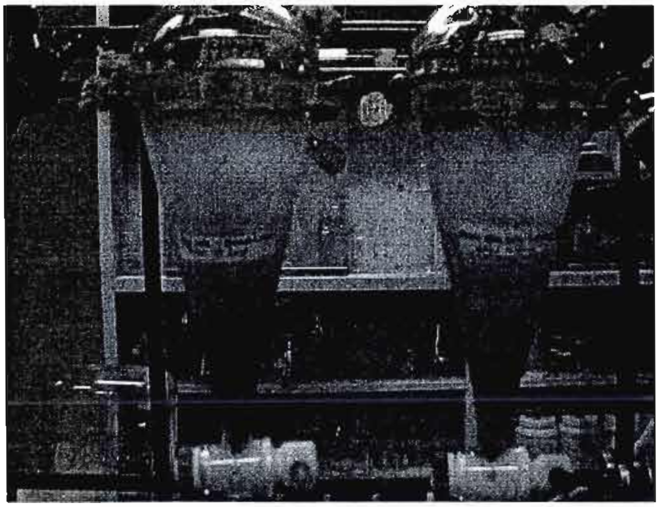


Figure 4.5 Wet-stored (left), and dry-stored (right) mineral slurries with saratan and 4 days decantation period. Note the stable suspension on top and the layered sediments at the bottom.

4.1.3 Fractionation and sampling procedures

The results of the titration and the corresponding visual observation indicated that a quantity of 2.7 % w/w of saratan be used in the slurry fractionation attempts. The samples were then left to decant and graded layer of sediment accumulated at the bottom and a strong suspension remained on top. A four (4) days decantation period was allowed. Figure 4.4 and 4.5 illustrate the layering obtained and the mean by which the layers were separated. Afterward, the suspension was removed and both liquid and solids were dried separately in such a way as to avoid disturbance and mixing of the layered phases. A total of 10 samples representing the different layers of the dried sediments and the suspension, were submitted to analyses.

4.1.4 Grain size distribution of the fractionated samples

Grain size distribution made with a laser apparatus indicated a gradual decrease in the grain size for the different layers from the first bottom layer to the suspension. The results are presented in tables 4.2 and 4.3.

Table 4.2

The mean and median size values for 3 layers of the wet-stored mineral slurries' mixture after saratan treatment. The sample numbering increases toward the upper layers of the sediment

Layer (from bottom to top)	Mean size (Micron)	Median size (Micron)
MixW4	18.5	17.05
MixW6	10.82	10.55
MixW9	2.46	2.32

The data indicate that sediments in layers MixD9 and MixW9 are roughly 6 to 8 times smaller in diameter than the coarsest bottom fractions represented by samples MixD3 and MixW4.

Table 4.3

The mean and median size values for 3 layers of the wet-stored mineral slurries' mixture after saratan treatment. The sample numbering increases toward the upper layers of the sediment

Layer (from bottom to top)	Mean size (Micron)	Median size (Micron)
MixD3	19.03	17.17
MixD6	9.26	8.91
MixD9	3.64	3.02

4.1.5 XRD evaluation of the fractionated samples

The mineralogy and the modal analysis were made by X-ray powder diffraction and the data are presented in table 4.4.

Table 4.4

Mineral composition determined by XRD for dried layers (MixD) and wet (MixW) from stored slurries after adding saratan. MixD1 and MixW1 are the bottom and MixD8 and MixW8 are the top layers. MixW10 and MixD10 are the solids from the suspensions

Sample	Qz	Ab	Mic	Mus	Bt	Cal	Ga	Sph	Py	Cpy	Total sulphide
MixW1	63.31	2.62	1.57	0.00	1.05	17.40	3.14	5.79	2.62	2.51	14.06
MixW2	59.88	4.88	1.05	0.00	1.05	20.89	2.79	5.22	1.74	2.52	12.26
MixW5	83.06	2.02	0.67	0.00	0.00	11.47	0.75	1.35	0.67	0.00	2.77
MixW7	74.29	4.33	2.58	0.48	2.15	10.82	1.72	1.72	0.86	1.03	5.34
MixW8	59.23	6.64	3.13	1.05	5.06	18.76	1.95	1.55	0.78	1.86	6.14
MixW10	60.59	13.11	3.04	0.00	1.04	21.19	1.04	0.00	0.00	0.00	1.04
MixD1	64.97	5.25	1.77	0.00	0.00	18.37	4.39	4.39	0.86	0.00	9.64
MixD2	67.53	2.47	0.61	0.00	0.61	16.78	3.72	4.97	1.86	1.46	12.01
MixD4	80.81	2.89	0.56	0.00	0.56	11.52	0.56	1.16	0.56	1.35	3.65
MixD8	69.76	5.14	1.92	0.50	1.92	16.04	1.29	1.29	0.63	1.51	3.43
MixD10	54.35	7.41	3.16	1.39	1.03	32.66	0.00	0.00	0.00	0.00	0.00

From the data it can be deduced that the sulphides are the first phase to decant, the quartz, albite and microcline increase toward the top or suspension and the phyllosilicates are also more concentrated toward the top layers.

4.1.6 SEM evaluations of the fractionated samples

An evaluation was made with SEM using electron back scattering. With this procedure the sulphides standout as white particles compare to the shades of grey representing the silicates and other mineral phases. Figure 4.7 shows a galena particle with a density 7.1 g/cc that standout as the brightest particle in the image.

The procedure allows a rapid identification of the sulphide particles and can also yield information on their corresponding diameter from which the surface area (table 4.5) could be measured and used to calculate an abundance value for the sulphides.

Table 4.5

SEM image analysis for sulphides fractionation in different layers of dry (MixD) and wet (MixW) stored slurries after saratan treatment. MixD1 and MixW1 are the bottom layers and MixD8 and MixW8 are the top layers. MixW10 and MixD10 are the suspensions.

Sample name	Sulphide particles' area sum $(\text{micron})^2$	Sulphide particles' diameter sum (micron)	Total particles' area sum $(\text{micron})^2$	Total particles' diameter sum (micron)	Percentage of sulphides based on the area	Percentage of sulphides based on the diameter
MixW1	16646.12	2364.55	198612.5	15516.96	8.38	15.24
MixW2	11179.99	1161.28	230831.5	15883.36	4.84	7.31
MixW5	1373.14	210.61	56442.11	5382.85	2.43	3.91
MixW7	229.57	103.17	31495.98	7573.99	0.73	1.36
MixW8	342.27	150.42	21702.13	5559.74	1.58	2.71
MixW10	0.76	1.37	1266.74	1226.84	0.06	0.11
MixD2	15792.93	2210.2	197982.6	18153.72	7.98	12.17
MixD4	1739.26	256.52	48441.95	5928.38	3.59	4.33
MixD8	12.37	15.62	1638.68	794.62	0.75	1.97
MixD10	135.8	106.89	33484.37	21524.37	0.41	0.50

The results of SEM evaluation presented in table 4.5 support the diffraction data for the concentration of sulphides with the bottom layers, which are controlled by their grain size and specific gravity data. Both XRD and SEM results support the conclusion that the fractionation process using saratan is an efficient process. In addition, the analysis indicated that sulphides' micron size particles where found with agglomerations of quartz and calcite. Reprocessing with a better dispersing technique the top layers could eventually fractionate these sulphides. This smaller size fractionation may require adjustment of the parameters already in use (figure 4.6).

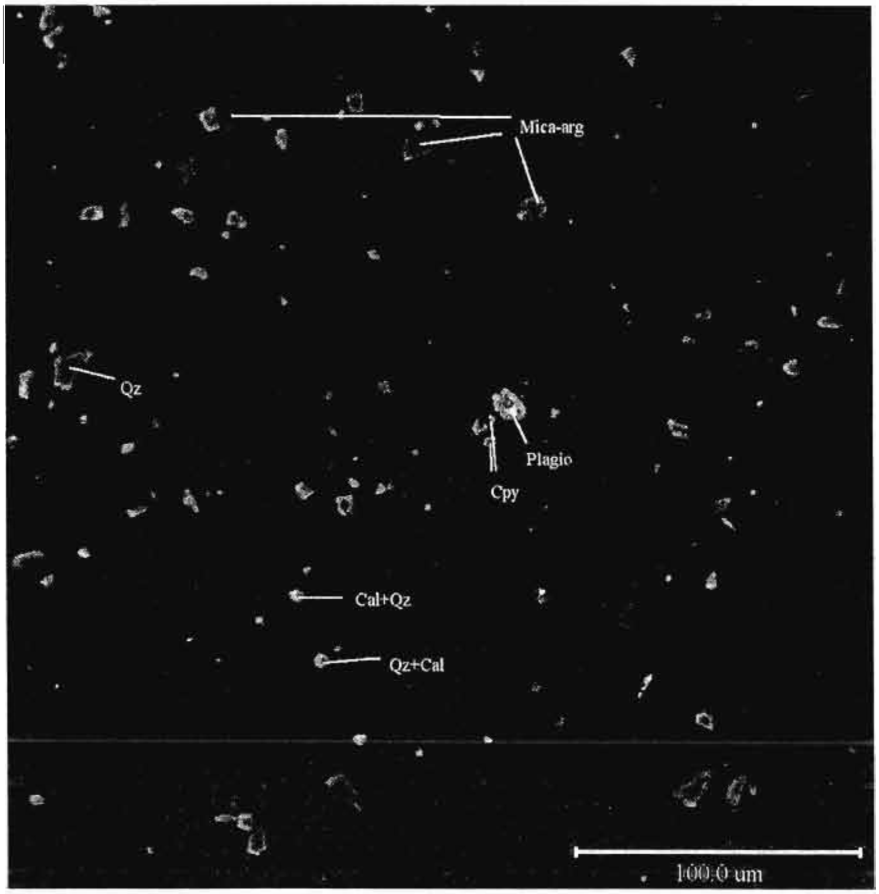


Figure 4.6 SEM photograph of an agglomeration with layer MixW7. Quartz, calcite and sulfides make up the agglomerates.

