



Swedish University of
Agricultural Sciences

Physico-chemical characteristics of some soils from Mali and their potential in heavy metal removal

Märit Sällström

Supervisor: Professor Ingmar Persson (Dept of Chemistry, SLU)
Examiner: Professor Dan Berggren Kleja

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Abstract

Rivers, streams and groundwater contaminated by heavy metals is a growing concern world wide as the pressure on existing water resources is increasing. Unfortunately, low income countries are afflicted the most. There is a need for cost efficient and simple methods and techniques to solve the problem. Previous studies have indicated great potential for clay minerals in pollution control. However, the studies have been carried out on synthesized clays and through modeling predictions. The objective for this study was to investigate natural mixed clays from Mali and their potential in heavy metal removal.

Experiments were carried out on three natural clay samples from Mali. Using X-ray diffraction and electron microscope the mineral composition and its morphology were investigated. The physico-chemical properties of the mixed clays were investigated by acid-base titrations preceded by a purification procedure. Finally, adsorption experiments were carried out with Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} ions in aqueous suspensions.

The mineralogical analyses showed that all three clay samples mainly consisted of crystalline quartz. According to the literature and previous modeling predictions carried out on quartz, the $\text{p}K_{\text{a1}}$ value is negative. Basically, it means that the hydrated quartz surface has no base properties, and that the only surface sites are $\equiv\text{Si-OH}$ and $\equiv\text{Si-O}^-$. It can therefore be assumed that rather than having a specific pH_{pzc} the surface is neutral over a wide pH range. $\text{p}K_{\text{a2}}$ was determined through alkalimetric titrations to 9.7 which is a value that corresponds relatively well with the literature. All clay samples proved to completely remove Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} from aqueous solution at different pH ranges. At $\text{pH} > 7$, all the studied metal ions are adsorbed to the mineral surface. Since the surface is neutral at this pH it can be assumed that all metals are adsorbed to the surface as inner-sphere complexes.

Using this clay mineral for heavy metal removal requires fairly high pH values for the water being treated. The pH has to be well above 7 to be certain that all metals are adsorbed. For a more wide spread application of clay minerals as heavy metal adsorbents further studies in clay mineral characterization are necessary. Every country has their unique soils with different properties and capacities that need to be mapped.

Keywords: Heavy metals, adsorption, natural clays

Sammanfattning

Floder och grundvatten kontaminerade med tungmetaller är ett växande problem när trycket på jordens existerande vattenresurser ökar. Tyvärr är befolkningen i låginkomstländer värst drabbade. Det finns därför ett behov av billiga och enkla metoder för att rena vatten från tungmetaller. Tidigare studier har visat stor potential för olika typer av lermineral. Dock har de flesta av dessa studier utförts på syntetiserade leror eller med hjälp av modeller vilket inte alltid ger en sann bild. Syftet med denna studie var att undersöka naturliga leror från Mali i Västafrika och deras förmåga att rena vatten från tungmetaller.

Experimenten utfördes på tre olika jordprover från Mali. Röntgendiffraktion och elektronmikroskop användes för att bestämma jordens mineraluppsättning och morfologi. De fysiokemiska egenskaperna bestämdes genom syra- basititreringar som föregicks av flera reningssteg där organiskt material, karbonater och järnoxider togs bort. Avslutningsvis utfördes adsorptionsexperiment med Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} i vattenlösning.

Experimenten för mineraluppsättning och struktur visade att alla tre jordprover bestod till största delen av kristallint kvarts. Enligt litteraturen och tidigare modelleringar har kvarts ett negativt $\text{p}K_{\text{a1}}$ värde. Detta betyder att den hydratiserade kvartsytan inte har några basiska egenskaper och att de enda ytpositionerna för kvarts är $\equiv\text{Si-OH}$ and $\equiv\text{Si-O}^-$. Därför kan det antas att ytan är oladdad eller neutral över ett vidare pH intervall snarare än vid ett pH_{pzc} . $\text{p}K_{\text{a2}}$ bestämdes genom basititrering till 9,7 vilket är ett värde som stämmer relativt bra överens med tidigare publicerade värden. Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} i vattenlösning renades med hjälp av jordproverna vid olika pH intervall. Vid $\text{pH} > 7$, var alla de studerade metallerna adsorberade till mineralytan. Eftersom ytan på kvarts till största delen är neutralt laddad vid detta pH värde kan det antas att metallerna binder som innersfärskomplex till ytan.

Att använda dessa jordar för rening av tungmetaller kräver ett relativt högt pH värde i vattnet som ska behandlas. pH måste vara över 7 för att med säkerhet veta att metallerna är adsorberade. För en vidare spridning av denna metod är det nödvändigt med fortsatta studier inom ämnet. Varje land har sina unika jordar med olika egenskaper och förmågor att adsorbera katjoner och detta behöver kartläggas.

Nyckelord: Tungmetaller, adsorption, naturliga lermineral

Table of contents

| | |
|---|--------------|
| Introduction | 7 |
| Overview | 7 |
| Basic Concepts..... | 10 |
| Soil Minerals..... | 10 |
| Mineral Characterization | 11 |
| Adsorption | 14 |
| Surface complexation | 16 |
| Surface charge and pH_{pzc} | 17 |
| Objectives | 20 |
| Materials and Methods..... | 21 |
| Sample Preparation..... | 21 |
| Purification Procedures | 21 |
| Removal of carbonates | 21 |
| Removal of iron oxides | 22 |
| Removal of organic matter..... | 22 |
| Physico-chemical experiments..... | 23 |
| Potentiometric titrations | 23 |
| CEC determination..... | 25 |
| Heavy metal adsorption..... | 26 |
| Preparation | 26 |
| AAS analysis..... | 29 |
| Mineralogical analysis | 30 |
| Scanning Electron Microscope (SEM) | 30 |
| Powder X-ray diffraction..... | 30 |
| Results and Discussion | 31 |
| Mineralogical analyses | 31 |
| Potentiometric titrations..... | 33 |
| Acidimetric titrations..... | 34 |
| Alkalimetric titrations..... | 35 |
| CEC determination | 36 |
| Heavy metal adsorption..... | 38 |
| Conclusions | 41 |
| Future perspectives | 42 |
| Thank you..... | 43 |
| References | 44 |
| Appendices 1-9..... | 47-54 |

Introduction

Overview

Heavy metals is a term applied to a large group of trace elements with an atomic density greater than 6 g/cm^3 (Alloway, 1995; Harrison, 1996). All trace elements are toxic to living organisms in high concentrations, although some are essential in low concentrations for plants, animals and humans. These trace elements are called micronutrients and include Zn, Cu, Mn and Co. Elements such as Ag, As, Ba, Cd, Hg, Pb, Sb, Tl have no known function for most living organisms and are poisonous even at very low concentrations. In an environmental and health perspective the most hazardous heavy metals are As, Cd, Cr, Hg, Pb and Zn (Alloway, 1995).

Heavy metals are non-biodegradable and cause various disorders and diseases in humans. The general symptoms for acute heavy metal poisoning are gastrointestinal disorders, diarrhea, paralysis, vomiting and convulsion, and depression and pneumonia when volatile vapors and fumes are inhaled (McCluggage, 1991). Lead is a cumulative poison, particularly for infants and pregnant women. It affects the central nervous system and causes mental retardation in children (WHO, 2006). For both men and women long term exposure to lead has shown reproduction dysfunction. The arsenic crisis in Bangladesh and India has resulted in extensive research on the health and environmental effects. There is overwhelming evidence that arsenic causes cancer in humans, particularly in skin, bladder and lung. Copper and cadmium causes serious failures of vital organs, for example liver and kidney. In addition, copper has a long-term effect on sensitive populations, such as carriers of the gene for Wilson disease and other metabolic disorders. Studies on cadmium have shown that it can be carcinogenic by inhalation. Mercury compounds damage the kidney and cause hemorrhagic gastritis and colitis. There is also evidence that mercury compounds have the potential to increase the incidence of some benign tumors. (WHO, 2006)

Heavy metals occur naturally in soils, deriving from the parent material in the bedrock. When found in nature, they are most likely from sources such as agriculture, industry, waste disposal, leaking landfills, mining etc. (Eriksson *et al.*, 2005). Leached into streams or groundwater reservoirs and displaced by atmospheric deposition, heavy metals eventually accumulate in the food chain in living organisms. Drinking water is not usually the sole source of human exposure to heavy metals. In many cases, the intake of toxic amounts of heavy metals from drinking water is small in comparison with that from other sources, such as food, air and consumer products. (WHO, guidelines for drinking water quality, 152)

Growing populations worldwide, urbanization and industrialization in developing countries are important factors for the increasing pressure on existing water resources (UNEP, 2006). The need for global agreements on a sustainable water resource management is rising on the agenda. The EU framework directive on water aims to establish a framework in Europe for the protection of surface and groundwater, as well as coastal waters. On a global level, The United Nations through organizations such as

UNEP, FAO, WHO and UNDP are taking action towards the right to access to clean and safe water as stated in the Millennium Development Goals (MDG's) (UN Millennium project, 2005). Guidelines for limit concentrations of heavy metals in drinking water have been set by WHO and the EU (Table 1.). A guideline value normally represents the concentration of a constituent that does not result in any significant risk to health over a lifetime of consumption.

Table 1. Guideline values for limit concentrations of heavy metals in drinking water by WHO and EU.

| Metal | Guideline values mg/l | |
|---|-----------------------|-------|
| | WHO | EU |
| Arsenic (naturally occ.) | 0.010 | 0.010 |
| Chromium (naturally occ.) | 0.050 | 0.050 |
| Manganese (naturally occ.) | 0.40 | 0.050 |
| Cadmium (industrial + human) | 0.003 | 0.005 |
| Mercury (inorganic, industrial + human) | 0.006 | 0.001 |
| Copper | 2.0 | 2.0 |
| Lead | 0.010 | 0.010 |
| Nickel | 0.070 | 0.020 |
| Zinc (Guideline value from 1984 based on taste considerations rather than toxicity) | 5.0 | - |

Source: Council Directive 98/83/EC 3/11 1998 and WHO, 2006

Several contaminated hotspots where chemical pollution poses significant risks for humans and wildlife have been located around the world. Unfortunately, low income countries make up the greater part of the list. The main areas reported in the GIWA final report (UNEP, 2006) include the river system of Ganges-Brahmaputra in India and Bangladesh, various countries in Central America and Africa, and the Arctic region. Yet, the concern is global as the pollutants travel long distances dissolved in water, adhered to sediments, transported by air or transferred in the food chain.

Therefore, global measures such as policy making, transboundary agreements and above all, proper treatment techniques for remediation of such contaminated sites are necessary in order to reach the fundamental steps in the progress towards the MDG's (UNESCO, 2006). For many contaminants, potentially several different processes could be appropriate, and the choice between processes should be made on the basis of technical complexity and cost, taking into account local circumstances. Existing treatment techniques for heavy metal contaminated water include: chemical precipitation, membrane filtration, ion exchange, co-precipitation, adsorption and sand filtration (Bailey *et al.*, 1999; Sajidu, 2008). Nevertheless, these methods are expensive and difficult to implement in developing countries. For that reason, cost effective alternative technologies or methods are needed. Bailey *et al.* (1999) presented a review of low cost sorbents for heavy metals. Montmorillonite clays were found to be a potential alternative to activated carbon for the adsorption of heavy metals, primarily because of their abundance, low cost and adsorption capabilities.

Many different civilizations have used clays as a natural purifier of water, for medical remedies etc. and the empirical knowledge is not to be despised. However, technical knowledge of the physico-chemical properties of the clays is necessary in order to achieve a wide spread application. Some of the clays that have been studied include kaolinite (Coles&Yong, 2002), vermiculite (da Fonseca, 2006) and bentonite (Khan *et al.*, 1995). Al Degs *et al.* (2003) compared four different clay types and their adsorbing potentials.

Most of the previous studies done in this field are focused on purified clays containing only one type of clay mineral. Sajidu *et al.* (2006) showed that the properties of mixed clay samples can vary extensively. Properties of purified clay samples do not give an accurate depiction. Further studies on mixed clay are essential in order to understand and map the possible mechanisms through which heavy metals are sorbed onto the clay surfaces. It is necessary to attract investments to actualize extended research in this area and develop sustainable future water schemes.

Mali is situated in western part of Africa with half of its surface area in the Sahara desert. The country is completely landlocked and dependent on the two major rivers, River Niger and River Senegal for water supply (UNESCO, 2006). The main heavy metals found in water and wastewater in the area for this study are chromium and manganese from tanneries, mercury and silver from hospitals and arsenic dissolved in groundwater (Plea, 2008). The recent extensive droughts in Mali have forced the government of Mali to act towards a more sustainable management of the water resources. Desertification, population growth, lack of waste treatment systems are just a few examples that have seriously affected the environment and water resources in Mali. As pointed out in the United Nations World Water Development Report 2 from 2006, one of the key factors for Mali's ability to address these issues are to raise the level of national technical expertise through increased educational programmes and research institutions (UNESCO, 2006).



Figure 1. Map of Mali and its surrounding countries.
Source: www.mapquest.com

Basic Concepts

In this part the fundamental principles behind the experimental work are described. Nevertheless, the descriptions should not be seen as complete but as useful information for a basic understanding of soil chemistry. The first part describes soil minerals and a few commonly used methods in characterizing unknown minerals. However, to gain a complete picture of a mineral, not only the structural features need investigation. In the second part physical and chemical principles of soils are reviewed.

Soil Minerals

Soils consist of minerals of the parent rock material from where they are formed and of organic residues. Their elemental composition, particle size and mineralogy depend in principal on the degree of weathering (McBride, 1994).

Soil minerals are divided into primary and secondary minerals. Primary minerals derive from the parent material and have been crystallized at high temperature and high pressure. The primary minerals are silicates and are classified structurally based on the arrangement of the connected silica (SiO_4) tetrahedral. Pyroxenes, amphiboles and micas are a few examples of silicate minerals. Quartz (Fig. 2) is a common rock forming silicate mineral and make up 11% of the earth crust (Eriksson *et al.*, 2005). It has the formula SiO_2 and since each oxygen binds to two silica the mineral is hard and resistant to weathering (McBride, 1994).

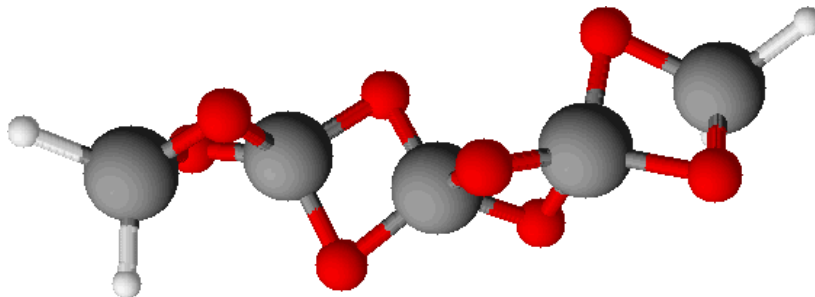


Figure 2. Structure of quartz.

Secondary minerals are weathering products of primary minerals. Particle size is typically $< 2 \mu\text{m}$ and by definition therefore belongs to the clay fraction of the soil (Eriksson *et al.*, 2005). Clay minerals have a high surface area and participate in many important chemical reactions in the soil.

Clay minerals have the structure of layer silicates which are stable and persistent in the soil. The structure consists of various combinations of stacked tetrahedral- and octahedral sheets.

The most weathered clay mineral is kaolinite, with the general formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is a 1:1 type mineral which means that it is built up by one tetrahedral sheet and one

octahedral sheet, held together by hydrogen bonds between the layers. The cation exchange capacity, CEC, is low due to very low isomorphous substitution¹. Halloysite is a similar clay mineral of 1:1 type but with the difference that it has water molecules between the layers.

The other common layer silicates that occur in the soil are: smectites, vermiculite, illite and chlorite. They are different types of 2:1 minerals with two tetrahedral sheets and a single octahedral sheet between. These minerals have a varying grade of isomorphous substitution and specific surface area. 2:1:1 minerals like chlorite have an interlayer composed of an extra octahedral sheet. Table 2 below describes some clay minerals in more detail.

Table 2. Common clay minerals and their characteristics.

| Clay | Halloysite | Kaolinite | Smectite | Vermiculite | Illite | Chlorite |
|---|------------------|------------------|----------|-------------|--------|------------------|
| Structure | 1:1 | 1:1 | 2:1 | 2:1 | 2:1 | 2:1:1 |
| Layer bond | Hydrogen bonding | Hydrogen bonding | Ionic | Ionic | Ionic | Hydrogen bonding |
| CEC (cmol _c /kg) | 2-10 | 2-5 | 80-120 | 100-180 | 0-40 | 10-40 |
| Specific surface area (m ² /g) | 78-112 | 10-30 | 550-700 | 600-800 | 0-100 | 70-100 |

Source: Gustafsson *et al.*, 2007, Takahashi *et al.*, 2001

Besides the sheet silicates, the clay fraction of the soil also consist of non silicate minerals as Fe and Al oxides and hydroxides but also of non crystalline minerals such as allophane and imogolite. Goethite, gibbsite and magnetit are examples of oxides and hydroxides; they have more simple structures than the sheet silicates. The structures are made up of close-packed oxygen and/or OH⁻ anions with Fe³⁺, Al³⁺, Mn⁴⁺, Mn³⁺ residing in the octahedral interstices. If no isomorphous substitution exists the surface charge relates to the pH of the surrounding solution (Gustafson *et al.*, 2007; Mc Bride, 1994; Eriksson *et al.*, 2005).

Mineral Characterization

Mixed natural clays are all different with respect to their components. Their abundance makes it economically valuable to determine the structure and chemical composition in order to evaluate their use as heavy metal adsorbents. Various methods exist to identify and classify clay minerals.

Electron microscopes are a group of instruments with a magnifying capacity up to 2 million times. It is based on the same principles as for light microscopes but uses accelerated electrons to produce images of the specimen. Today, the most commonly used electron microscope is the Scanning Electron Microscope (SEM) (www.ne.se). The accelerated electrons are focused in to a fine beam with a diameter that can be as small as 1 nm. The beam is scanning the sample building up an image by detecting signals from

¹ Isomorphous substitution is the replacement of one structural ion by another of equal or different charge, without fundamentally altering the structure.

the sample. If the SEM instrument is equipped with an x-ray detector it is also possible to analyze the chemical composition of the sample. When irradiated with electrons the sample is emitting x-ray radiation with different wave lengths. The emitted wave lengths can be measured and related to the elements present on the surface.

X-ray diffraction is a technique used to identify and classify unknown crystalline structures. In a crystal the atoms or molecules occupy specific positions. The crystal has a highly ordered structure and the atoms or molecules are arranged three dimensionally so that the net attractive intermolecular forces are at their maximum and the energy level at its minimum. The smallest divisible unit of a crystal is the unit cell. It is a basic, three-dimensionally repeated unit that makes up the lattice structure of a crystal (Fig. 3). The first step to identify an unknown mineral is by measuring the size and shape of the unit cell. If the crystals in the mineral are well defined the angles and lengths of the unit cells are determined with x-ray diffraction technique.

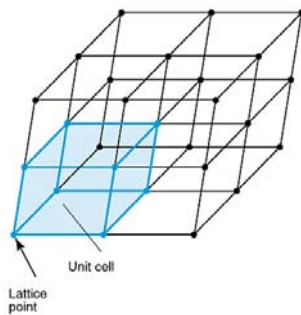


Figure 3. Basic lattice structure.

Two methods exist where the single crystal method is used for bigger crystals that are easy to isolate. Powder x-ray diffraction is an alternative approach which enables identification of a sample consisting of many different components. The x-rays are generated in a sealed tube where a heated tungsten filament emits electrons which are accelerated by an electric potential. The electrons hit a metal target, commonly made of copper or molybdenum, and K_{α} radiation is emitted with wavelengths of 1.5418 and 0.7107 Å, respectively. The mineral to be identified is ground to a fine powder, ideally consisting of randomly oriented crystallites with lattice planes available in all possible orientations. The radiation is directed onto the sample and when the x-rays strike a crystal a diffracted beam is formed. Beams are diffracted from every layer lattice but they all need to interact in order to give a reflection (Fig. 4). The waves have to be in phase according to Bragg's law, otherwise no reflection will be projected.

$$2d \sin\theta = n\lambda$$

Where d is the spacing between the Miller planes, θ is the angle of the incident rays, n is the order of the diffracted ray, and λ the wavelength of the incident x-ray beam.

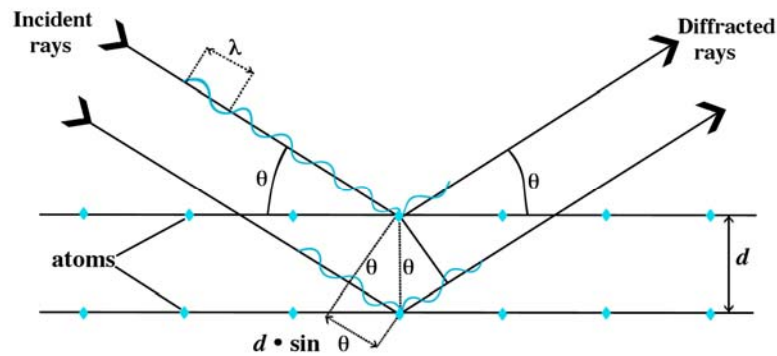


Figure 4. X-rays satisfying Braggs law.

The intensities of the diffractions are recorded on an x-ray radiation sensitive detector as a function of the scattering angle θ . The diffracted beams from each plane form a pattern with rings. Each crystalline solid has its unique characteristic x-ray powder pattern which may be used as a "fingerprint" (Fig. 5) for its identification. From the distances between the rings and the dimension of the film, the angle θ can be calculated and then plotted against the diffracted intensities. The last step in the process of identifying the mineral is searching the Mineralogy Database for compounds with the same or similar "fingerprint".

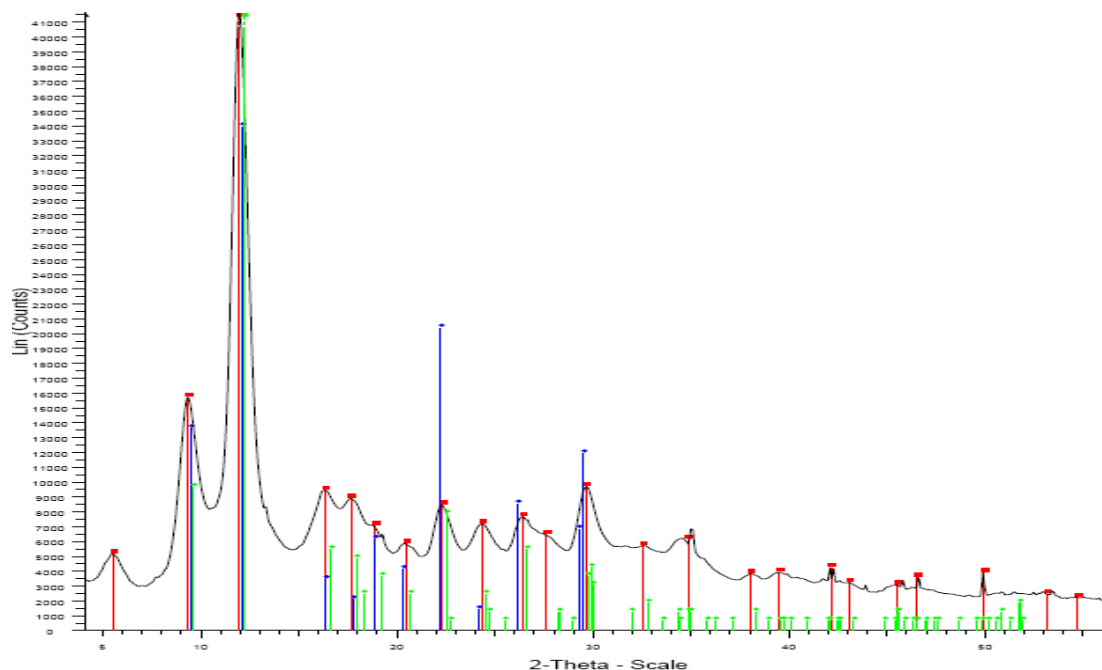
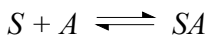


Figure 5. Example of a diffraction plot.

Adsorption

Adsorption is a general term of intermolecular interaction between a solute and a solid phase. Adsorption data is most commonly represented by an adsorption isotherm where the quantity adsorbed specimen onto a solid adsorbent is plotted as a function of the equilibrium concentration (McBride, 1994). According to Alloway (1995), adsorption of metal ions has traditionally been described by either the Langmuir or the Freundlich adsorption isotherm. The Langmuir isotherm is the simplest description of adsorption assuming single layer adsorption. The adsorption sites, S , on the surface of the solid becomes occupied by a sorbate from the solution, A , implying 1:1 stoichiometry (Stumm, 1992).



The Langmuir equation has the form:

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b}$$

Where C is the concentration of the ion in the equilibrium solution, x/m is the amount of C adsorbed per unit of adsorbate, K is a constant related to the bonding energy and b is the maximum amount of ions that will be adsorbed by a given sorbent (Alloway, 1995). The Langmuir model is useful when there is strong specific interaction between the surface and the adsorbate so that a single adsorbed layer forms and no multi-layer adsorption occurs (Ng *et al.*, 2002). The other model widely used for describing adsorption is the Freundlich isotherm. The equation has the form:

$$x = kc^n \quad \text{or} \quad \log x = \log k + n \log c$$

Where x is the amount adsorbed per unit of adsorbent at concentration of c of adsorbate, and k and n are constants (Alloway, 1995). Regardless of which model that is used neither of them provide information on the adsorption mechanisms, and both assume a uniform distribution of adsorption sites and the absence of any reaction between adsorbed ions. Even so they are still considered useful. Figure 6 present examples of Langmuir and Freundlich isotherms compared with a linear isotherm.

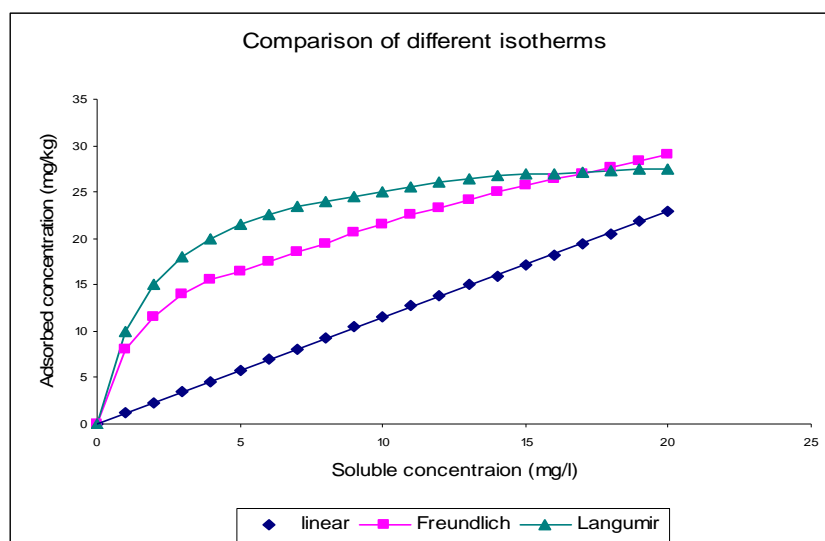


Figure 6. Linear, Freundlich and Langmuir adsorption isotherms.

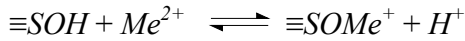
The adsorption reactions that are of importance in waters, sediments and soils are listed in table 3. This area is extensively researched and for this report only the adsorption mechanism of value will be reviewed. For a more thorough description, refer to literature cited in this section.

Table 3. Descriptions of different types of adsorption reactions (Stumm, 1992).

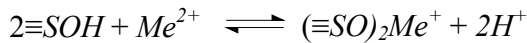
| Chemical reactions with surfaces | Electrical interactions at surfaces | Interactions with solvent |
|----------------------------------|-------------------------------------|---------------------------|
| Surface hydrolysis | Electrostatic interactions | Hydrophobic expulsion |
| Surface complexation | Polarization interactions | |
| Surface ligand exchange | | |
| Hydrogen bond formation | | |

Surface complexation

Ions can adsorb to a mineral surface either as inner-sphere complexes or outer-sphere complexes. The inner-sphere complex formation takes place directly on the surface with ions that do not have a complete hydration shell (McBride, 1994). The bond is specific and mainly covalent and the ions are difficult to exchange. In the inner-sphere reactions one proton per bound surface site is released:



Bidentate surface complexes can also be formed:



Where $\equiv\text{S}$ is the adsorption site on the surface and Me^{2+} a divalent metal ion.

Outer-sphere complexes require a charged surface since the ions bind electrostatically. The ions have a hydration shell and are rather easily exchangeable. Outer-sphere complexes are formed immediately outside the surface within the electric double layer (Eriksson *et al.*, 2005). The adsorbents show differences in selectivity for cations or heavy metals. Generally, it can be explained by the Lewis hard-soft acid-base (HSAB) principle. Hard Lewis acids prefer to react with hard Lewis bases, and soft acids prefer soft bases. Cr^{3+} is a hard Lewis acid, while the other heavy metals included in this study are border-line Lewis acids (Alloway, 1995).

The diffuse ions are hydrated ions further out in the electric double layer. They take care of charge that is “left over” and are very easy to exchange.