Figure 4.8 illustrates a SEM photograph of the sample MixD2, which is the second lowest layer of the decanted column. This layer in general contains the coarse-grain particles such as large grain of calcite in the middle of the photo with approximate diameter of 25 microns. The strong positive surface charge of calcite can adsorb the negatively charged quartz and sulphide particles forming larger and heavier agglomerate that will be more susceptible to decant.

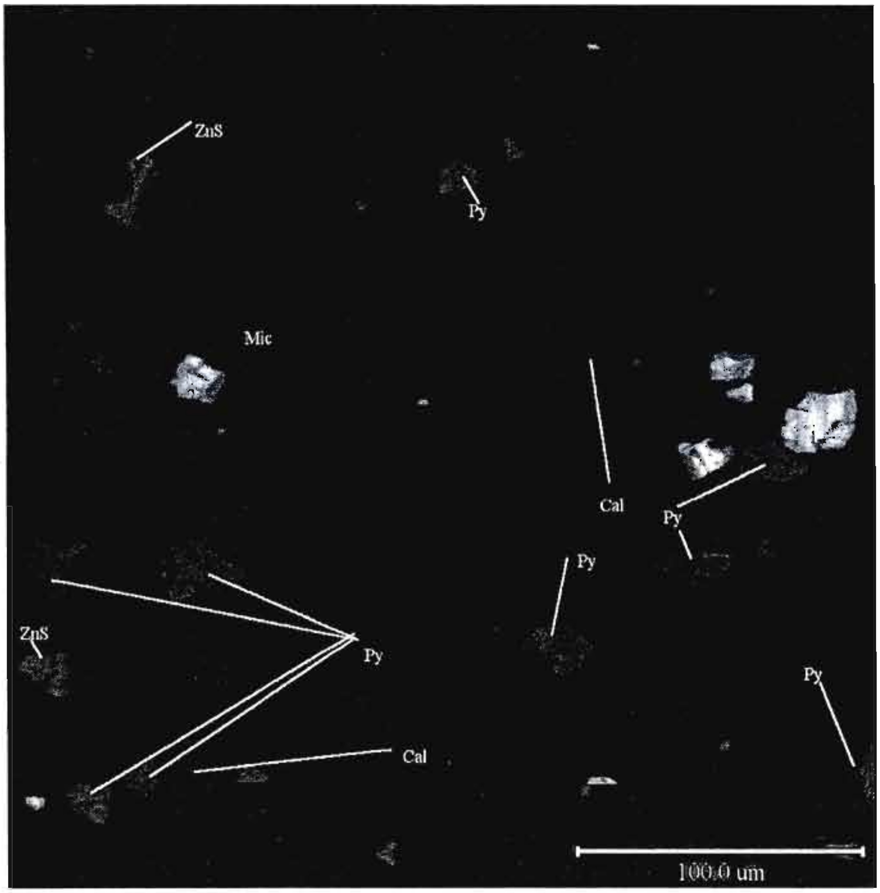


Figure 4.7 SEM image of the MixW1, the bright particles are high density sulfides minerals. The brightest particles in the middle section of the photo (such as particles no. 1), are galena particles.

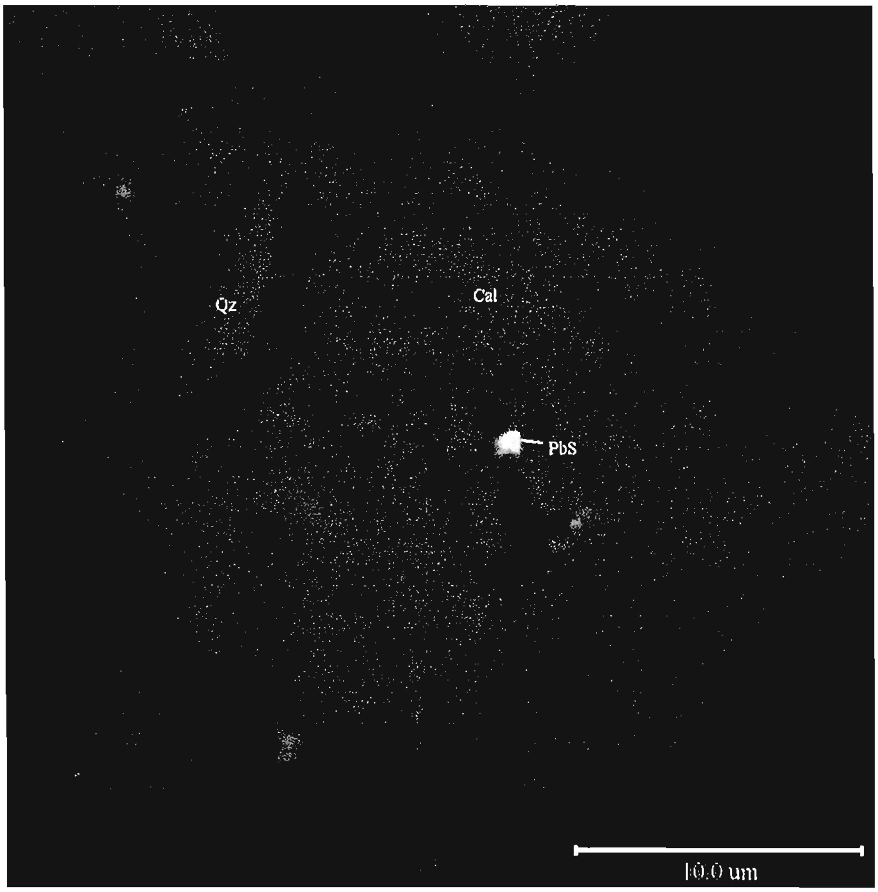


Figure 4.8 SEM photograph of an agglomeration with the MixD2 layer. A large calcite particle with a diameter of 25 micron adsorbed quartz and very small grains of sulphides at its surface.

4.2 Fractionation of the Sweet-Lake natural contaminated sediments

The results from the artificial prepared mineral equivalent system paved the way to selected attempts of fractionating the multiphase complex contaminated natural system represented by the Sweet lake sediments. These sediments were selected because of the accumulated knowledge acquired by our group throughout the years on the environmental problem, the area and the solid involved. Lortie[15] was successful in fractionating the sediments, but the process was not efficient and the fractionation was still somewhat empirical. Nevertheless, it was anticipated that with a better dispersion of the agglomerations using mechanical means aided with an optimized quantity of a chemical dispersant a good separation and fractionation of the system could be achieved.

4.2.1 Sweet Lake slurry titration with saratan followed by mechanical dispersion

With the ESA equipment 240 ml of the Sweet-Lake's slurry (C = 5% w/w) was titrated with saratan solution of 10%w/w. The titration curve of figure 4.9 indicates that after attaining 3%w/w of saratan a linear relationship is displayed for the surface charge or the zeta value.

From these results, a quantity of 30 ml of saratan (C= 10%) was added to 2 kg of the Sweet-Lake slurry with solid concentration of 5%w/w and the mixture was homogenized with a double blade high-speed disperser for 10 minutes. An additional amount of surfactant was added to the slurry to ensure that the value of 3.5%w/w of saratan was reached for a maximum dispersion. After 16 hours of decantation in a graduated cylinder, three layers were distinguishable in the sample:

a) a stable suspension on top;

b) a very fine-grain sediment in the middle;

c) a coarse-grain sediment with a graded bedding type.

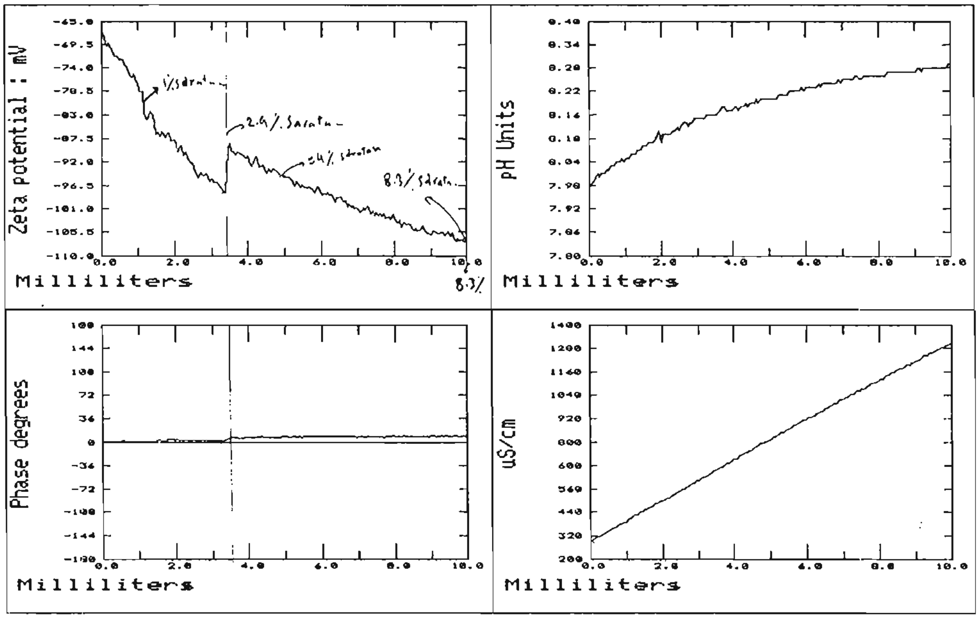


Figure 4.9 Titration of Sweet Lake slurry ((240 ml C = 5%w/w) with saratan (C= 10%w/w). The surfactant increment was of 0.05ml/15sec with the ESA titration unit.