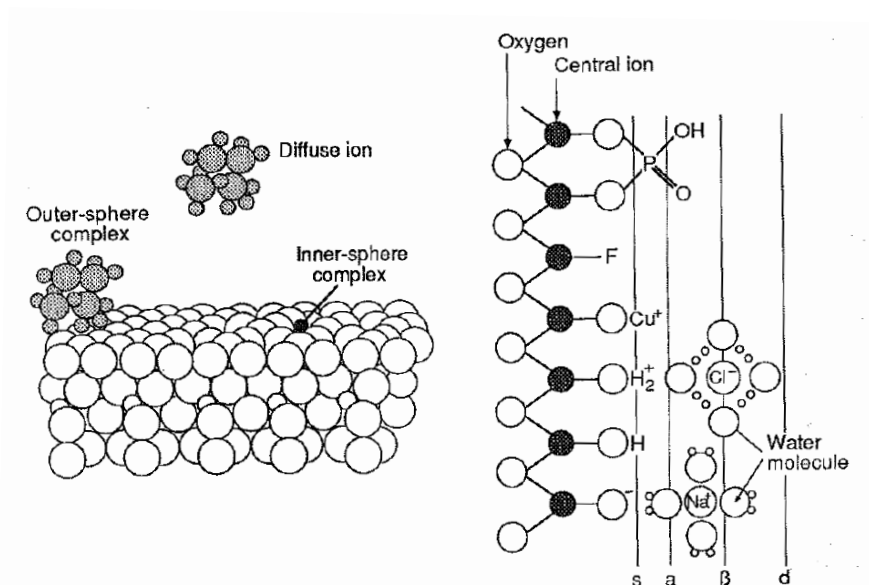


Figure 7. Complexation reactions on a surface. From Stumm, 1992.

Surface charge and pH_{pzc}

The surfaces of oxides and hydroxides contain $\equiv\text{SOH}$ groups in aqueous suspensions, where $\equiv\text{S}$ represent the surface of the clay mineral and OH is the attached hydroxyl group (Fig. 8). In the presence of water they behave as Lewis acids and bases releasing or taking up protons (Stumm, 1992).

When solid soil particles are in contact with water electrical charge may develop on the surface. As described in Stumm (1992), this charge has three different sources. The permanent charge originates from structural imperfections (isomorphous substitution) in the tetrahedral and octahedral sheets of a secondary mineral. The charge is independent of pH and in most cases negative. In ion exchange reactions on the negatively charged surface cations are attracted electrostatically to balance the charge difference.

The second type of charge arises from acid-base-reactions on the surface of the soil particle. On the edges of the clay the active surface site, in this case $-\text{OH}$ groups participate in the uptake and release of protons and OH_2^+ or OH^- is formed. For oxides and sulfides the active surface groups are $-\text{OH}$ and $-\text{SH}$. Other types of minerals can have other active surface groups such as $-\text{OPO}_3\text{H}_2$. If the material contains organic matter, carboxylic acids, $-\text{COOH}$, participate in the acid-base-reactions. This charge is obviously pH dependent and therefore variable. pH values below pH_{pzc} generate a positively charged surface. When pH increases above pH_{pzc} the functional surface groups dissociate and the surface becomes negatively charged.

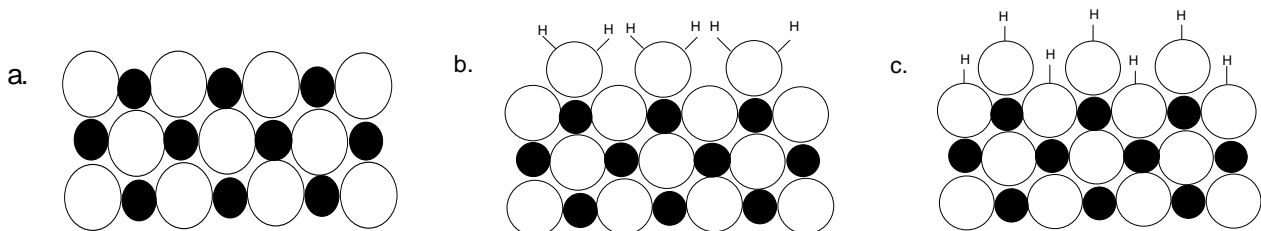


Figure 8. Cross section of an oxide surface layer. Black represents metal ions and white are oxides or hydroxide ions. a. is a close packed oxide in vacuum. Water is added to oxide/hydroxide, b. and H_2O molecules bind to metal ions in the surface. This is not a stable thermodynamic situation, some metal ions have a proton, some not. c. this is a charge neutral surface. It has amphoteric (protolytic) properties and behaves as a Lewis acid or base depending on the pH of the solution. (From Stumm, 1992)

The third source of surface charge, and probably the least significant one for this paper, is the surface charge established by adsorption of a hydrophobic species or a surfactant ion. This involves organic solutes such as humates and fulvates and for this reason of little interest for this study.

The pH at which the surface charge is zero is called point of zero charge (pH_{pzc}). pH_{pzc} is a term used when considering all surface conditions where charge is established by proton exchange. This usually coincides with the isoelectric point. Some prefer to use the term pH_{pzse} , point of zero salt effect, since pH_{pzc} is independent of ionic strength. If specifying the pH_{pzc} as solely due to H^+ or OH^- binding it is referred to as point of zero net proton charge, pH_{pznpc} . The pH_{pzc} is an important parameter since it determines the acidity and basicity of the hydrated oxides/hydroxides which control the adsorptive potential of a particular oxide. When $\text{pH} > \text{pH}_{\text{pzc}}$ the surface is negative, and cations will be adsorbed electrostatically. Conversely, when $\text{pH} < \text{pH}_{\text{pzc}}$ the surface becomes positive and anions will be adsorbed. Generally, Al- and Fe oxides have pH_{pzc} in the range from 7 to 10; hence these minerals have a positive surface charge in acidic and slightly alkaline soils. Kaolinite and montmorillonite on the other hand have low pH_{pzc} and are therefore negatively charged in almost all types of soils (Stumm, 1992; Eriksson *et al.*, 2005).

Another term frequently used in soil science is cation exchange capacity (CEC). It is referred to as the clay's total capacity to exchange and electrostatically adsorb cations. The CEC is partly a result of the amount of permanent charge that has developed on secondary minerals through isomorphous substitution in the tetrahedral and octahedral sheets. It is also a result of dissociated edge groups on the mineral which generates a pH dependent CEC. In addition, humus content plays a significant role, increasing the CEC greatly due to humic acids (Eriksson *et al.*, 2005)

A charged particle will be surrounded by an electrical field, commonly referred to as the electrical- or diffuse double layer (Gustafsson *et al.*, 2007). The distribution of cations and anions around the surface is illustrated in figure 9. The cations in the inner solution are subject to two equally strong forces. The electrical potential gradient that is directed towards the negatively charged surface and the concentration gradient directed towards the bulk solution. Hence, there is a surplus of cations in the inner solution that corresponds to the particle's inherent negative charge. In the bulk solution the cation and anion charges balance each other. There are no ways of measuring the potential gradient; instead different theories have been developed, for example the Gouy-Chapman theory (Gustafsson *et al.*, 2007).

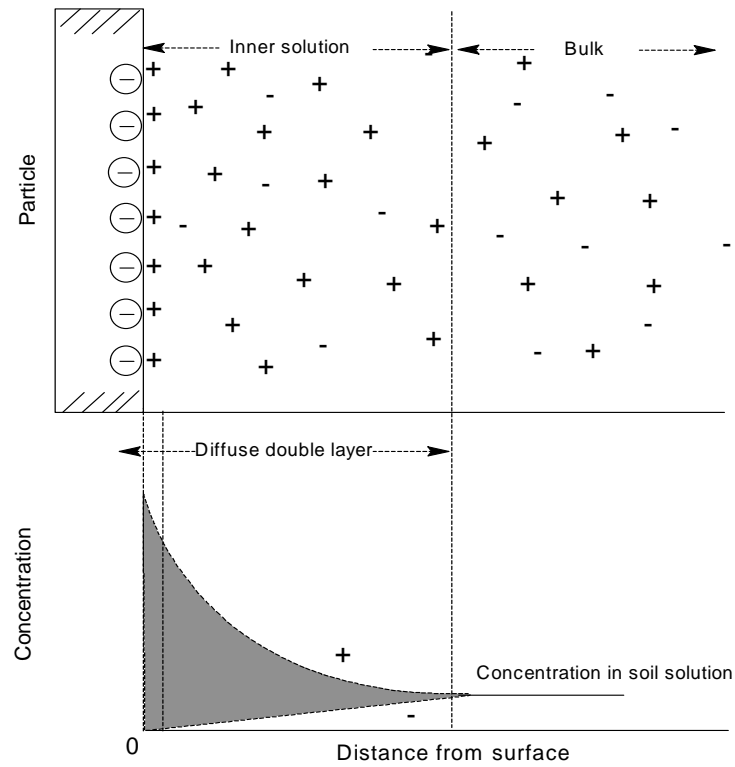


Figure 9. Distribution of exchangeable cations and anions in the surrounding area of a negatively charged particle surface (From Eriksson *et al.*, 2005).

Objectives

The general objective was to investigate the physico-chemical properties of natural mixed clays from Mali and their implementation as a remediation for heavy metal removal of contaminated water. This study also aims at the understanding of the chemical mechanisms. An important intention with this study is to open up for further research in the area of soil chemistry and to stimulate a more applied research project for heavy metal treatment.

Specifically the objectives are:

- To identify and classify some mixed clay samples from Mali.
- To investigate the clay's physico-chemical parameters.
- To investigate the acid-base properties of the clay.
- To determine the clay's metal ion binding capacity.
- To understand the possible mechanisms through which heavy metals are sorbed onto the clay surfaces.

Materials and Methods

The clays samples investigated were collected from two different locations in Mali in the western part of Africa. The samples named BN1 and BN2 are from the village Banambani situated 25 km north of the capital Bamako. The GPS coordinates for the pit are 8 02' 38.6"N, 12 47' 53.0"W and the altitude 379 m a s l. BN1 was sampled from a depth between 0.20 and 0.51 m and BN2 between 0.51 and 0.81 m. The third sample, named MB, was collected from the village Markabassy north of Niono, in the center of Mali. The GPS coordinates are 14 55' 03.78"N, 6 00' 00.77"W and the altitude 272.3 m a s l. The sample is taken from a depth between 0.5 and 1 m.

Sample Preparation

The samples were sifted with an automatic sieve (Retsch Vibro) partitioning the samples in five fractions; >0.125 mm, >0.063 mm, >0.045 mm, >0.032 mm and <0.032 mm. For the analysis of BN1 and BN2 the fractions $0.045 < 0.125$ mm were used and for MB the fractions $0 < 0.063$ mm were used.

Purification Procedures

The purification procedures were designed in accordance with the thesis *Evaluation of water/wastewater quality in Blantyre city and heavy metal removal using alkaline clays and moringa seeds* by Sajidu (2008). The steps described below serve to remove impurities that can affect diffraction patterns for the x-ray analysis and other analytical methods. The three main categories of impurities are carbonates, iron oxides and organic matter. Presence of carbonates in the clay sample results normally in a poor x-ray diffraction pattern due to their poorly crystalline structure. In addition, the efficiency of hydrogen peroxide for organic matter removal is reduced. The carbonates are removed by reacting the clay with a buffer solution containing acetic acid and sodium acetate until no more evolution of carbon dioxide is evident. Iron oxides also disturb the x-ray diffraction pattern. In the purification procedure, Fe(III) is reduced by sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) to dissolved free Fe(II), sodium citrate is used to form chelates with both Fe(III) and Fe(II) in the clay. Finally, the organic matter has to be removed since it “glues” the clay together preventing the particles to disperse and separate, which is necessary for the following analysis. Hydrogen peroxide is used to oxidize the organic matter. The experimental methods for the purification procedures are designed to affect the actual components of the clays as little as possible.

Removal of carbonates

The clay fractions selected for the experiments were weighed in a glass beaker. The clays were then dispersed in 1 M sodium acetate-acetic acid buffer (8.2 g sodium acetate and 6 g pure acetic acid per 100 ml of water) in the relation 1:1 (for BN1 and BN2). More buffer solution was necessary for MB since smaller sized fractions were used resulting in a greater surface.

Table 4. Amount of clay and buffer solution added.

| Sample | Amount clay (g) | Amount buffer solution (g) |
|--------|-----------------|----------------------------|
| BN1 | 86.41 | 86 |
| BN2 | 74.50 | 74 |
| MB | 37.55 | 95 |

Bubbles of carbon dioxide, CO₂, emerging from the mixture indicate presence of carbonates. BN1 and BN2 were swirled around once a day for 6-7 days until no more carbon dioxide bubbles appeared. MB was swirled around once a day for seven days. Seeing that a significant number of bubbles were still emerging, the mixture was put on magnetic stirrer for four days to speed up the reaction. The mixtures were then centrifuged (Kubota KS-5200C) and washed several times with distilled water to reach a pH around 6.

Removal of iron oxides

The centrifuged clay samples were dispersed in a citrate buffer (108.8 g sodium citrate dehydrate, 8.4 g sodium hydrogen carbonate and 70 g sodium chloride per liter of water). pH was adjusted to 8.3 for each sample with drops of 2 M sodium hydroxide. Sodium dithionite was added and the mixtures were stirred for 70 hrs with magnetic stirrer.

Table 5. Amount of citrate buffer and sodium dithionite added for the Fe removal experiment.

| Sample | Volume citrate buffer (l) | Amount sodium dithionite (g) |
|--------|---------------------------|------------------------------|
| BN1 | 0.201 | 14.9 |
| BN2 | 0.233 | 17.32 |
| MB | 0.102 | 7.54 |

Next, the mixture was centrifuged and washed four times with a solution of 0.5 M sodium chloride and 0.025 M hydrochloric acid. The purification process for iron oxides was then repeated once more. The stirring part however, was replaced by end over end shaker with the mixture in a polypropylene centrifuge bottles to avoid grinding of the magnet by the hard clay material releasing unwanted components. The Fe that was not extractable by citrate-dithionite was assumed to be part of the layer silicate structure.

Removal of organic matter

The washed and centrifuged clay sample was transferred over to a glass beaker. 500 ml 0.1 M sodium acetate solution and 170 ml hydrogen peroxide solution (30%, aqueous) were mixed with the clay sample. The mixture was stirred with magnetic stirrer for 10 hrs at 90 °C. In the beginning, drops of octyl alcohol were added to break the surface tension and hamper the foam formation. Subsequently, the mixture was shaken in end over end shaker for 20 hrs at room temperature. In the last step, excess salt were taken out by washing the clay sample with distilled water. Finally, the clay was dried in a vacuum oven at 50 °C for approximately one week.

Physico-chemical experiments

In order to fully understand the reactions taking place on a mineral surface it is important to investigate its physico-chemical properties. As described in literature, essential parameters to determine are: specific surface area, charge density (Bolt, 1957), pH_{pzc} (Stumm, 1992), CEC and the acidity constants (Sverjensky&Sahai, 1996). Various methods have been developed and the following experiments were designed as described in Sajidu (2008) and references therein. Potentiometric titrations were performed on the purified samples of BN1 and BN2; there was not enough material for carrying out titration experiments on the MB sample. CEC determination experiments were carried out on all samples, both raw and purified material.

Potentiometric titrations

Potentiometric acid- base titrations are utilized to study amphoteric properties of the clay and how surface charge varies with pH. Data obtained from the experiments is also intended for calculation of the amount of active surface sites, acidity constants; both microscopic and intrinsic, and pH_{pzc} .

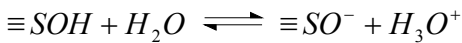
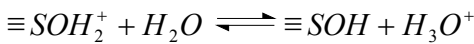
Acidimetric titrations

The experiment was set up with an automatic burette (Metrohm 665 Dosimat) filled with 20.078 mM nitric acid. 0.5 g of clay was dissolved with 50 g 0.100 M sodium nitrate as ionic medium and stirred with magnetic stirrer. 0.20 ml nitric acid was added stepwise up to 26 ml. The pH value was recorded at each equilibrium point using Ross Sure-Flow combination pH electrode. An additional titration was done with 2.5 g of clay in order to obtain more reliant measurements with larger surface area.

In contact with water the surface of a clay mineral contains $\equiv\text{SOH}$ groups that can dissociate or be protonated in the same way as water and form $\equiv\text{SO}^-$ or $\equiv\text{SOH}_2^+$, respectively. The total concentration of active acid- base sites is expressed by:

$$\{\equiv\text{SOH}_{\text{tot}}\} = \{\equiv\text{SOH}_2^+\} + \{\equiv\text{SOH}\} + \{\equiv\text{SO}^-\}$$

Where $\{\}$ denotes concentration of species on a solid surface whereas $[\]$ denotes concentration of species in solution. $\{\equiv\text{SOH}_2^+\}$ is considered to be a two-protonic acid with the following dissociation steps:



The uptake and release of protons is described with the acidic constants:

$$K_{a1}^s = \frac{[\equiv\text{SOH}] \cdot [\text{H}_3\text{O}^+]}{[\equiv\text{SOH}_2^+]}$$

$$K_{a2}^s = \frac{[\equiv\text{SO}^-] \cdot [\text{H}_3\text{O}^+]}{[\equiv\text{SOH}]}$$

From the titration plot the V_e value, which is the total volume of active surface sites, was approximated. The total concentration of active surface sites, $\{\equiv\text{SOH}_{\text{tot}}\}$, in each point was calculated using the V_e value in moles divided with the total volume:

$$V_e (\text{mole}) = 20.078 \text{ mM } H_3O^+ \cdot V_e (\text{ml}) \quad \{\equiv \text{SOH}_{\text{tot}}\} = \frac{V_e (\text{mole})}{V_{\text{tot}} (\text{l})}$$

The total concentration of surface charge Q was calculated using the added acid concentration in each point minus the measured acid concentration:

$$Q = [H_3O^+]_{\text{added}} - [H_3O^+]_{\text{measured}}$$

The mean number of protons, or charges, adsorbed per surface site was calculated by dividing Q with $\{\equiv\text{SOH}_{\text{tot}}\}$ for each equilibrium point:

$$Z = \frac{Q}{\{\equiv \text{SOH}_{\text{tot}}\}}$$

Furthermore, microscopic K_{a1} values were calculated according to equations above. $\text{p}K_{a1}$ versus Z in each point were plotted in a diagram to obtain intrinsic $\text{p}K_{a1}$ through linear extrapolation to charge zero.

Alkalimetric titrations

A similar titration on a new suspension was done with 20.00 mM sodium hydroxide. First, 2.5 g of clay was used. After no equilibrium point was reached the experiment was repeated once more with 0.5 g of clay.

Data from the alkalimetric titrations was treated similar as described above. Using the V_e value obtained from the acidimetric titration plot the total concentration of active surface sites, $\{\equiv\text{SOH}_{\text{tot}}\}$, in each point was calculated:

$$\{\equiv \text{SOH}_{\text{tot}}\} = \frac{V_e (\text{mole})}{V_{\text{tot}} (\text{l})}$$

The total concentration of surface charge Q was calculated using the added base concentration in each point minus the base concentration (calculated from the recorded pH value):

$$Q = [OH^-]_{\text{added}} - \left[\left(\frac{10^{-14}}{[H_3O^+]_{\text{meas.}}} \right) \right]$$

The mean number of protons, or charges, adsorbed per surface site was calculated by dividing Q with $\{\equiv\text{SOH}_{\text{tot}}\}$ for each equilibrium point:

$$Z = \frac{Q}{\{\equiv\text{SOH}_{\text{tot}}\}}$$

Furthermore, microscopic K_{a2} values were calculated according to equations above. $\text{p}K_{a2}$ versus Z in each point were plotted in a diagram to obtain intrinsic $\text{p}K_{a2}$ through linear extrapolation to charge zero.

From $\text{p}K_{a1}$ and $\text{p}K_{a2}$ pH_{pzc} could be determined:

$$\text{pH}_{\text{pzc}} = 0.5(\text{p}K_{a1} + \text{p}K_{a2})$$

CEC determination

Cation exchange capacity (CEC) is the clay's total capacity to exchange and electrostatically adsorb cations. CEC is expressed as cmole_c/kg and corresponds to the total amount of negatively charged sites on the surface of the clay mineral.

Methods for determination of CEC are commonly based on saturating a sample with one cation, washing the excess, followed by replacement of the added cation with another cation. The amount of the replaced cation is then determined analytically. In this work, CEC was determined using copper bisethylenediamine according to the method described in Sajidu (2008) and references therein.

13.445 g CuCl_2 was dissolved in 100 ml distilled water. 30.07 g ethylenediamine was dissolved in 500 ml distilled water. 50 ml of the CuCl_2 solution and 102 ml of the ethylenediamine solution were mixed together. The solution was then diluted to 1 l with distilled water to give 0.05 M $[\text{Cu}(\text{EDA})_2]^{2+}$. The slight excess of ethylenediamine solution ensures complete complex formation.

1 g of dry clay was weighed in centrifuge tubes. Each sample was repeated three times for statistical reasons. 4 ml $[\text{Cu}(\text{EDA})_2]^{2+}$ solution was added and diluted with 25 ml of distilled water. After being shaken for approximately 30 minutes the samples were centrifuged. The supernatant were diluted 100 times and the absorbance was determined by atomic absorption spectroscopy (AAS) using Perkin Elmer AAnalyst 100.

A calibration curve was created. The concentration of $\text{Cu}(\text{II})$ adsorbed to the mineral was calculated by subtracting the measured copper concentration in the supernatant with the total concentration of copper in the solution. The CEC in cmole_c/kg was then calculated by dividing the amount of adsorbed copper times two by the weighed amount of dry clay.

Heavy metal adsorption

The influence of pH on adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} to the mineral surface was investigated. Results from the titration and structural experiments show very little difference between BN1 and BN2 they were treated as one sample for this experiment.

0.5 g clay was suspended in 1 mM metal solutions and pH was adjusted to a certain value with 0.1 M nitric acid or 0.1 M sodium hydroxide. The mixtures were shaken for 48 hrs and then centrifuged for 15 minutes at 3000 rpm in (Kubota KS-5200C). The pH value in the supernatant was recorded and then the supernatant was diluted and analyzed for the given metal concentration on AAS (Perkin Elmer AAnalyst 100).

Preparation

A certain amount of the metal was mixed with 0.1 M sodium nitrate in a 100 ml flask. 1 ml 0.1 M nitric acid was added to avoid hydrolysis and keep the ionic strength stable.

Table 6. Metal solution preparation data

| Metal | Pb | Cu | Cd | Cr | Zn |
|--------------------|----------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|
| Species | $\text{Pb}(\text{NO}_3)_2$ | $\text{Cu}(\text{NO}_3)_2$ | $\text{Cd}(\text{NO}_3)_2$ | $\text{Cr}(\text{ClO}_4)_3$ | $\text{Zn}(\text{NO}_3)_2$ |
| Amount (g) | 0.033 | 0.024 | 0.034 | 100 μl | 0.030 |
| Concentration (mM) | 1 | 1 | 1 | 1 | 1 |
| g/l | 0.33 | 0.24 | 0.34 | | 0.30 |

In a centrifuge tube 0.5 g of clay was weighed. To each tube 9 ml of metal solution was added. The volume metal solution was calculated based on the V_e value obtained from the first titration experiment as follows:

$$V_e\text{-value} = 0.45 \times 10^{-3} \quad \text{Acid conc.} = 0.020 \text{ M}$$

$$n = C \cdot V$$

$$0.45 \times 10^{-3} \cdot 0.020 = 9 \times 10^{-6} \text{ moles surface positions/0.5 g clay} \rightarrow 18 \times 10^{-6} \text{ moles surface positions per gram clay}$$

$$1.0 \times 10^{-3} \cdot X = 18 \times 10^{-6} \rightarrow X = 0.018 \text{ l}$$

0.5 g clay, 9 ml metal solution

pH was adjusted in each tube using 0.1 M nitric acid or 0.1 M sodium hydroxide.

Table 7. Data for mixture preparation

| Metal | | Pb | Cu | Cd | Cr | Zn |
|------------------------|---|-------|-------|-------|-------|-------|
| EXP. 1 (BN): | | | | | | |
| Amount clay | | | | | | |
| Sample | 1 | 0.500 | 0.502 | 0.499 | 0.502 | 0.500 |
| | 2 | 0.507 | 0.503 | 0.501 | 0.510 | 0.499 |
| | 3 | 0.500 | 0.500 | 0.500 | 0.503 | 0.500 |
| | 4 | 0.501 | 0.500 | 0.514 | 0.505 | 0.500 |
| | 5 | 0.503 | 0.500 | 0.506 | 0.502 | 0.500 |
| | 6 | 0.500 | 0.505 | 0.507 | 0.509 | 0.500 |
| pH (start) | | | | | | |
| Sample | 1 | 2.93 | 2.98 | 2.96 | 3.17 | 3.13 |
| | 2 | 5.04 | 5.44 | 4.99 | 4.92 | 4.92 |
| | 3 | 6.91 | 7.01 | 7.04 | 7.05 | 7.00 |
| | 4 | 7.98 | 7.68 | 8.32 | 7.93 | 7.91 |
| | 5 | 8.93 | 9.11 | 8.88 | 9.27 | 9.42 |
| | 6 | 10.82 | 10.78 | 10.92 | 10.77 | 11.06 |
| Added acid (µl) | | | | | | |
| Sample | 1 | 100 | 100 | 100 | 100 | 100 |
| | 2 | | 90 | 30 | | |
| | 3 | | | 10 | | |
| | 4 | 10 | 30 | | | |
| | 5 | 5 | | | | |
| | 6 | | | | | |
| Added base (µl) | | | | | | |
| Sample | 1 | | | | | |
| | 2 | 30 | 130 | 80 | 45 | 10 |
| | 3 | 145 | 190 | 75 | 200 | 105 |
| | 4 | 175 | 225 | 100 | 220 | 190 |
| | 5 | 190 | 200 | 140 | 250 | 240 |
| | 6 | 300 | 320 | 300 | 325 | 300 |
| EXP. 2 (MB): | | | | | | |
| Amount clay | | | | | | |
| Sample | 1 | 0.497 | 0.501 | 0.506 | 0.505 | 0.512 |
| | 2 | 0.490 | 0.503 | 0.507 | 0.511 | 0.497 |
| | 3 | 0.519 | 0.499 | 0.505 | 0.513 | 0.503 |
| | 4 | 0.504 | 0.495 | 0.495 | 0.494 | 0.511 |
| | 5 | 0.505 | 0.499 | 0.496 | 0.505 | 0.516 |
| | 6 | 0.495 | 0.496 | 0.502 | 0.505 | 0.500 |
| pH (start) | | | | | | |
| Sample | 1 | 3.52 | 3.86 | 3.59 | 3.78 | 3.24 |
| | 2 | 4.67 | 5.62 | 5.16 | 5.15 | 5.20 |
| | 3 | 6.67 | 6.46 | 7.38 | 6.68 | 6.93 |
| | 4 | 8.10 | 8.69 | 8.31 | 7.85 | 8.20 |
| | 5 | 8.90 | 9.10 | 8.87 | 8.64 | 8.87 |
| | 6 | 10.41 | 10.38 | 10.76 | 10.43 | 10.74 |
| Added acid (µl) | | | | | | |
| Sample | 1 | 500 | 500 | 500 | 500 | 700 |

| | | | | | | |
|------------------------|---|-----|-----|-----|-----|-----|
| | 2 | 200 | 100 | 200 | | 200 |
| | 3 | 250 | | | | |
| | 4 | 80 | | 40 | | |
| | 5 | | | | | |
| | 6 | | | | | |
| Added base (μl) | | | | | | |
| Sample | 1 | | | | | |
| | 2 | | | | | |
| | 3 | 100 | | | 60 | |
| | 4 | 200 | 100 | 100 | 150 | 100 |
| | 5 | 120 | 120 | 100 | 200 | 130 |
| | 6 | 240 | 200 | 300 | 400 | 300 |

AAS analysis

The supernatant was diluted to fit the linear range given in Analytical Methods for Atomic Absorption Spectrometry. The absorbance was measured and from a calibration curve the adsorbed concentration could be calculated.

Table 8. AAS data

| Metal | Pb | Cu | Cd | Cr | Zn |
|------------------------|---|---|---|---|---|
| Stock soln. conc. (mM) | 1 | 1 | 1 | 1 | 1 |
| Wavelength (nm) | 217.0 | 324.8 | 228.8 | 213.9 | 357.9 |
| Linear range (M) | $2.0 \times 10^{-6} - 1.0 \times 10^{-4}$ | $1.6 \times 10^{-6} - 7.9 \times 10^{-5}$ | $3.6 \times 10^{-7} - 1.8 \times 10^{-5}$ | $2.0 \times 10^{-6} - 1.0 \times 10^{-4}$ | $3.0 \times 10^{-7} - 1.5 \times 10^{-5}$ |
| Dilution (times) | 20 | 20 | 100 | 20 | 100 |

Table 9. Equilibrium pH and measured absorbance

| | | Table 9: Equilibrium pH and measured absorbance | | | | |
|----------------|---|---|-------|-------|-------|-------|
| Metal | | Pb | Cu | Cd | Cr | Zn |
| EXP. 1 (BN): | | | | | | |
| Equilibrium pH | | | | | | |
| Sample | 1 | 3.59 | 3.32 | 3.79 | 3.43 | 3.35 |
| | 2 | 4.72 | 5.02 | 5.24 | 4.04 | 4.63 |
| | 3 | 4.74 | 6.24 | 6.30 | 6.58 | 6.42 |
| | 4 | 6.54 | 6.73 | 6.92 | 6.94 | 6.93 |
| | 5 | 6.86 | 7.87 | 7.32 | 7.94 | 7.34 |
| | 6 | 10.24 | 9.96 | 10.27 | 10.21 | 10.18 |
| Absorbance | | | | | | |
| Sample | 1 | 0.412 | 0.163 | 0.212 | 0.038 | 0.195 |
| | 2 | 0.345 | 0.138 | 0.200 | 0.023 | 0.177 |
| | 3 | 0.060 | 0.006 | 0.192 | 0.001 | 0.163 |
| | 4 | 0.006 | 0 | 0.122 | 0.001 | 0.03 |
| | 5 | 0.001 | 0 | 0.082 | 0.001 | 0.003 |
| | 6 | 0.001 | 0 | 0.001 | 0.001 | 0.002 |
| EXP 2. (MB): | | | | | | |
| Equilibrium pH | | | | | | |
| Sample | 1 | 4.11 | 4.37 | 4.14 | 3.99 | 3.92 |
| | 2 | 5.01 | 6.10 | 5.92 | 6.09 | 5.74 |
| | 3 | 7.00 | 7.08 | 7.12 | 6.65 | 6.97 |
| | 4 | 7.80 | 8.46 | 7.78 | 7.35 | 8.23 |
| | 5 | 8.32 | 8.76 | 8.25 | 7.79 | 8.67 |
| | 6 | 9.95 | 9.96 | 10.35 | 10.02 | 10.34 |
| Absorbance | | | | | | |
| Sample | 1 | 0.070 | 0.061 | 0.011 | 0.005 | 0.117 |
| | 2 | 0.021 | 0.003 | 0.152 | 0 | 0.057 |
| | 3 | 0.004 | 0.001 | 0.109 | 0 | 0.006 |
| | 4 | 0.002 | 0.001 | 0.028 | 0 | 0 |
| | 5 | 0.001 | 0.001 | 0.005 | 0 | 0 |
| | 6 | 0.001 | 0.002 | 0.003 | 0.003 | 0 |

Mineralogical analysis

Two techniques were used in order to characterize the mineral composition, structure and morphology of the clay.