The stable suspension was removed and left to decant separately and the solid was left at 40 °C to dry. To avoid any disturbance of the solid cake by cracking of the sediment and possible mixing of the layered phases, we interrupted the drying of the sample as soon as the solid cake could be handled and sampled for the different layer present. Thirteen samples from the layers were prepared for XRD and SEM analyses. The results indicated that the dispersion was still not adequate. Trapped sulphides are noticed on figures 4.10 and 4.11. Fine particles of sulphides were still found within agglomerations with the matrix and as a result they could not be dispersed by the surfactant. A better mechanical dispersion technique was required to break the fine agglomerations and freed the micron to sub-micron size sulphides for a fractionation under the influence of the surfactant.

Figure 4.10 SEM microphotograph of Sweet-Lake sediment with saratan (3.5w/w%) followed by homogenizing and drying. The presence of high density fine particles surrounded by a matrix material confirms the need for a more efficient dispersion process.

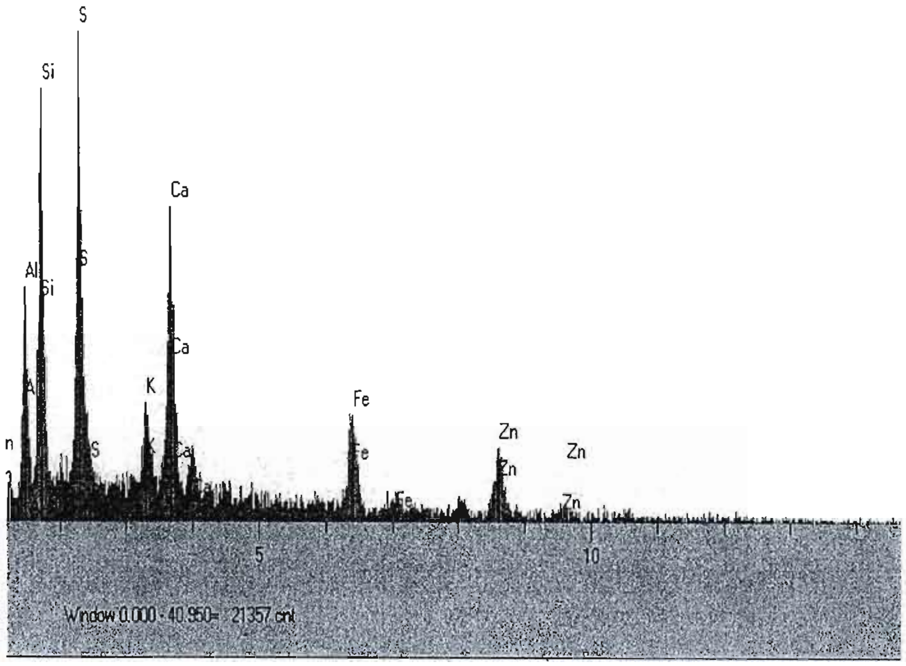


Figure 4.11 The SEM general analysis of the agglomerate of figure 4.10 indicating a high amount of sulphur, iron and zinc elements, which corresponds to trapped sulphides.

4.2.1.1 Wet attrition with ceramic beads

By means of a wet attritor filled with ceramic beads of 0.6 to 0.8 mm in diameter, Sweet-Lake sediment was attrited for 30 minutes. The grain size reduction observed was significant; the volume median of the sample was reduced from 11.04 micron to 8.63 micron.

4.2.1.2 Titration of an attrited sample

A titration of the attrited slurry resulted in an initial decrease of the surface-charge followed by a further decrease with the addition of 10 ml of saratan (4%w/w) on a different slope for the zeta curve. This break in the linear relationship indicated the end of the fastest change for the zeta. As shown by figure 4.12, by adding more saratan (4%w/w) this results in a smaller effect on the surface charge of the particles.

The break in the curve indicating the corresponding 4%w/w of saratan is considered as the possible optimum addition of surfactant.

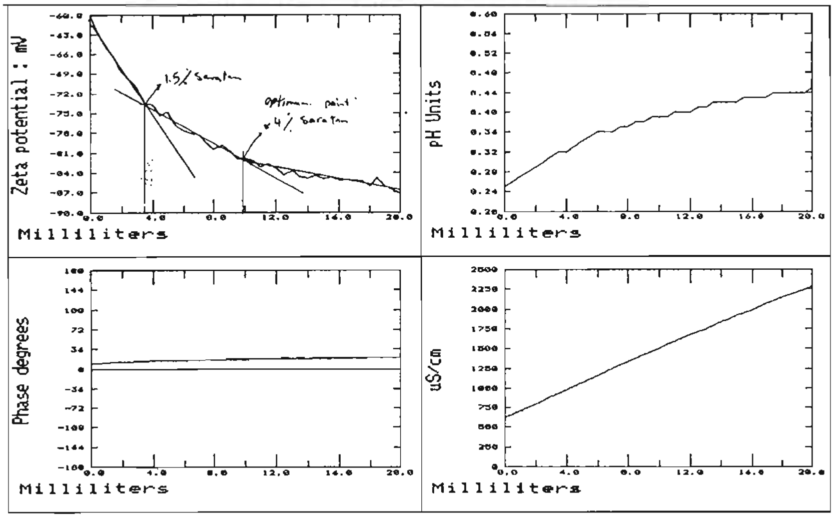


Figure 4.12 Titration with saratan (C= 10%w/w), using 250ml of Sweet Lake's attrited slurry with a concentration of solid 9.5%w/w. The increment interval was 0.05ml/15sec.

4.2.1.3 Dispersion evaluation

From the titration curve, it was calculated that 29.6 ml of saratan (10%w/w) solution was required for to 2 kg of the attrited slurry (C = 3.7%w/w). The saratan was added before the attrition so that the best repulsion effect between the particles would be achieved and this procedure would prevent any re-agglomeration of the fines. The sample was attrited for 30 minutes.

Based on visual observations the attrition with the addition of surfactant was more effective since a strong and stable suspension was induced in the slurries (figure 4.13).

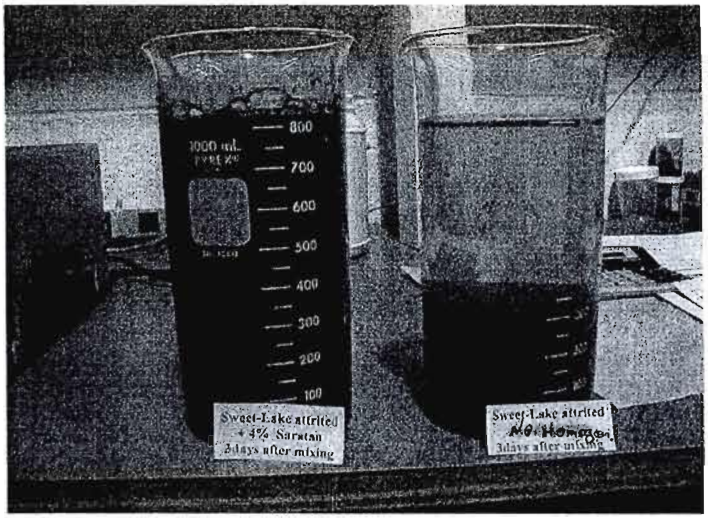


Figure 4.13 (left) An attrited sample with an addition of saratan prior to milling (right) a non attrited sample and no saratan addition. Even after 3 days of decanting the saratan treated sample has a strong suspension.

For the fractionation process, the sample was left to decant for one hour. Two zones were noticed, the upper part with a weaker suspension and lower part with a strong one. Consequently the sample was divided in three parts and dried separately:

a) -The lowest part of the beaker (100 ml), containing the first decanted particles (few minutes);

b) -The lower and stronger suspension;

c) -The upper and weaker suspension.

4.2.1.4 Drying and further decanting

Beakers (a) and (b) were left to dry at 40 °C and to avoid disturbance by cracking of the solid cake, the procedure used previously was applied to attain a reduced amount of humidity for sampling of the cake. Beaker (c) was left to decant, and after 30 days the clear liquid on top was removed and the rest of the sample was dried at 40 °C.