Scanning Electron Microscope (SEM)

Electron microscopes produce micrographs that cannot be seen with light microscopes. It uses electrons instead of light to produce an image of the sample by detecting low energy secondary electrons which are emitted from the surface. In the SEM, the electron beam is rastered across the sample, with detectors building up the micrograph by mapping the detected signals with beam position. (Chang, 2005)

The samples; BN1, BN2, MB, both raw and purified were attached to carbon sticker and placed in the SEM Hitachi TM-1000 at the Department of Chemistry, SLU. The images obtained were analyzed with the computer software program SwiftED-TM. Elemental analyses were carried out with the same program. This was made scanning part of the surface. The system detects Na and heavier elements. Consequently, elements such as C, H, O and N cannot be detected. In the case for minerals, oxygen is assumed to be the dominating element adjacent to the detected elements.

Powder X-ray diffraction

X-ray powder diffraction (XRD) analysis was performed on all samples; BN1, BN2 and MB, both purified and raw. Images of XRD patterns for the samples were collected using the software program SMART CCD 1 K at the Department of Chemistry, SLU with monochromatic MoK α ($\lambda = 0.7093 \text{ \AA}$) radiation. The XRD patterns were integrated and converted to a 2D diffraction pattern with peaks to be identified. The software program EVA was used to identify the “fingerprint” and give suggestions on possible minerals.

Results and Discussion

The experimental part of this study has provided useful information about the structural and physico-chemical properties of the unknown mineral. The essential question to bear in mind throughout the whole experimental procedure is: what information is obtained in each method? The picture of putting a puzzle together has been a way of visualizing the task better. Below the findings from the mineralogical experiments with SEM and X-ray powder diffraction (XRD) are summarized. After that, the results from the potentiometric titrations and metal adsorption experiments are presented. Accompanying each result is a brief discussion.

Mineralogical analyses

The shape of the particles is important to account for since edges tend to be more reactive than “flat” surfaces (Stumm, 1992). The SEM gives an indication whether the material is crystalline or amorphous. Micrographs of BN1 and BN2 (Figs. 10 and 11) give a rather clear indication that the material is crystalline. Most particles have sharp edges typical for a crystalline structure. Some particles have a rough surface that most likely is even smaller particles attached to the surface. The particle sizes are ranging from 8 μm to 30 μm . There is also a few bigger “clumps” sized 80 μm that can either be small aggregated particles that are crystalline or one big amorphous “clump”. The elemental analyses for BN1 and BN2 show that the dominating element in the samples is silica (Appendix 1 and 2). There is also a small fraction of aluminum and, in BN2 some iron and titanium. These amounts however are negligible since it is measured by weight percent and iron and titanium have greater molecular weight than silica. As pointed out in the materials and method section, oxygen is assumed to be the dominating element for clay minerals.

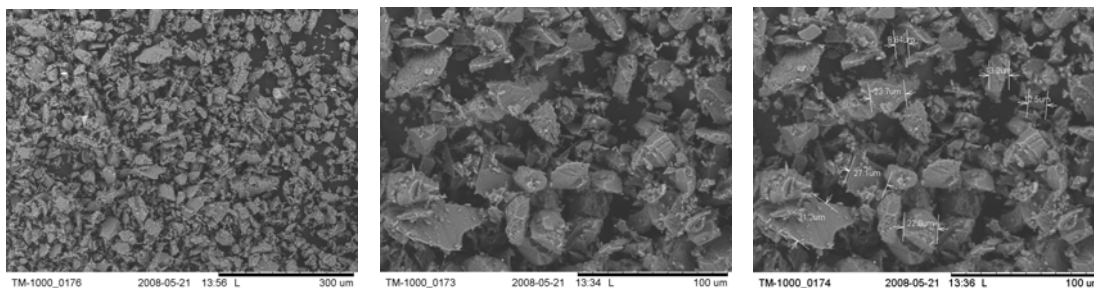


Figure 10. SEM micrographs of BN1.

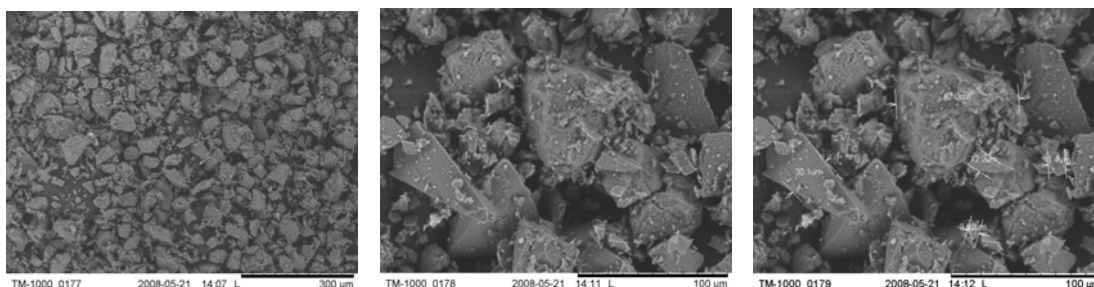


Figure 11. SEM micrographs of BN2.

The SEM images of the MB sample give a somewhat different picture. In figure 12 it is difficult to distinguish separate particles and the clumped together material is either amorphous or very small aggregated, crystalline particles. In order to clearly settle on a crystalline structure, the samples have to be analyzed with x-ray diffraction. The elemental analysis also shows that MB differs from the two other samples. The main components are aluminum and iron and to a lesser extent silica (Appendix 3). An incomplete purification procedure might be the answer to the high iron content but the fact that the silica fraction is low indicates that MB has a different mineral composition than BN1 and BN2.

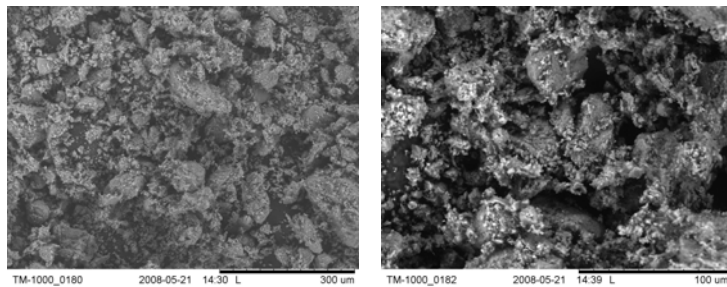


Figure 12. SEM micrographs of MB.

BN1, BN2 and MB are all confirmed to consist of crystalline material through the x-ray powder diffraction analysis. The diffracted beams give a diffraction pattern with distinct ring formation which is the ultimate evidence for a crystalline structure (Fig. 13). The diffraction plots for all samples show similar patterns and peaks (Appendices 4-9). The raw samples of BN1 and BN2 have peaks at the expected positions for quartz (Appendices 4, 5) and when comparing them with the purified samples (Appendices 7, 8) there is little difference. In the raw and pure samples of MB the diffraction plot have peaks with heights and positions expected for quartz (Appendices 6, 9). There are also peaks that correspond to minerals like halloysite. A few unidentified peaks are present but are assumed to be Al-hydroxides since the purification procedure did not remove impurities such as Al-hydroxides and the element analysis with the SEM indicate a small amount of aluminum in all samples. Important to remember is that with x-ray diffraction only crystalline material will appear. This method does not reveal possible presence of amorphous material. Iron could not be detected in any sample. Therefore, the iron found in MB through the SEM elemental analysis must therefore be amorphous.

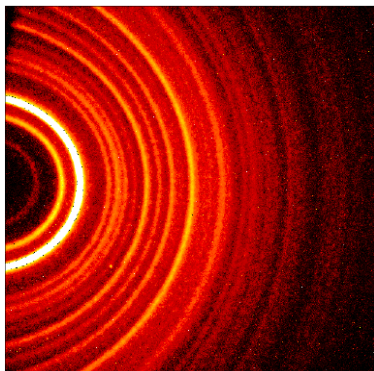


Figure 13. Diffraction pattern

In summary, the mineral characterization point out quartz as the dominating component in all three samples. With less certainty, Al-hydroxide could also be present, but to a lesser extent. The MB sample also has halloysite as a major component and probably amorphous iron compounds.

Potentiometric titrations

Initial pH measurements of the purified clay samples of BN1, BN2 and MB show neutral, or close to neutral, natural pH values ranging from 6.51 to 7.54 (Table 10). This is also the case for the raw clay samples. Slightly lower pH values are noted in the raw samples. This can be explained by the presence of acidifying factors such as humic acids in the unpurified (raw) samples. Note however that a greater amount of clay material results in a higher pH, which may be explained by the increased amount of surface sites that act as bases, i.e. $\equiv\text{SO}^-$.

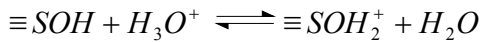
Table 10. Natural pH values of BN1, BN2 and MB

| Sample | Amount (g) | pH |
|---------|------------|------|
| BN1:raw | | 6.23 |
| BN1 | 2.5 | 7.54 |
| BN1:1 | 0.502 | 6.81 |
| BN1:2 | 0.501 | 6.73 |
| BN1:3 | 0.503 | 6.87 |
| BN2:raw | | 5.88 |
| BN2:1 | 0.501 | 6.58 |
| BN2:2 | 0.500 | 6.51 |
| BN2:3 | 0.501 | 6.68 |
| MB:raw | | 5.38 |
| MB | 0.500 | 9.35 |

Acidimetric titrations

From the acidimetric titrations made on 1 g clay/100 ml ionic medium a V_e value was estimated from the titration plot to be 0.45 ml. This gives an amount of 1.83×10^{-5} moles active surface sites/g, a relatively low value that indicate that very little of the added acid has reacted with the surface.

Acidimetric titrations were carried out with the intention to determine the first acidic constant of the clay material. This protonation reaction is assumed to take place, leading to a positively charged surface:



From where the K_{a1} can be calculated using:

$$K_{a1}^s = \frac{[\equiv\text{SOH}] \cdot [\text{H}_3\text{O}^+]}{[\equiv\text{SOH}_2^+]}$$

Microscopic pK_a values were calculated for each equilibrium point in the titration curve. These pK_a values were plotted against the charge of the surface (Z). Through extrapolation to charge zero, the intrinsic pK_a value could be obtained (Fig. 14 a, b). Plots for BN2 were almost identical with initial pH as the only varying factor. This gives a pK_{a1} value close to 5. According to theoretical predictions through modeling, $\log K_1$ for quartz is -1.6 (Double Layer Model) and -1.3 (Triple Layer Model) (Sverjensky&Sahai, 1996). Basically this means that the first acidic constant for quartz is not measurable. Consequently, the protonation reaction of the surface cannot occur and the surface is never positively charged over a “normal” pH range. The first protonation constant for quartz can then only be indirectly estimated as concluded by Pokrovsky et al (2005).

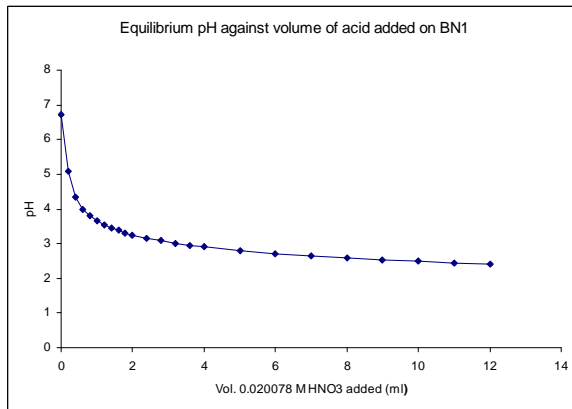


Figure 14a. Titration plot for BN1.

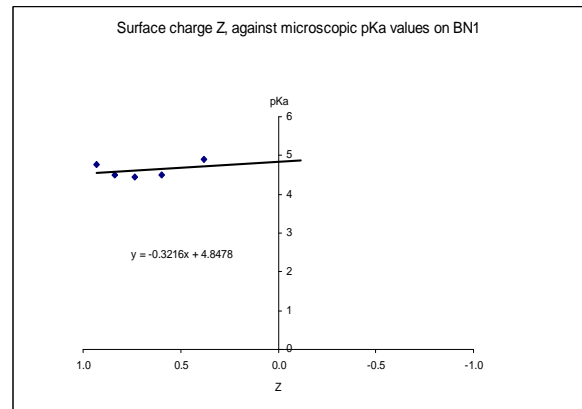


Figure 14b. Intrinsic pK_a value.

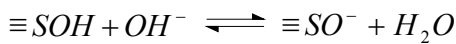
From the mineralogical analysis it was concluded that the dominating material in all clay samples is quartz. Quartz reacts like a strong acid, never holding $\equiv\text{SOH}_2^+$ sites in the

surface. Therefore, the plots from the acidimetric titration do not give an accurate description of the reactions that takes place on the surface of quartz. On the other hand, it gives an indication that something else is present besides quartz in this material and that this impurity has a buffer capacity and acid-base properties since protonation of a surface obviously takes place. The pK_{a1} value obtained from the acidimetric titration represents an average pK_a for the uptake of protons that the unidentified impurity possesses.

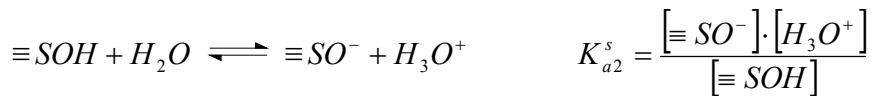
Alkalimetric titrations

Similar V_e value was obtained from the alkalimetric titration plot, 0.465 ml. This slightly higher volume results in an amount of 1.868×10^{-5} moles active surface sites/g or a concentration of 1.82×10^{-4} M. Usually the alkalimetric titrations are the most uncertain measurements in potentiometric experiments; the titration is sensitive to carbonate formation and the deprotonation reaction taking place on the surface is not always complete. For this study however, it turned out to be the most reliable parameter.

Deprotonation reaction:



The K_{a2} value can be calculated using the following reaction:



Similar data treatment was carried out for the alkalimetric titrations resulting in the following plots, (Fig. 15 a, b, c, d).

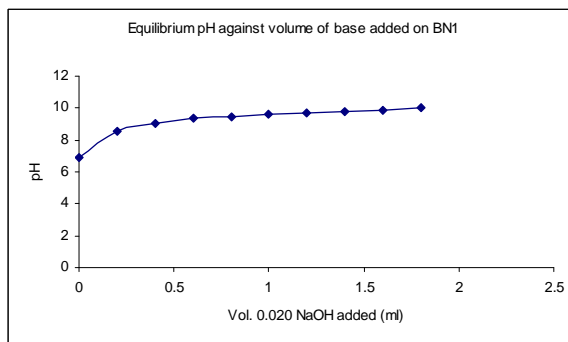


Figure 15a. Titration plot for BN1

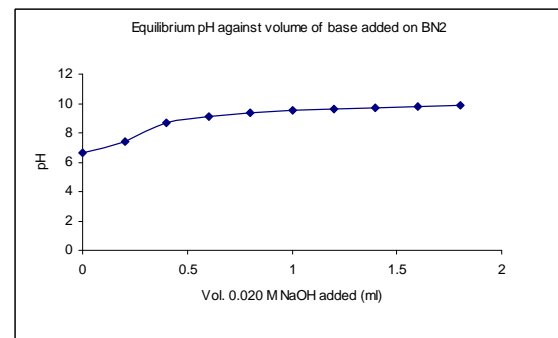


Figure 15b. Titration plot for BN2

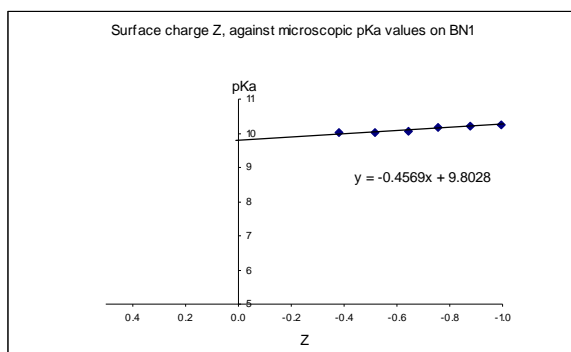


Figure 15c. Intrinsic pK_a value for BN1.

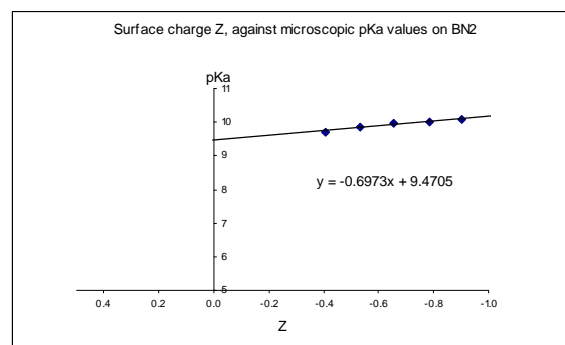


Figure 15d. Intrinsic pK_a value for BN2.

This gives an average pK_{a2} of 9.72. These values seemed to be somewhat closer to previous predictions. In Sverjensky's modeling predictions (1996) $\log K_2$ is 7.6 in the Double Layer Model and 7.1 in the triple Layer Model. Nevertheless, modeling predictions are precarious and exact results are not always achieved.

This leads to complications in determination of the pH_{pzc} , since only one plausible acidic constant is available. The concept of pH_{pzc} is therefore not applicable in this case and the surface is neutral over a wide pH range rather than at a specific point. However, Sverjensky (1996) predicts the pH_{pzc} for quartz to be 3.0 or 2.9. Parks (1965) came to a similar conclusion in his study where a large number of quartz materials were investigated. The pH_{pzc} values predicted were ranging from ≈ 2.5 -2.9. pH_{pzc} can be discussed whether it is a concept relevant for all types of minerals. Clearly, for this quartz dominating material it is not.

Conclusively, the surface is neutral up to pH values around 9, where the surface charge starts to become negative. If too much base is added in the alkalimetric titration, quartz starts to dissolve. In order to obtain reliable results the material is required to be chemically stable over the investigated pH range. If not, one is simply directed to theoretical extrapolations.

CEC determination

It is generally considered that quartz does not possess a measurable capacity to exchange cations (Eriksson, 2008). Previous studies on quartz show that the cation exchange capacity (CEC) is low, 0.26 cmolc/kg (Kelm&Helle, 2005). The low or non-existent CEC is explained by the absence of structural charge and high level of weathering.

CEC proved to be low in all samples, with almost no difference between BN1 and BN2 (Table 11). As explained above a low CEC is logic due to lack of permanent charge. Furthermore, there is a low level of organic matter which is an important contributor to CEC through humic acids. The only source of charge is then the variable charge, or the pH dependent. Since the surface is neutral up to pH 9, there will be no negatively charged surface positions giving rise to a CEC until the pH value reaches above 9. MB samples had somewhat higher values. The MB sample has possibly a fraction of halloysite which

may be the reason to a slightly higher CEC in those samples. Takahashi *et al.* (2001) have investigated the cation exchange capacity for halloysite and found values as high as 19-26 cmolc/kg. These values are considered unusually high and values from 4.9 and up seem more common (Guiliano *et al.*, 1999; Lee&Kim, 2001). Raw samples had slightly higher values in comparison to purified samples (Fig. 12). This is explained by iron oxides and organic material in the raw samples contributing to a higher capacity of exchanging cations. The moles adsorbed correspond to 1.868×10^{-5} moles active surface sites/g obtained from the potentiometric titrations.

Table 11. CEC and μ moles cations adsorbed on purified clay samples

| Purified samples | μ moles adsorbed per gram | CEC (cmole _c /kg) |
|-------------------|-------------------------------|------------------------------|
| BN1:1 | 2.89 | 0.586 |
| BN1:2 | 1.95 | 0.374 |
| BN1:3 | 1.38 | 0.276 |
| mean value | 2.07 | 0.412 |
| BN2:1 | 1.26 | 0.245 |
| BN2:2 | 1.08 | 0.215 |
| BN2:3 | 1.11 | 0.218 |
| mean value | 1.15 | 0.292 |
| MB:1 | 5.73 | 1.166 |
| MB:2 | 5.54 | 1.113 |
| MB:3 | 5.54 | 1.142 |
| mean value | 5.60 | 1.140 |

Table 12. CEC and μ moles cations adsorbed on raw clay samples

| Raw samples | μ moles adsorbed per gram | CEC (cmole _c /kg) |
|-------------------|-------------------------------|------------------------------|
| BN1R:1 | 3.38 | 0.460 |
| BN1R:2 | 2.10 | 0.416 |
| BN1R:3 | 2.41 | 0.449 |
| mean value | 2.63 | 0.442 |
| BN2R:1 | 2.13 | 0.418 |
| BN2R:2 | 2.10 | 0.421 |
| BN2R:3 | 2.04 | 0.401 |
| mean value | 2.09 | 0.413 |
| MBR:1 | 5.51 | 1.079 |
| MBR:2 | 5.79 | 1.098 |
| MBR:3 | 5.97 | 1.100 |
| mean value | 5.75 | 1.092 |

Heavy metal adsorption

In this study the clay material from BN1 and BN2 have shown to completely remove Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} from aqueous solution at different pH ranges (Fig. 16). In the pH range from 4.7 to 6.5 lead is removed from 0% to 100%. Copper is 100% removed at pH 6.2. Chromium was gradually adsorbed to the clay material in the pH range of 3.4 to 6.6. For zinc there was a rapid change in percent adsorbed taking place at around pH 7. Cadmium on the other hand was gradually adsorbed from pH 6.3 with complete removal at pH 10.3.

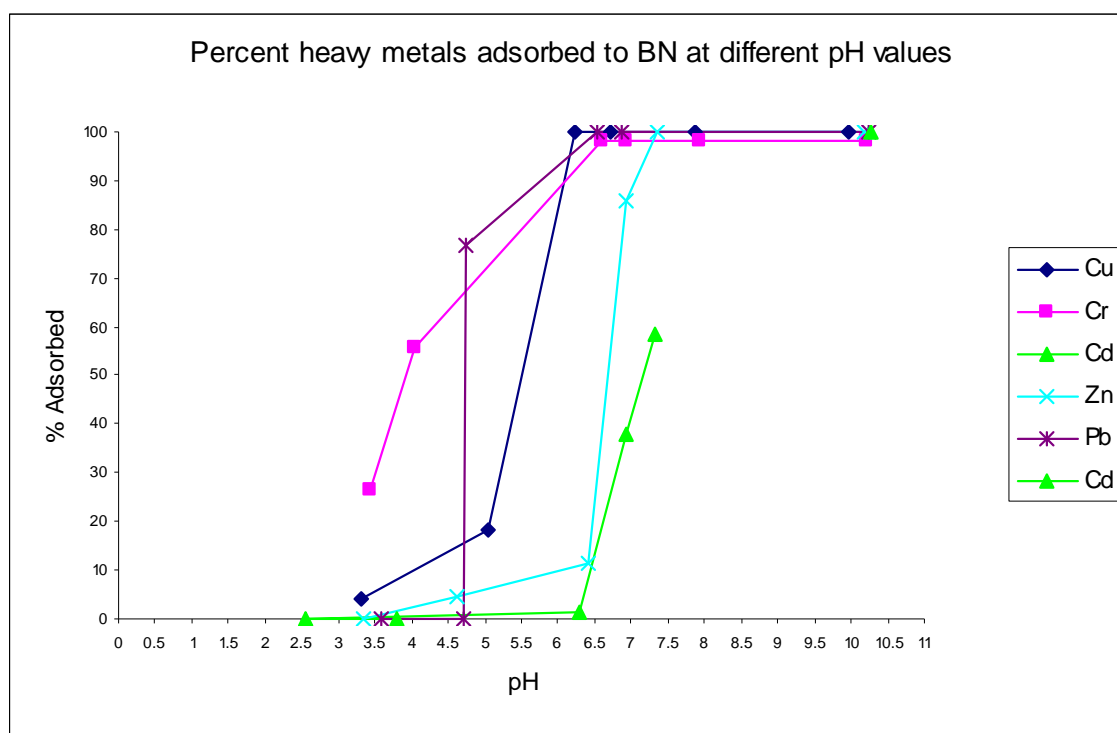


Figure 16. Adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} to BN.

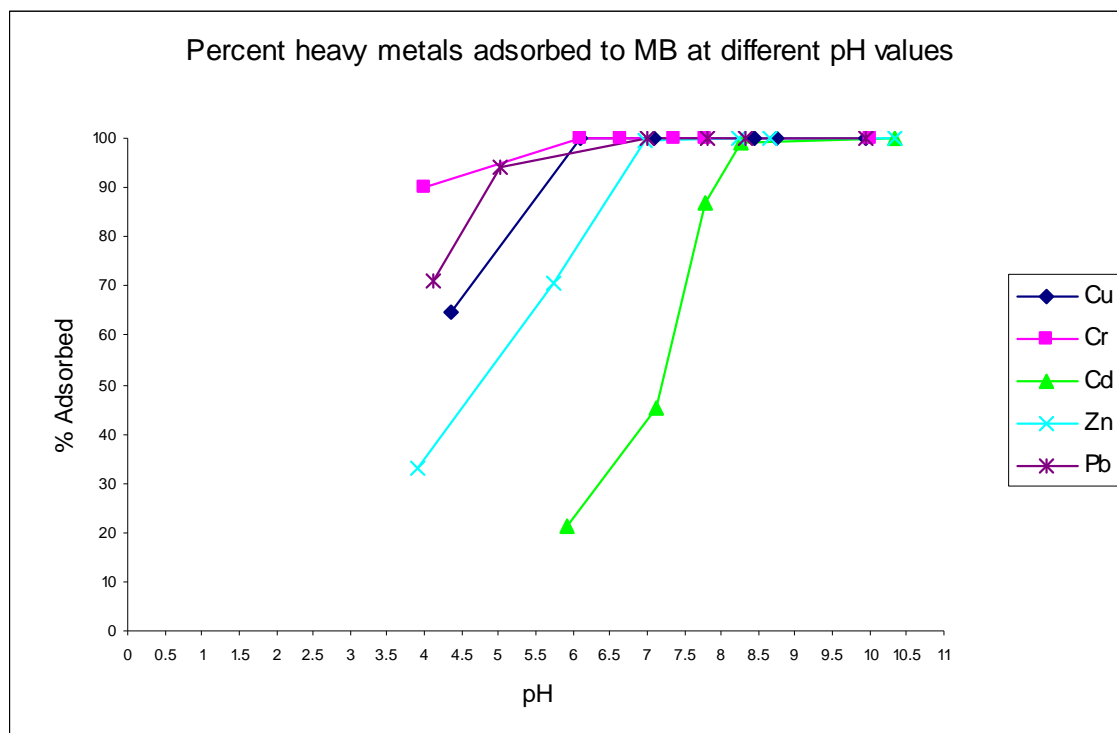


Figure 17. Adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} to MB.

Similar results were obtained from experiments with the MB sample (Fig. 17). Lead is adsorbed to 70% at pH 4 and at pH 7 a complete removal was observed. Copper behaved in the same way as in the first experiment; at pH 6.1 100% was removed. The adsorption of chromium was slightly different with a nearly complete removal at pH 4. However, the 100 % adsorption took place at almost the same pH value as for BN, pH 6. Zinc was not adsorbed as rapidly in MB as it was in BN. On the contrary, a gradual adsorption took place between pH 3.9 and 7. Nevertheless, at pH 7 zinc was 100% adsorbed in both clay samples. Cadmium adsorbed gradually as in BN but reached complete adsorption at a lower pH value than for BN.

Conclusively, the two clay samples are more or less identical in their capacity of completely remove the metals. At pH 7 all metals except cadmium are 100% adsorbed. The only difference is the pH where the least amount of metal is adsorbed. This is less significant since the importance is at which pH value a complete removal takes place.

The potentiometric titrations showed that the clay has a wide pH range rather than a specific point (pH_{pzc}) where the surface is neutral. The pK_{a2} value was determined to be around 9 which means that above pH 9 the surface starts to become deprotonated and negatively charged. Cations that adsorb to the surface when it is neutral presumably form inner-sphere complexes. Since 100 % adsorption is in effect at pH 7 all metals are adsorbed to the surface as inner-sphere complexes. In addition, electrostatic forces come into effect above pH 9 making the bond even stronger. However, to claim the sorbent to be quartz is arguable. With an unidentified amorphous material being present and also

some Al-hydroxides there is a chance that the adsorption takes place on those surfaces. Thus, it is not certain that inner-sphere complexes are formed. For example, if the Al would come from muscovite with a pH_{pzc} of 6.3 (Sverjensky&Sahai, 1996) lead, chromium and zinc could be adsorbed outer-spherically. But, if the Al-hydroxide would be gibbsite, inner-sphere complex formation would take place rather than outer-sphere since the pH_{pzc} for gibbsite is 9.0 (Sverjensky&Sahai, 1996). It is Important to remember that values of pH_{pzc} can differ significantly between published papers. Purenness and age of the clay mineral can be the key factors. It is important to bear in mind that values for pH_{pzc} for clay minerals are neither absolute nor something that is agreed upon. To determine the type of complex formation with higher certainty experiments with Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) have to be performed.

Using this clay mineral, dominated by quartz, for heavy metal removal requires fairly high pH values for the water being treated. Measured natural pH values for the BN samples and for MB are between 5 and 7. If this would be the case also for the water in need of treatment it is questionable if this specific clay mineral is suitable. The pH has to be well above 7 to be certain that all metals are adsorbed. On the other hand, if the heavy metal problem is mainly concerning copper, lead and possibly chromium, the treatment can be successful even if the pH is below 6.