4.2.1.5 Sampling

From the portion A, (beaker (a)) two samples were taken SS1 close to bottom and SS6 close to top. The lowest part of the beaker (b) had the same characteristics of SS1 and the layer on top was exactly the same as SS13 and as a result these two parts are removed and became SS12. The samples SS8 to SS11 are numbered from the bottom to the top of the beaker (b) sediments (figure 4.14). Beaker (c) contained homogenous fine grain sediment similar to SS13 and was combined with the latter. In table 4.6 weight and weight percent of each sediment sample are presented.

Table 4.6
Weight and weight percent of the different samples fractionated from Sweet Lake sediments, attrited with 4%w/w saratan surfactant and dried at 40 °C

	SS1	SS2	SS3	SS4	SS5	SS6	SS7	SS8	SS9	SS10	SS11	SS12	SS13	SUM
Weight	1,03	0,68	2,16	3,52	5,60	1,77	1,40	20,34	7,78	18,49	2,06	5,03	6,90	76,75
Weight percent	1,34	0,88	2,81	4,59	7,29	2,31	1,83	26,50	10,13	24,09	2,68	6,55	8,99	100,00

Figure 4.14 Decanted sediment cake of beaker (b) after drying. Different textures and layering in sample are evident.

4.2.1.6 XRD evaluations of the fractionated Sweet Lake sediments after attrition with saratan

For each sample the X-Ray diffraction were made so that the mineralogical composition could be determined and the results are given in table 4.7

Table 4.7

The XRD mineral composition for the different decanted Sweet Lake sediment. The samples were attrited with 4%w/w saratan

Mineral	SS1	SS3	SS5	SS8	SS10	SS13
Quartz	89,41	79,52	71,65	55,93	57,11	39,39
Calcite	1,30	7,92	14,47	16,47	14,79	25,22
Albite	3,27	4,19	4,19	6,09	4,44	2,33
Clinochlore	1,30	1,05	2,00	3,25	5,67	7,42
Microcline	4,57	3,14	2,30	6,82	3,70	3,81
Chalcopyrite	0,00	0,13	0,00	0,41	1,23	2,54
Pyrite	0,15	1,31	1,30	2,27	2,96	2,97
Sphalerite	0,00	0,39	0,00	0,57	2,22	3,18
Galena	0,00	0,79	0,50	0,89	2,22	4,87
Illite	0,00	1,57	3,59	7,30	5,67	8,26
SUM	100,00	100,01	100,00	100,00	100,01	99,99

The changes in mineral concentration in the different fractionated layers, for all phases, (table 4.7) indicate an efficient separation or fractionation process. Quartz has a higher concentration in lower layers and gradually decreases in the upper layers. Calcite displays its own relationship, very low for the bottom layer, an intermediate concentration for the middle layers and a high value in the suspension. The phyllosilicates show a low concentration in the first three (3) layers followed with a sharp increase for the last three (3) layers. The most surprising and significant results are the sulphides, contrary to all expectation; they display a steady increase in concentration toward the suspension (figures 4.15 and 4.16).

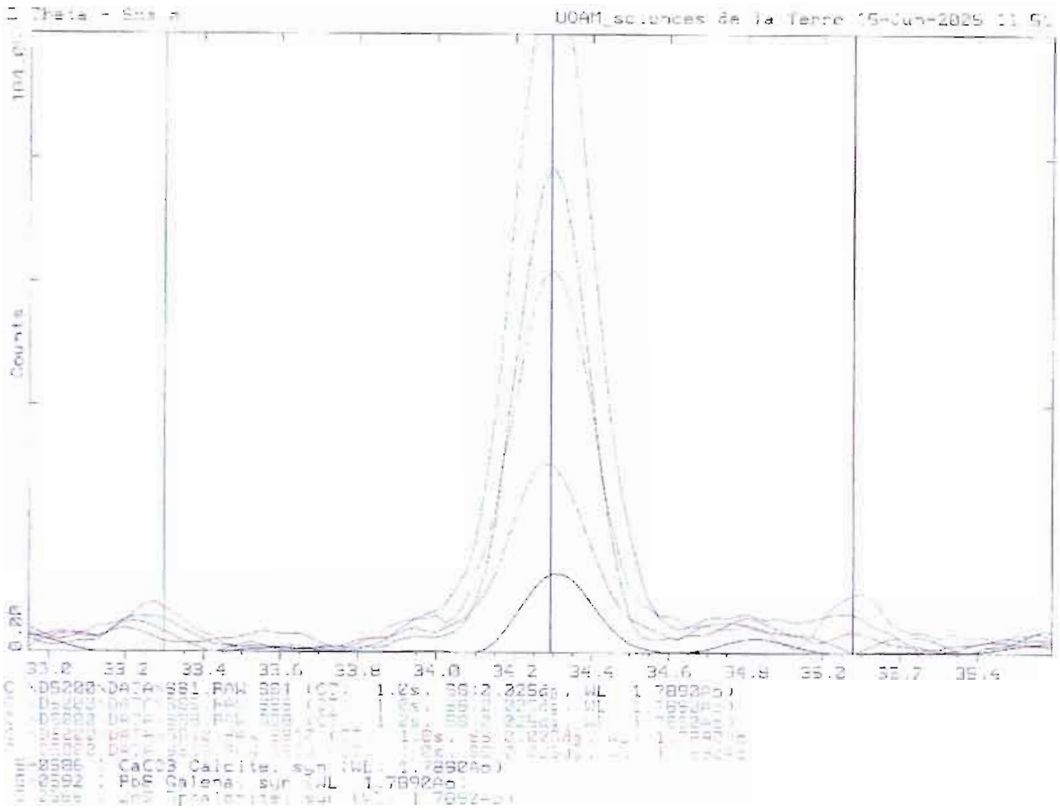


Figure 4.15 Overly plots of X-Ray diffractograms showing the intensity variations for calcite, galena and sphalerite for different layers of the Sweet-Lake sediment after attrition with 4%w/w saratan surfactant.

X-ray diffraction of untreated Sussersee Lake sediments does not show the presence of sulphides, the latter being below the detection limits of 1 or 2% concentration. The fractionated layers obtained with the surfactant treatment displays the highest intensities for sulphides galena and sphalerite in layer SS13. (figure 4.15). The bottom layer SS1, on the other hand, displays the highest intensities for calcite and quartz but no evidence of a diffraction patterns for the sulphides (figure 4.16).

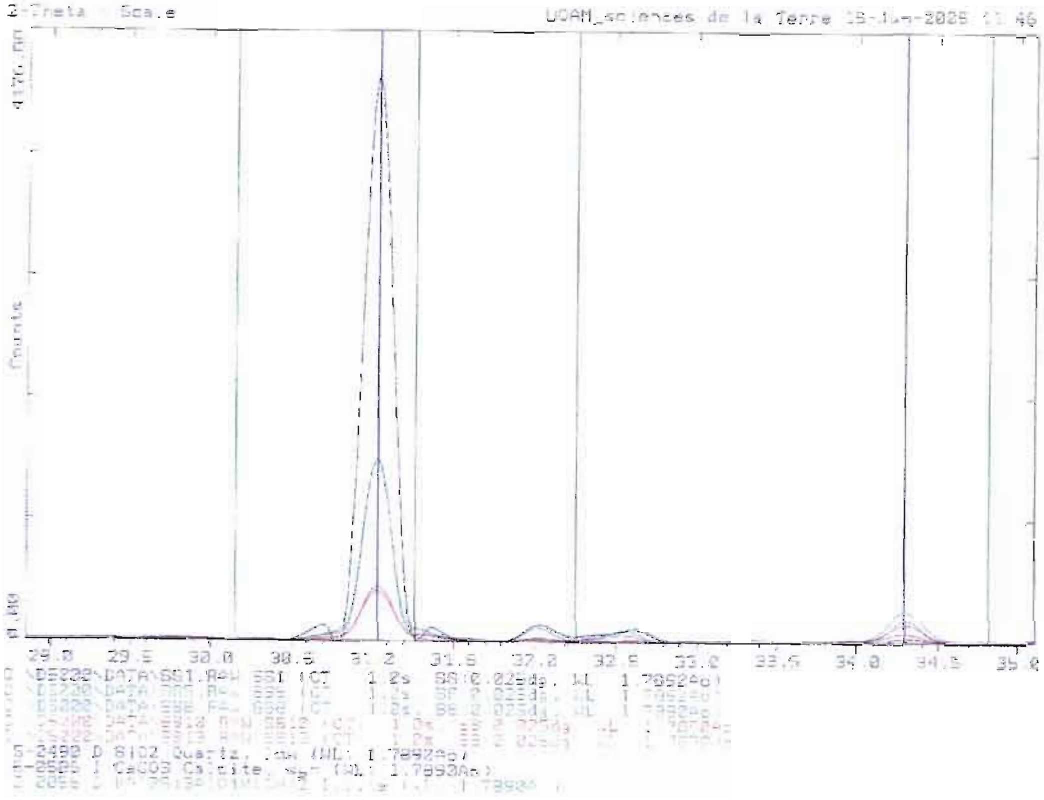


Figure 4.16 Overly plots of X-Ray diffractograms comparing the intensity for quartz, calcite and illite in different layers of the Sweet-Lake sediment after the attrition with 4%w/w saratan.