The equilibrium and kinetics of natural sorbents was studied by Al-Degs *et al.* (2006). They found that natural mineral consisting of mainly primary minerals, i.e., quartz and aluminosilicates and secondary minerals, i.e., calcite and dolomite was efficient in removal of Zn(II), Pb(II) and Co(II) from aqueous solution.

Conclusions

The following conclusions can be drawn with the combined information from all experiments carried out:

All three samples have crystalline quartz as the dominating component. Quartz is giving the clay minerals their characteristic properties.

The surface charge is neutral at normal soil- and water pH values.

The capacity of exchanging cations is exceptionally low.

Metal cations are 100 % adsorbed to the surface from pH 7 and up.

A few general conclusions on clay minerals and their use in experimental work and as heavy metal sorbents are as follows:

The material need to be chemically stable over the studied pH range, otherwise one is directed to predictions and theoretical extrapolations.

Different clays have different properties primarily depending on their physico-chemical characteristics and mineralogical structure

Future perspectives

There is a clear consensus all over the world and within organizations such as the UN and EU that the water crises in many parts of the world are becoming increasingly severe. Whether the problems concern too much water or not enough, pollution or water-borne diseases, water remains as the essential factor for social and economic development. As stated in a number of UN reports the solution for many water related problems is better governance. However, technical development also plays an important role in ensuring access to safe water. The source of heavy metal pollution is not always poor management or weak legislation. In many cases heavy metal pollution of waters derives from sources that are difficult, or sometimes even impossible to control, for example natural leakage from bedrocks or sediments, or fertilizing agents used in agriculture. In addition, a number of rivers, streams and ground-water reservoirs are already contaminated and in urgent need of remediation measures. Technology and science play therefore a central role in the necessary steps towards the fulfillment of the MDG's.

Historically, development policies have been dominated by the idea that aid or, *development assistance*, is the transfer of wealth and specialized knowledge from one side to relatively passive recipient. With lessons learned from non-sustainable development projects in many countries, new more modern policies have been developed. The most important one, the Paris declaration from 2005, revolutionized development aid or *development cooperation* as it is now termed, where mutual responsibility, better coordination and important commitments is the motto. In their updated report: New Policy for Global Development, The Swedish International Development Cooperation Agency (Sida) point out education and shared knowledge as key factors for reaching the MDG's.

As pointed out in the introduction, developing countries need cost-effective methods that are easy to implement. The use of natural clay minerals for heavy metal removal has satisfied both these requirements and also proven to be very useful and efficient. However, from the ratiocinated conclusions in this study it becomes obvious that further research in this field is necessary. Every clay mineral has its own properties and characteristics, for example the Mali soils demonstrate completely opposite properties compared to the Malawi soils used in another, similar study. In order to develop solutions applicable in different countries clay minerals and their characteristics and capacity of adsorbing pollutants need to be investigated and mapped.

With rather simple methods this research is feasible. However, to make efficient use of science and technology a scientific base is essential. With the new policies for development cooperation in mind sharing knowledge and supporting education in the basic sciences such as chemistry and biology is a first step. Aid donors, for example Sweden, have the role of providing knowledge and support the countries own initiative and work.

Thank you...

Ingmar, for excellent supervision during this work. I have learned more than I could ever imagine and you have triggered my curiosity. My interests for science and research work have certainly grown and I am hoping that someday we will work together again.

Bernt, for all the help in the lab.

Ania, my coffee mate and source of fun during the “last pull”.

Marcus, for all those small little things that make my everyday life easier, funnier, better.

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APPENDIX 1

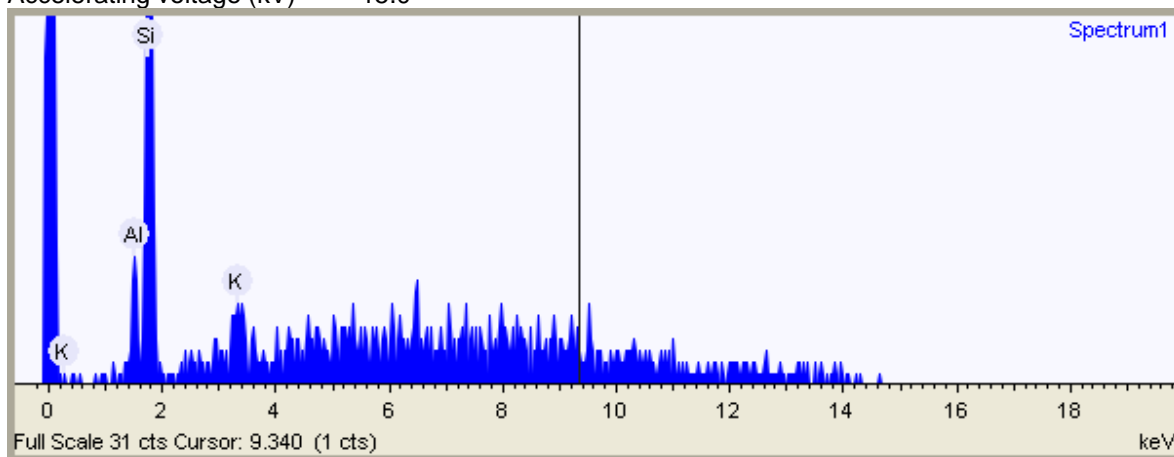
Project BN1

Acquisition conditions

Acquisition time (s) 60.0

Process time 4

Accelerating voltage (kV) 15.0



Quantification Settings

Quantification method All elements (normalised)

Summary results

| Element | Weight % |
|-----------|----------|
| Aluminum | 9.3 |
| Silicon | 83.5 |
| Potassium | 7.1 |

APPENDIX 2

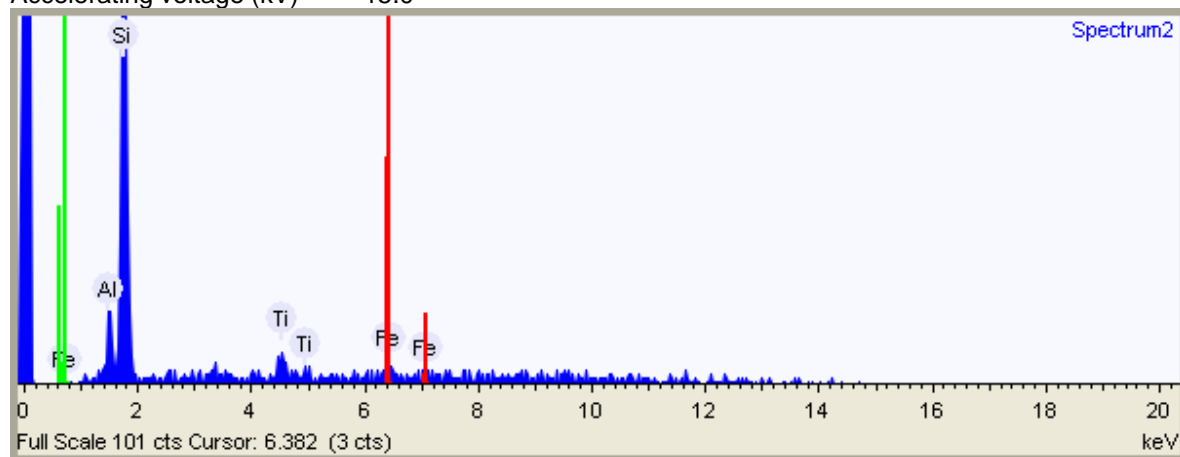
Project BN2

Acquisition conditions

Acquisition time (s) 60.0

Process time 4

Accelerating voltage (kV) 15.0



Quantification Settings

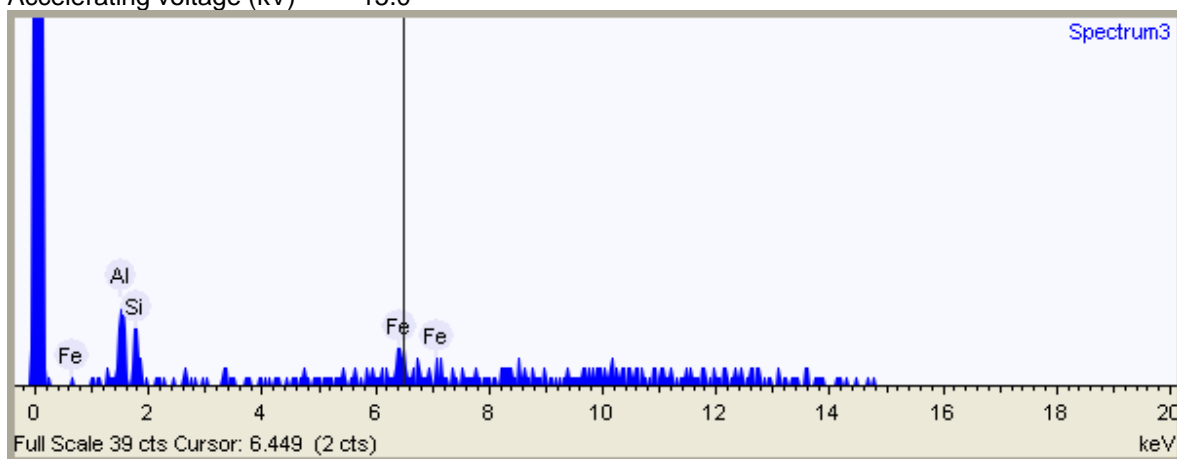
Quantification method All elements (normalised)

Summary results

| Element | Weight % |
|----------|----------|
| Aluminum | 8.9 |
| Silicon | 71.7 |
| Titanium | 11.4 |
| Iron | 8.0 |

APPENDIX 3

Project MB
Acquisition conditions
Acquisition time (s) 60.0
Process time 4
Accelerating voltage (kV) 15.0



Quantification Settings

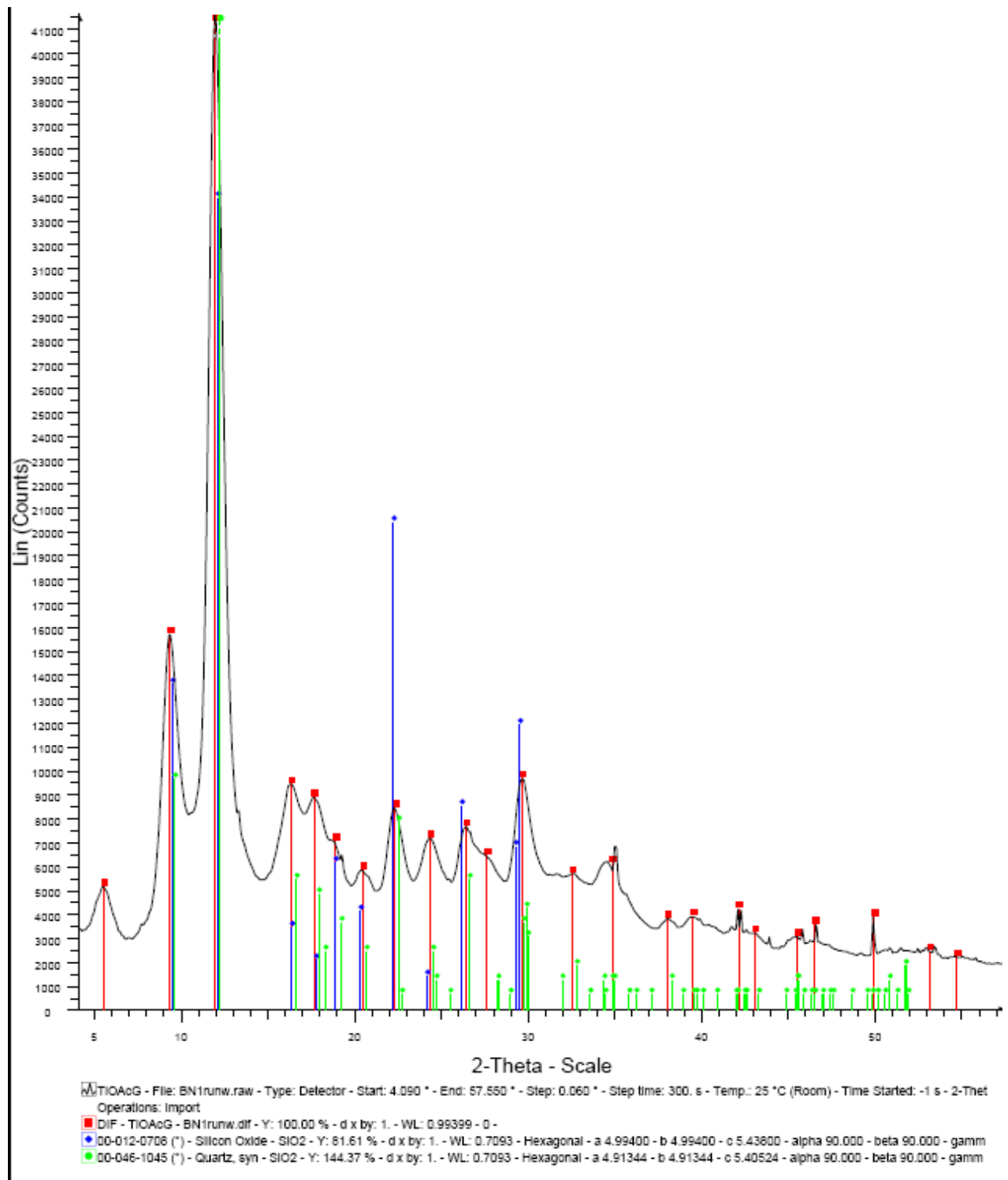
Quantification method All elements (normalised)

Summary results

| Element | Weight % |
|----------|----------|
| Aluminum | 31.3 |
| Silicon | 17.9 |
| Iron | 50.7 |