4.2.1.7 SEM evaluations of the fractionated Sweet Lake after attrition with saratan

The electron microscope images show that most of the matrix has been dispersed releasing the small particles of sulphides. The amount of trapped particles or agglomerations that were not dispersed are rare and their concentration should not impact the efficiency of the process nor affect the results as far as decontamination is concerned (figure 4.17).

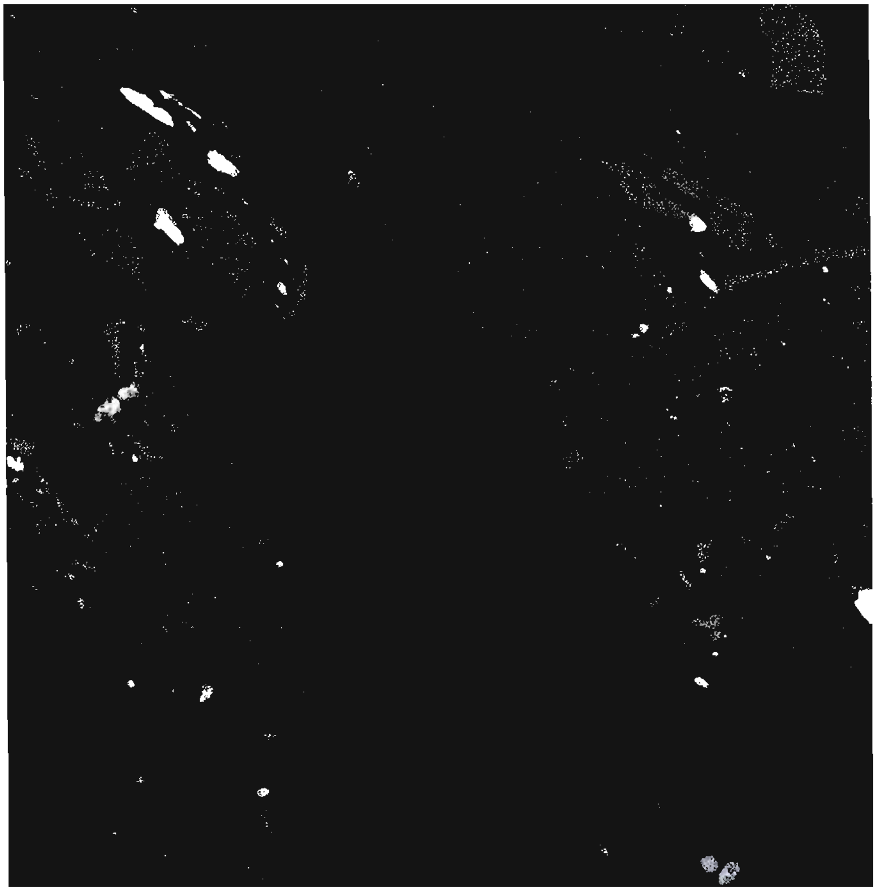


Figure 4.17 SEM photograph from sample SS3 illustrats the large agglomerations with sulphide grains trapped and also partly dispersed.

4.2.1.7.1 Analysis of the individual particles and their relationship to the fractionation process

The high-density grains in SEM photographs of Sweet-lake sediment are not only sulphides. Determination of the composition of several particles revealed that apatite and ilmenite could also display that high-density property (figure 4.18).

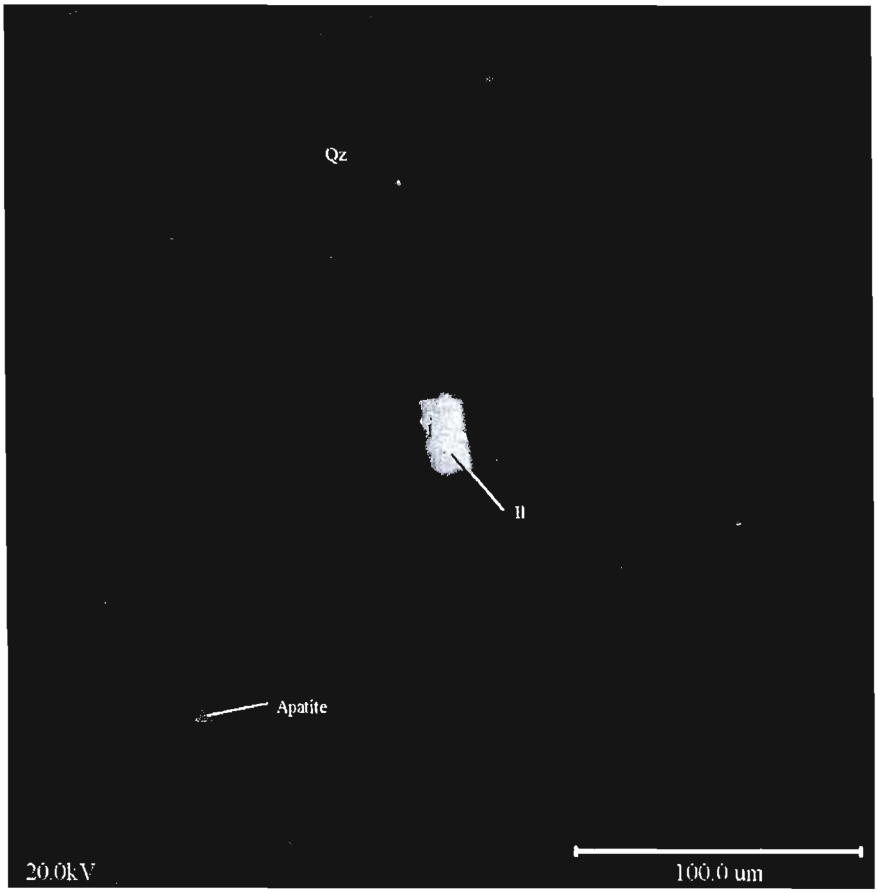


Figure 4.18 SEM photograph from sample SS1, consisting of quartz particles and heavy minerals such as apatite and ilmenite.

This method provides valuable information about individual particles, their composition, shape and size variations, but it is time consuming and does not provide reliable statistic data to compare the different samples based on the amount of sulphide particles present (figure 4.19).

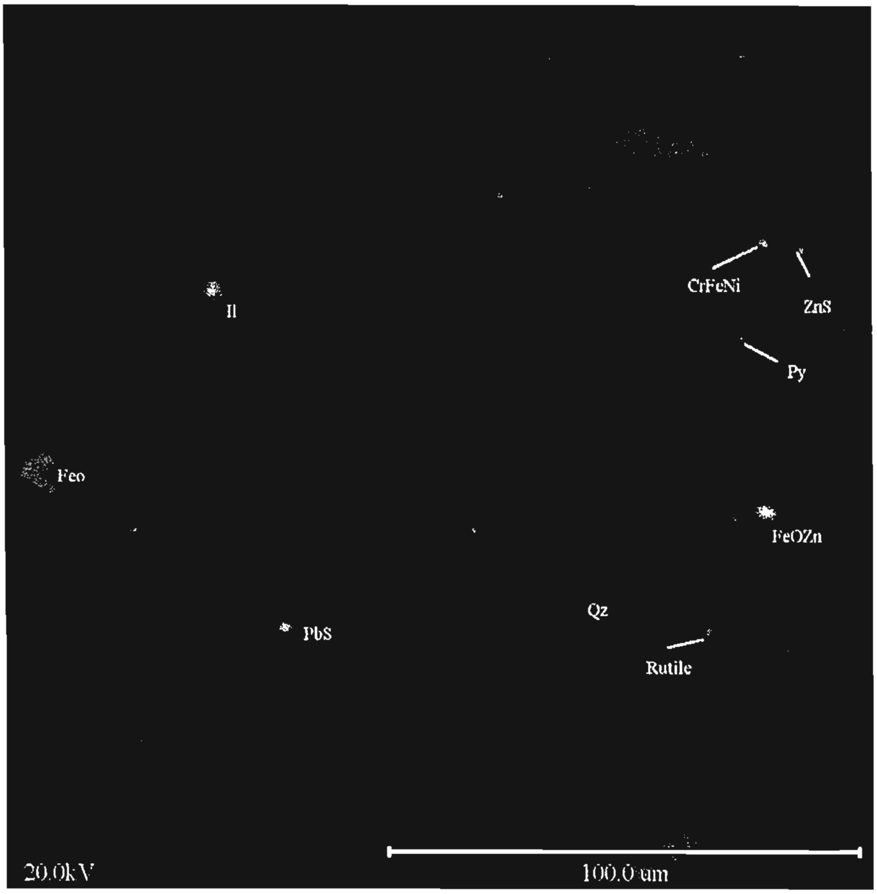


Figure 4.19 The SEM analysis of the particular minerals in sample SS3.

The results presented in figures 4.18 to 4.20 also show a gradual reduction in the grain size of the particles from sample SS1 at the bottom of the decanted column to the top corresponding to sample SS13. In general based on the SEM observations, the size of the sulphide particles in Sweet-Lake sediments is smaller than 3 microns, which is much smaller than the artificially prepared mineral slurry used to simulate or model the Sweet Lake sediments.

4.2.1.7.2 Mapping the elemental distribution of the solid from the fractionated layers

In this method the dispersive x-ray fluorescence of the electronic microscope locates and maps an image of the emission for a particular element. In figure 4.20 to 4.22 are the maps of silicium, aluminium, calcium, iron, sulphur, copper, lead and zinc elements for different samples from the fractionated Sweet Lake sediments.

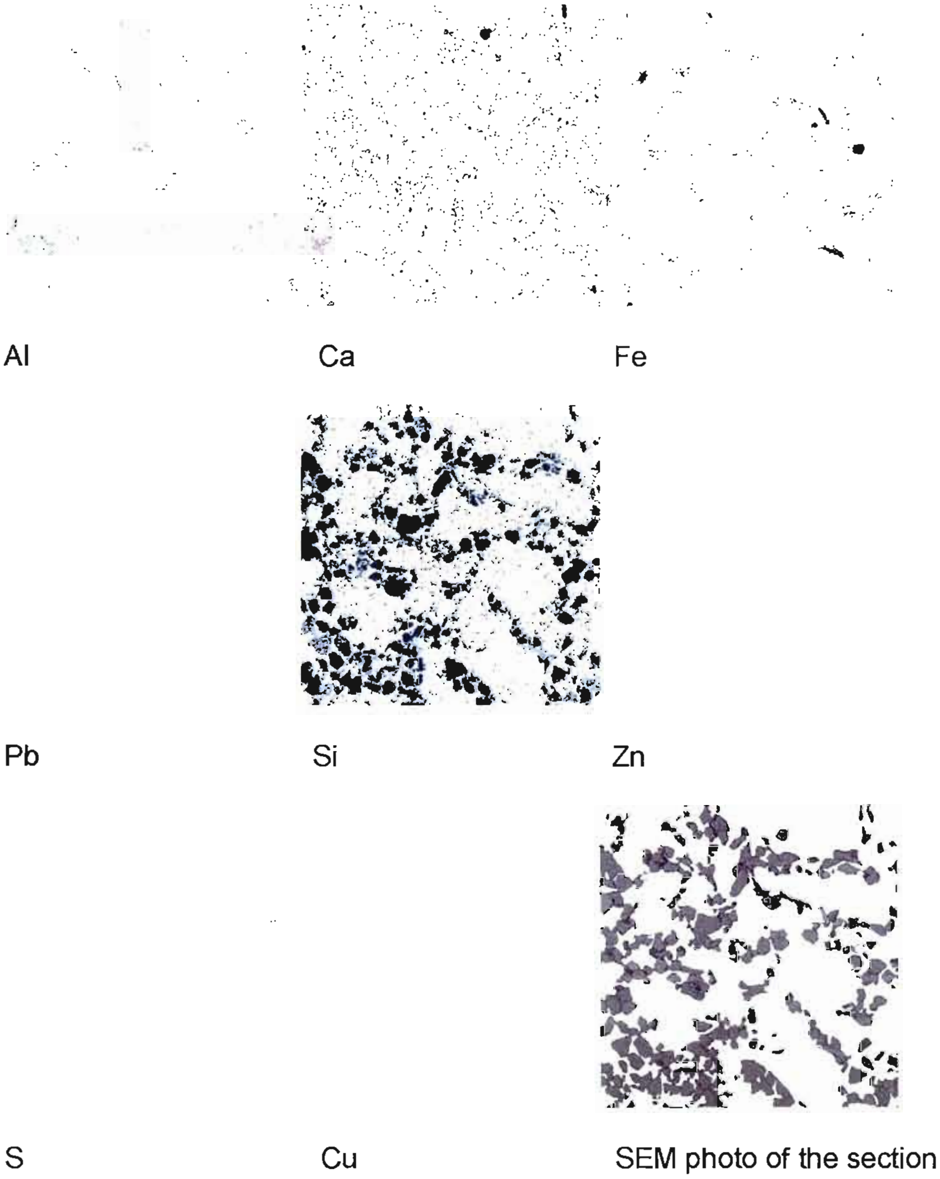
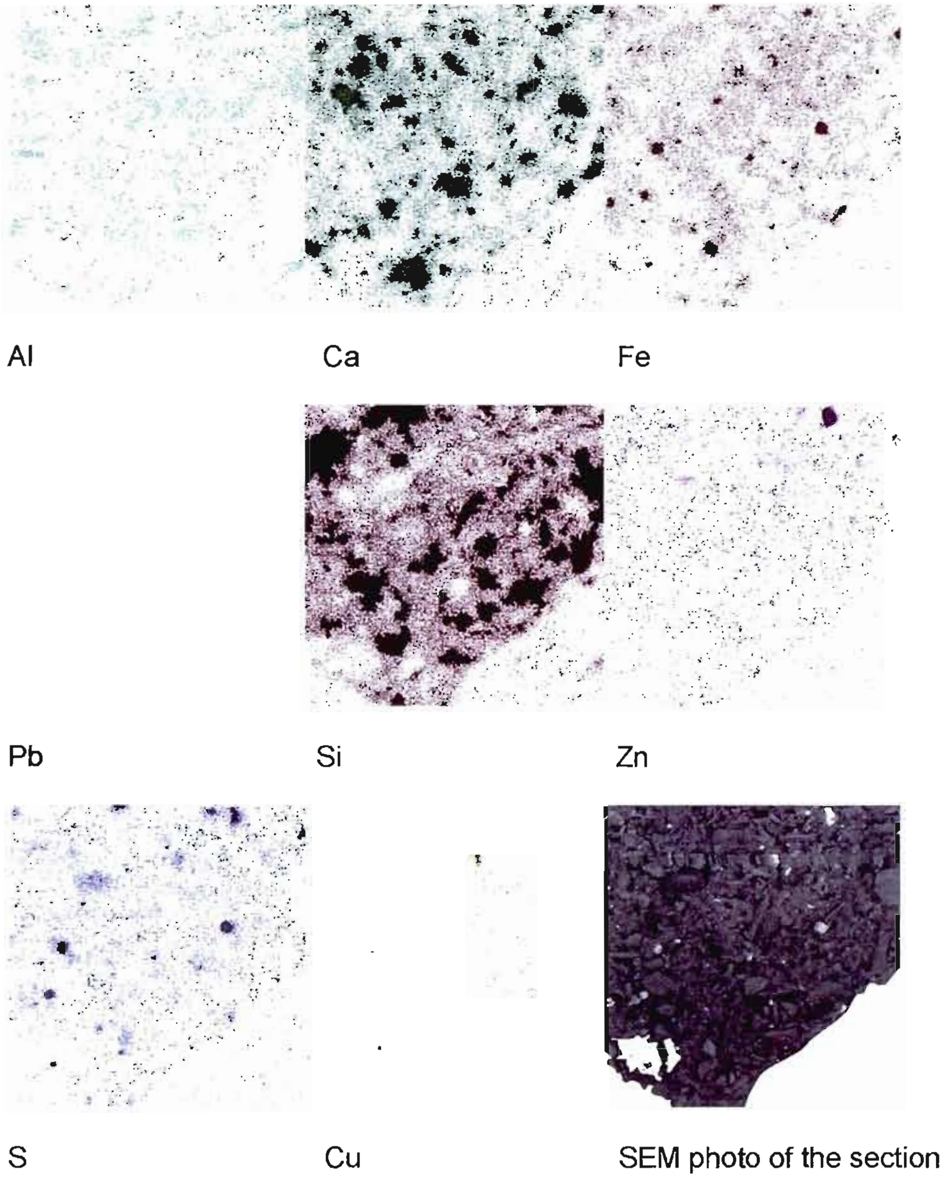


Figure 4.20 The X-ray Maps of the sample SS1 for aluminium, calcium, iron, lead, silicium, zinc sulphur and copper elements

The measured area in which the detected elements are shown can be related to their concentration in the sample.