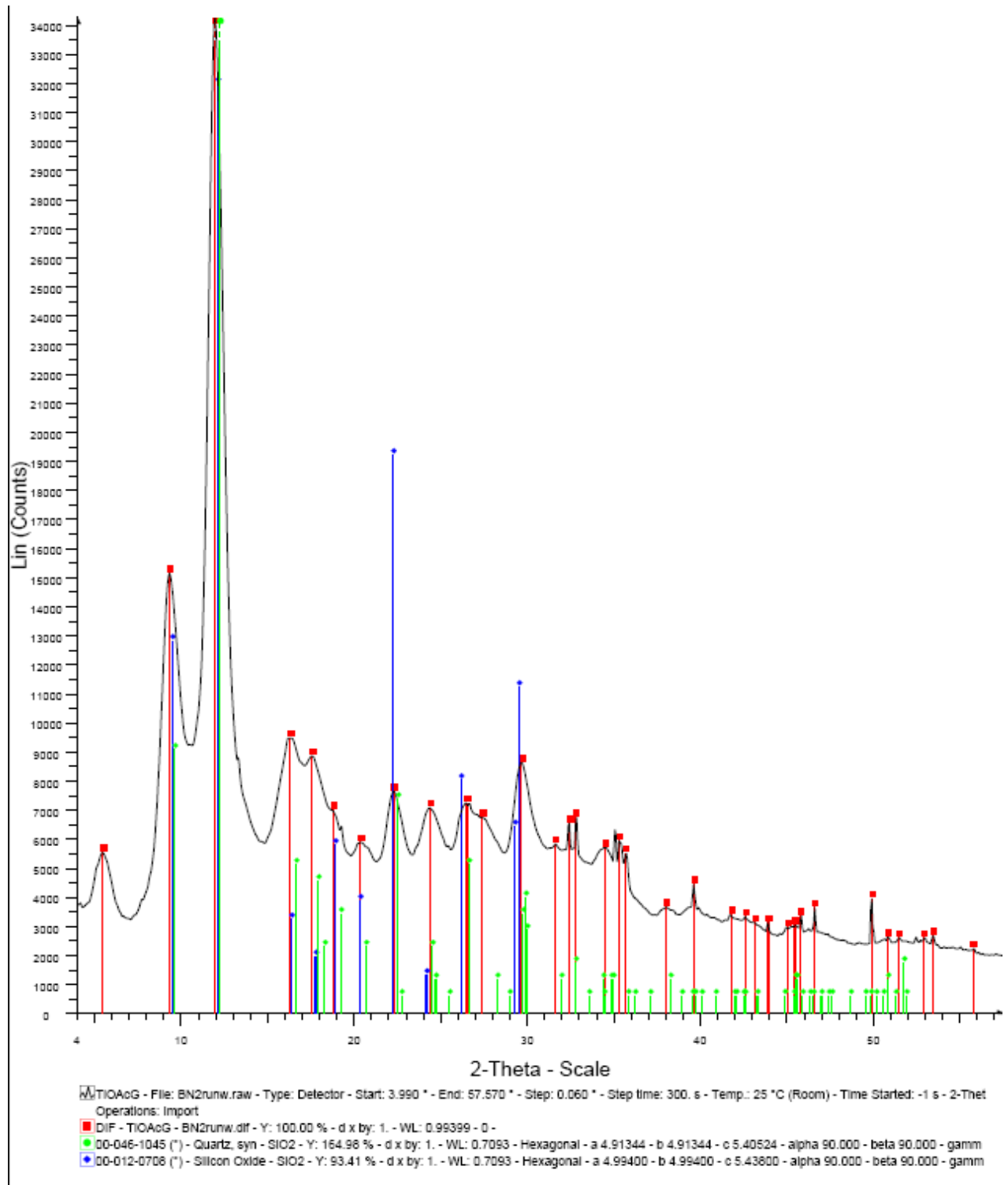
APPENDIX 4

BN1 (Raw)



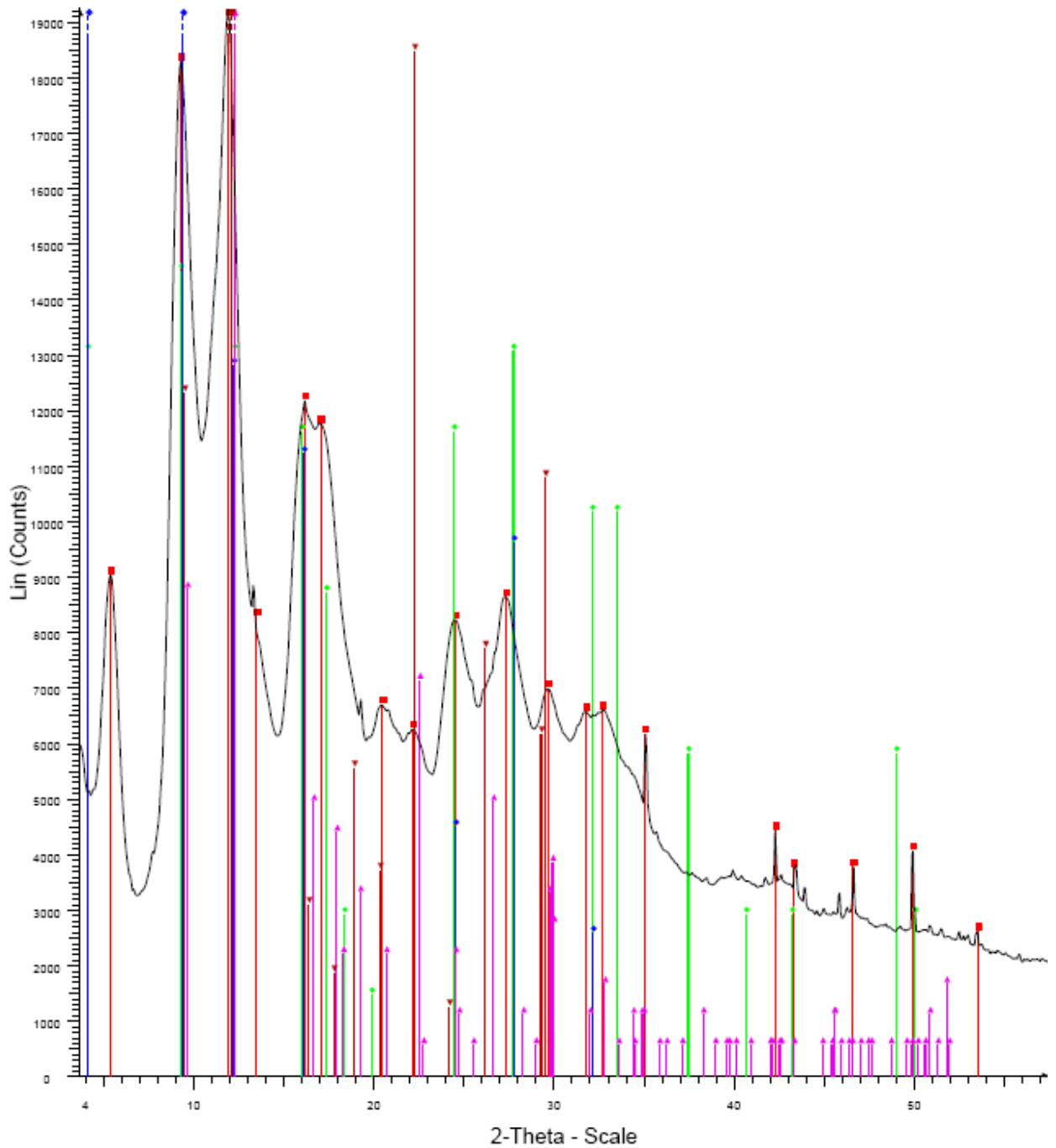
APPENDIX 5

BN2 (Raw)



APPENDIX 6

MB (Raw)



TiOAcG - File: MBrunw.raw - Type: Detector - Start: 3.640 ° - End: 57.520 ° - Step: 0.060 ° - Step time: 300. s - Temp.: 25 °C (Room) - Time Started: -1 s - 2-Theta
Operations: Import

■ DiF - TiOAcG - MBrunw.dif - Y: 100.00 % - d x by: 1. - WL: 0.99399 - 0 -

● 00-009-0451 (l) - Halloysite-10A - $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ - Y: 75.50 % - d x by: 1. - WL: 0.7093 - Hexagonal - a 5.12200 - b 5.12200 - c 10.03000 - alpha 90.000 -

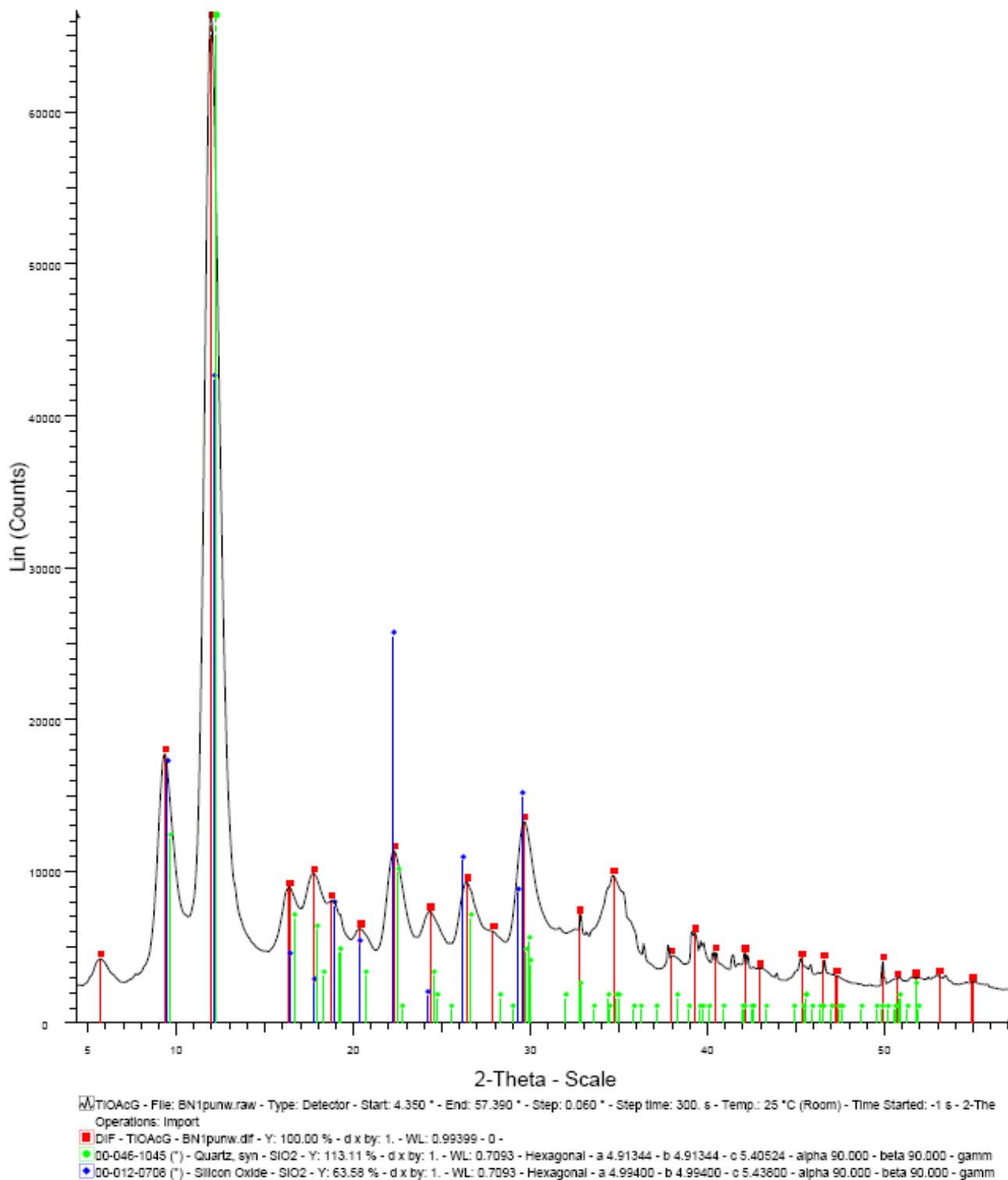
◆ 00-029-1489 (*) - Halloysite-10A - $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ - Y: 166.56 % - d x by: 1. - WL: 0.7093 - Hexagonal - a 5.11800 - b 5.11800 - c 10.03000 - alpha 90.000 -

▲ 00-046-1045 (*) - Quartz, syn - SiO_2 - Y: 285.12 % - d x by: 1. - WL: 0.7093 - Hexagonal - a 4.91344 - b 4.91344 - c 5.40524 - alpha 90.000 - beta 90.000 - gamma 90.000 -

▼ 00-012-0708 (*) - Silicon Oxide - SiO_2 - Y: 160.08 % - d x by: 1. - WL: 0.7093 - Hexagonal - a 4.99400 - b 4.99400 - c 5.43800 - alpha 90.000 - beta 90.000 - gamma 90.000 -

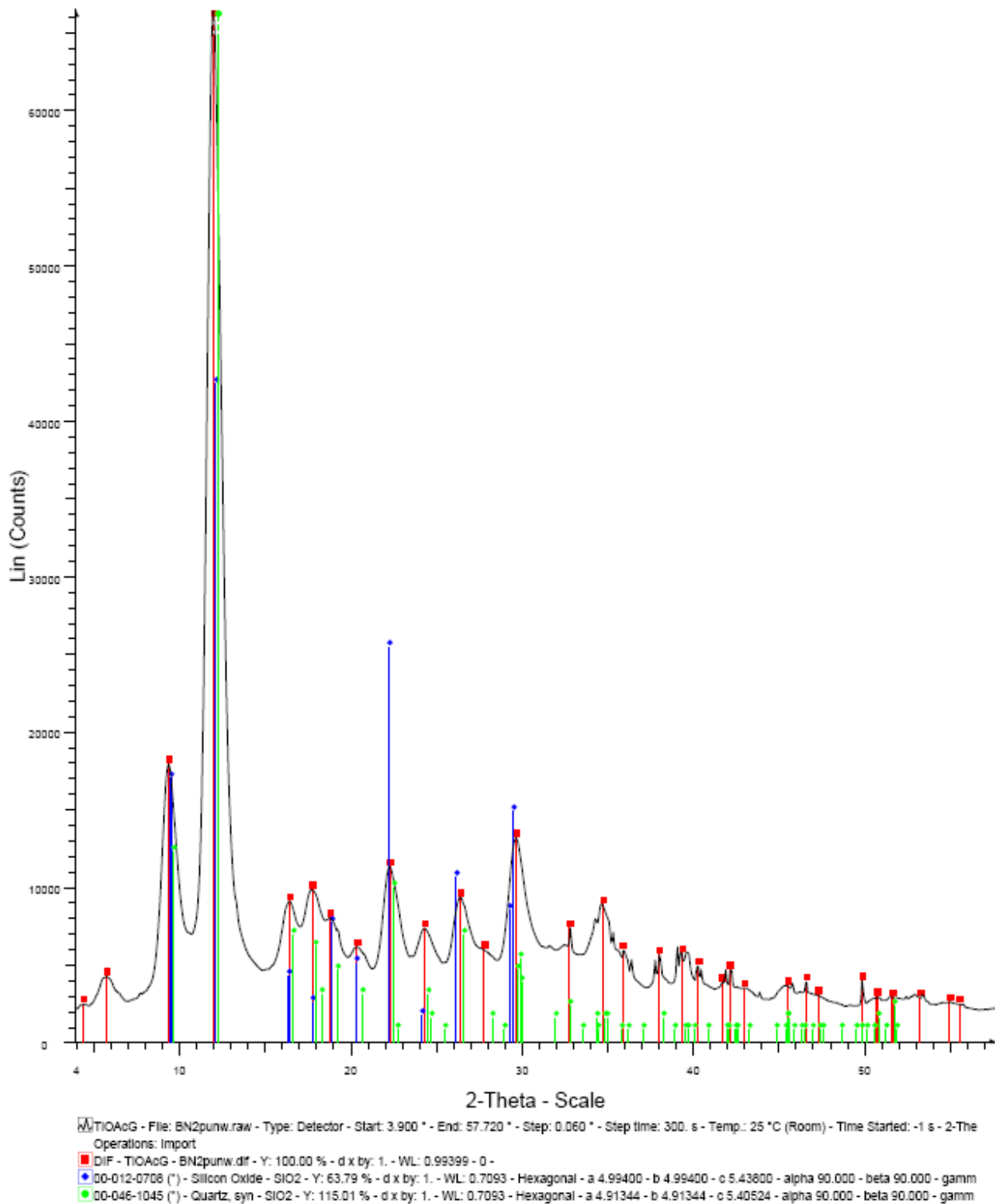
APPENDIX 7

BN1 (pure)



APPENDIX 8

BN2 pure



APPENDIX 9

MB (pure)