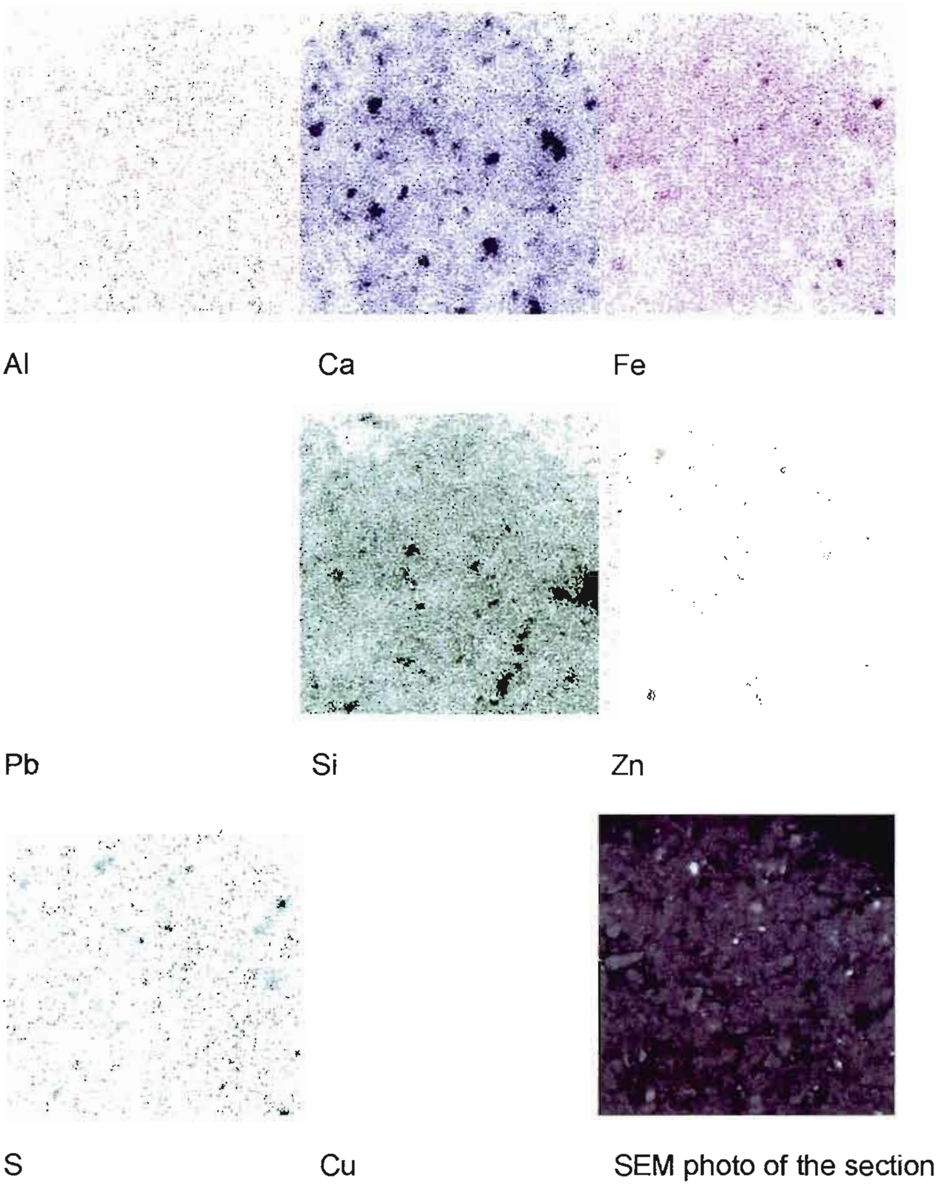


Al Ca Fe

Pb Si Zn

S Cu SEM photo of the section

Figure 4.21 The X-ray Maps of the sample SS10 for aluminium, calcium, iron, lead, silicium, zinc sulphur and copper elements.



Al Ca Fe

Pb Si Zn

S Cu SEM photo of the section

Figure 4.22 The X-ray Maps of the sample SS13 for aluminium, calcium, iron, lead, silicium, zinc sulphur and copper elements.

Table 4.8, Presents the results of the concentrations for the elements and different samples. From sample SS1 (bottom) to SS13 (top) the total percentage of the Si, an indicator for the total silicates, decreases; on the contrary, considering Ca as a carbonate indicator, a gradual increase in percentage of the carbonates from bottom layers to top is evident. From bottom to the top sample SS1 to SS13 the amount of aluminium increases, which can reflect the increase in alumino-silicates and phylosilicates. If this consideration is exact, it should be accompanied by a reduction in the quartz percentage. The percentage of sulphide minerals, from sample SS1 to SS13 also increases gradually.

Table 4.8
The approximate percentage of the minerals based on the SEM X-ray maps of Si, Al, Ca, Zn, Pb and Cu elements

	SS1	SS3	SS5	SS8	SS10	SS13
Si (silicates including alumino-silicates).	82,89	81,09	60,28	63,76	60,52	56,77
Ca (carbonates)	16,98	18,77	39,52	36,04	38,87	42,46
Zn (sphalerite)	0,05	0,07	0,11	0,10	0,44	0,56
Pb (galena)	0,02	0,02	0,02	0,03	0,03	0,07
Cu (chalcopyrite or Oxides)	0,07	0,05	0,07	0,07	0,14	0,14
SUM	100	100	100	100	100	100
Percentage of alumino-silicate minerals in total silicate minerals, calculated based on Al %	0,2	8,1	25,8	21,0	21,5	100,0

The SEM evaluations are in agreement with XRD results (table4.7), which confirm that our last procedure for dispersing the sediment is more efficient and result in a much improved separation and/or fractionation. As pointed out by the results, this process is able to concentrate the bulk of the sulphides and silicates with a non-negligible fraction of the carbonates in layer SS13. In other word, by using this procedure we can fractionate our complex system in at least two simpler systems: (i) system rich in quartz and poor in sulphides and carbonates (bottom layers); (ii) system rich in phylosilicates, carbonates and sulphides (upper layers).

4.3 Discussion

In a complex multiphase system the polarity of the initial zeta will dictate the choice of surfactant that can be used. In our case the initial negative charge indicated the use of an anionic surfactant. Further selection is possible using our approach by measuring the zeta intensity change by mean of a titration curve and in our case the surfactant saratan was our best choice. A faster testing procedure was demonstrated by Lortie,[15] that viscosity modification versus the amount of surfactant used is also very effective and reliable for an accurate selection.

The addition of an anion surfactant will increase the negative charges at the surfaces of all solid with an inherent negative charge. This will in turn increase the repulsion forces between the particles which will respond by forming a layering system that will reflects the variation in the charge intensities of the phases and their abundance. For our study the selection of saratan, a sodic organic compound, increased the conductivity of the liquid in a linear fashion but the pH remains essentially constant.

We have found that using dried or wet solids affects the fractionation process. This may relate to some of the hydrated hydroxides making them more suceptible to chemical reactions. On the other hand, by using dried surfaces we avoid a ponctual surface dilution phenomenon and a reduction of the surfactant effect with the hydration water. It is also possible that other factors are at work but this is beyond the scope of this study.

A titration of complex system with the selected surfactant should produce a change of the slope or break on the zeta curve. This break corresponds to the surfactant related to a saturation value attained for the double layers present in the system. This quantity of surfactant required to attain the maximum repulsion could represent the optimized quantity for the system. In our study, averages of slopes for the different sections of the zeta curve were used to obtain the intersecting point and its corresponding optimum surfactant value. It is anticipated that this procedure analysis can also be used to determine the optimum surfactant value in other systems.

If the contaminants are the sulphides and are associated with silicate and carbonate mixtures, then the fractionated sulphides pattern will be with the top layers in association with phyllosilicates and the carbonates. These layers can be separated from others by physical means.

The efficiency of the fractionation is a direct function of the dispersion that can be achived with simultaneous insertion of the chemical additives and utilizing the mechanical devices.

CONCLUSION

This study addressed several questions related to aqueous system containing fine micron size solid particles in the environmental field of anthropic residues and anthropogenic materials from rivers and lakes. Previous studies were successful in establishing the potential of such a technique to contaminated industrial residues and sediments but the parameters were not fully understood and the technique relied mainly on empirical rules.

The main goal was to finalize the development of a surfactant enhanced hydrometallurgical separation technique applicable in the realm of the colloid fraction size. The technique procedure presented in this memoir applies to micron size particles for which the surface charges are the guiding parameters for their behaviours. In this technique the surfactant alters the surface charges of the solids that dictate flocculation and suspension for the some phase. Because of the small mass of the particles, gravity will play a role that is time dependant, a function related to the grain size of the solids involved. For example a montmorillonite suspension can be stable for a year if the system is shielded from disturbance but nevertheless the amount of solid in such a suspension will be substantially reduced, which means that gravity still has an effect on the system.

Environmental problems are also difficult to study because they are multiphase complex systems, which cannot easily be studied by using the conventional separation techniques such as dry or wet magnetic separation, electrostatic separation or by heavy liquid separation.

The fundamental parameter, the zeta potential, is a key factor for the surface charge measured with an acoustic technique ESA that also gives a mobility value to the solid from which a zeta potential can be calculated which further defines a suspension or flocculation. The other parameters are measured simultaneously by the ESA equipment are chemistry parameters for the liquid reflected by the pH and the conductivity values.

This enhanced surfactant colloid separation was found to induce fractionation in a natural multiphase system for grain size distribution with a median of 2 to 3 µm in which the separated smallest sulphide grain had a diameter of approximately 0.2 µm measured with a scanning electron microscope (SEM). Our results indicate that the sulphides initially were not detectable in the natural sediment by X-ray diffraction but could be analysed after its fractionation in layers. These phases can after concentration process, be available for more exhaustive characterization even including radiochemical analysis if radiometric lead is involved. The total amount that was fractionated appeared sufficient for a remediation for which the neutralization potential of the solid would exceed its potential for acid generation.

This project initiated its investigation by characterizing simple mineral slurries and by increasing the number of phases until a complex natural mineral equivalent system was simulated for which similarities and differences could be measured and established.

The results verified the initial assumption that a natural mineral had the same surface polarity and similar intensity value as its anthropic compound if the phases had similar chemistry and structure. The results also established that in a multiple phase system, the measured zeta would have a value dictated by the overall summation of the individual zeta of the constituent phases. We were able to verify the equation of state:

$$\zeta \text{ (zeta) mV for the system} = \Sigma\zeta_a \text{ X } C_a + \zeta_b \text{ X } C_b + \ldots\ldots$$

By knowing the initial zeta potential value of a system and its major mineral components natural or anthropic an evaluation for its remediation potential can be assessed or its mobility with a risk factor can be determined.

Using artificial mineral system, data and guidelines were defined and measured for suspension, flocculation and fractionation of simple and complex systems.

Finally the study applied the learned data to the contaminated sediments of the Sweet-Lake, a receptacle pond for the industrial region of Mansfeld in Germany. The successful fractionation of this system could be used to decontaminate the sediments and extract enough sulphides so that its potential acid generating sulphides is lower than its neutralization capacity.

Our study started to establish a database for surface characteristics of mineral in an aqueous fine grain system. It was further established that these characteristics can be used in evaluating the potential remediation and fractionation of other contaminated sites and be useful in assessing a mobility or risk factor. The mineral study indicated that certain minerals have a larger impact in a system and can modify the measured parameter to an extent that important compensation need to be done before extrapolating to final conclusions. Montmorillonite is such a problem phase and should merit additional study in order to fully understand its impact and possibilities.

Other phases could be problematic and certainly oil and grease will require an adjustment or a pre-treatment prior to forecasting results.

The relatively close correspondence between a complex system of equivalent mineral and its natural counterpart implies multiple applications for environmental studies, risk assessments and other evaluations. The simple equation that links its initial zeta value to a summation of the zeta of its component mineral phases confirms the potential for its fractionation and its remediation. In other words, the zeta value can be substituted in a complex natural system by the value of the equivalent mineral to evaluate if anomalies related to organic or problematic anthropic phases could prevent the fractionation into simpler systems.

It is also possible to extrapolate for a natural system if the zeta and the mineral composition are known if such a system can easily be mobilized by natural event like flooding. If the system is mobilized can adding other stable inorganic phases like calcite, dolomite and quartz stabilize it or can a risk evaluation be made.

With this fractionation process the separation of different phases in the realm of the fine particles has been extended to the micron and sub-micron size particles. This exceeds the limits set by the conventional physical techniques of magnetic, electrostatic or even heavy liquid separation.

Potential new environmental techniques applicable to fine and ultra fine contaminated soils and residues from industrial, mining operations

From the results of this study, two different procedures have been highlighted and two potential new techniques have been defined for handling, characterizing and treating micron to sub micron size anthropogenic residues. In order to persue further this development, trial applications have to be conducted from which more detailed step like procedures could be given and applicable parameters better defined.

The first technique or process will stabilize the soils or residues and prevent the dispersion of contaminants in the environment. The stabilization will have to prevail under extreme events associated with weathering processes including flooding.

The second process allows the fractionation of the solid phases so that the contaminant fraction can be separated and handled separately which results in the decontamination of the residue.

Preliminary analyses required before selecting the applicable technique

- Grain size distribution by laser or by other techniques;
- XRD mineralogical analysis for phase identification and relative abundance in the system;
- SEM can determine the element association for particular grains and their respective morphology. This evaluation can also determine the dispersion state for the contaminants which can be determinant in the selection process between stabilization or fractionation;
- Zeta potential determination for the system using the Electroacoustic Sonic Amplitude (ESA) signal measurement. This value will help determine the mineral phase or surfactant to be used for either stabilizing or fractionating the system.

The first technique, the stabilizing procedure

The stabilization process can successfully be done when large opposite sign charges are involved. In this case inorganic fine mineral powder (carbonates, silica, clays) can be advantageously used instead of an organic surfactant (sodium metaphosphate, saratan), although the latter case is also feasible. A list of natural mineral with their surface charge characteristics are given in tables 1.1 and1.2 for a specific grain size. The goal with this technique is to bring the system to its isoelectric zero point with a neutral pH.

Guidelines for its application

- With an ESA titration using the surfactant or mineral additive the zero point charge has to be attained and the amount of additives used is noted;
- The stability of the system should be evaluated periodically for changes in the ESA signal with time, a phenomenon associated with ageing;
- Surface characteristics and quality can be analysed with SEM or other surface analyzing techniques like atomic force microscope or electron diffraction.

The second technique, the fractionation procedure

In this process the key for success is to increase the charge of the system to its maximum intensity so that decantation slowdowns or becomes sluggish allowing for the different mineral phases and the contaminants to fractionate and segregate into layers. For this process to work, the mineral phases have to be completely dispersed and only then, can the surfactant play its role. Depending on the system under study, the dispersion techniques used can vary from a simple washing and replacement of the pore water to strong mechanical stirring, ultrasonic vibration, homogenizing techniques or wet attrition with ceramic beads.

Guidelines for its application

- With the initial zeta measurements for the system, the charge polarity will dictate the family of surfactant that can be used. A more refine selection of a surfactant will require visual evaluation of the fractionation ease for the system or from viscosity measurement with the addition of a specific surfactant;
- The final surfactant selection will be made after titration of the slurry with the surfactant and with the determination of the precise quantity of surfactant required;
- The visual observation of the fractionation process should yield information on the separation method that could be used to recover the fractionated layers that will form;
- Sampling of the different layers and their evaluation with XRD or SEM procedures will yield the efficiency for the fractionation process;
- It is conceivable that a layer obtained with a first separation could require further fractionation with the above steps.

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APPENDIX

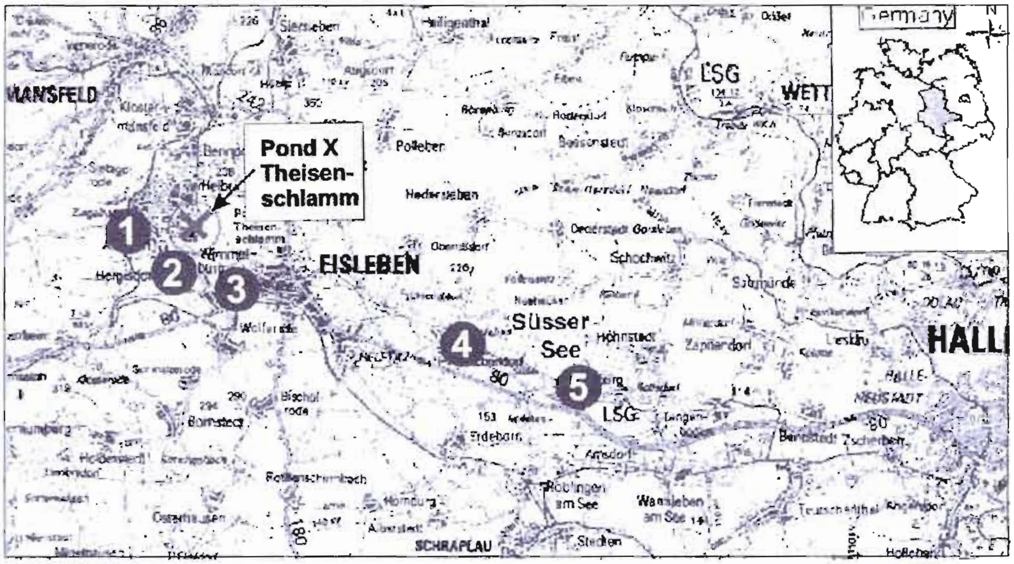

Figure A.1 Map of the Mansfeld Mining Area including Sweet Lake (Susser See).[10]

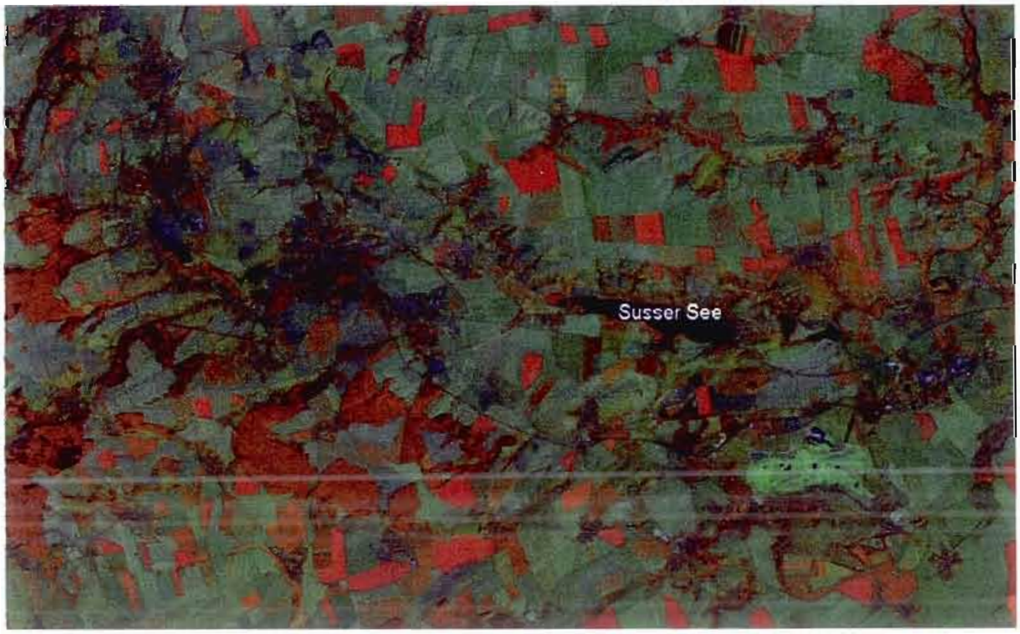

Figure A.2 An aerial photograph of the Mansfeld Mining Area including Sweet Lake (Photo provided by UFZ